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Cu-ZSM-5 Zeolite Catalysts for the Selective Catalytic Reduction of NOx

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Abstract

The relationship between copper content and activity for the selective catalytic reduction of NOx by propene in the presence of excess oxygen, of Cu-ZSM-5 catalysts was investigated. Turnover numbers were determined for Cu-ZSM-5 catalysts prepared from an aqueous ion exchange solution, with different copper contents. Turnover number was constant at copper contents < 90-100% exchange. Above this degree of exchange turnover increased by a factor of two, then remained constant up to the highest extent of exchange studied. Results suggest that both isolated copper ions and small metal/oxygen clusters, including dimers catalyse the SCR reaction, with the clusters being twice as active per copper ion. Retention of copper (II) acetate in the dimeric form in ethanol, introduces copper with greater unit activity for the SCR reaction per copper ion, than an aqueous ion exchange solution. XPS/XAES and EXAFS shows that copper is well dispersed within the zeolite matrix; in overexchanged Cu-ZSM-5 copper is present as both isolated Cu(II) ions and small Cu-O clusters. In Cu-ZSM-5 with a low level of ion exchange, copper is present in the form of isolated ions. Entities introduced by overexchange are thus dimers or small metal/oxygen clusters such as [Cu-O-Cu]²⁺, these species were shown to exhibit the highest turnover number for selective catalytic reduction.

The reactivity of carbonaceous material deliberately deposited on Cu-ZSM-5 catalysts under lean SCR reaction conditions was examined. The coke deposit exhibited significant activity for NOx reduction. Differences in reactivity were noted, with the rate of reaction, for catalysts with higher degrees copper exchange, reaching a maximum at lower reaction temperatures than catalysts with lower levels of copper ion exchange. The total amount of NOx converted was of the same order of magnitude as the amount of deposited coke. A simple kinetic model was formulated in an effort to understand the differences in reactivity. There was very good agreement between calculated and experimental values. The greater activity of coked catalysts with higher levels of copper exchange was mainly due to a lower activation energy, compared with coked catalysts with lower levels of copper ion exchange. These results showed a variation in the stability of the coke deposit towards NO, which was inversely dependent on copper content; suggesting that the residual acidity of the zeolite could be a factor in determining how catalyst activity varies with copper loading. The results suggest an inverse correlation between Bronsted acidity and catalyst activity. FTIR spectroscopy confirmed the presence of a polyaromatic coke deposit. Characteristics of an adsorbed cyanide species were also observed. The presence both of =NH and -NH₂ groups was suggested indicating that organic nitro groups may undergo sequential reduction to form cyanide. Powder XRD revealed that Cu-ZSM-5 undergoes a displacive transformation from monoclinic to orthorhombic framework symmetry upon internal coke deposition. This transformation was reversible upon the removal of coke, by reaction with NO and O₂.

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Chapter 1 Introduction

1.1 The Need for Pollution Control

The substantial increase in anthrapogenic air pollution experienced by industrialised nations between the eighteenth century and the present day is primarily associated with the industrial revolution [1]. The most significant early cases of man made air pollution were the "peasouper" smogs of Victorian London. The major irritants in these smogs were smoke and sulphur dioxide (SO₂) formed during the combustion of coal. These, when combined with water vapour in the atmosphere, formed a lethal aerosol of sulphurous acid on carbon particles. This smog, as well as reducing visibility, was especially harmful to the breathing of persons suffering from bronchitis and other respiratory ailments. Atmospheric pollution in the UK reached a peak in the early 1950's, severe smogs over London in 1952 contributed to the premature deaths of around 4000 people. In 1956 these problems resulted in the introduction of a clean air act of parliament which permitted the burning of smokeless fuels only in specific zones of high pollution risk [1-3].

The next occasion where air pollution became a major public concern was in Los Angeles, California, in the 1950's due to the formation of a type of pollution termed photochemical smog. Photochemical smog is formed by a complex series of reactions between hydrocarbons (HC), oxides of nitrogen (NOx) and oxygen (O₂), catalysed by sunlight. The products of these photochemical reactions are manyfold but include ozone (O₃) and other reactive species such as aldehydes and peracetylnitrates. In addition to the visual effects associated with this phenomenon, photochemical smog also affects plant growth and at low concentrations (0.1 ppm) it is irritating to the eyes, at higher concentrations (>0.6 ppm) it affects the function of the pulmonary alveoli and can cause severe bronchial and respiratory problems. The source of the precursor emissions was identified to be the large and ever increasing number of motor vehicles on the road. The US clean air act was passed in 1970 and included stringent regulations covering emissions of the three major pollutants, carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx) [1-3].

The problems of air pollution unfortunately do not end with photochemical smog, further phenomena have now been identified and include acid rain, global warming and O_3 layer depletion [1-3].

1.2 Motor Vehicle Exhaust Pollution

Motor vehicles using petrochemical fuels are generally recognised as the source of more air pollution than any other single human activity. Road transport is the dominant source of CO, NOx, hydrocarbons (referred to collectively as VOC's) and is a substantial contributor of greenhouse gases such as CO₂, as well as toxic substances such as SO₂, fine particulates and lead. Recent studies also indicate that motor vehicles are a source of other toxic air pollutants including 1,3 butadiene, benzene and other carcinogens. Without significant controls, these emissions will continue to increase because of the inevitable growth in the motor vehicle population [4-6]. Motor vehicle emissions are associated with air pollution problems at local, regional and global levels [4,7].

In built up urban areas, large proportions of the population are regularly exposed to high concentrations of pollutants as a result of motor vehicle exhaust emissions. Pollutants are often present in concentrations which exceed international health guidelines and can cause acute and chronic health problems. Aggravated respiratory problems and decreased pulmonary function are associated with exposure to NOx and photochemical oxidants. Exposure to gaseous VOC's and particulate matter are known to have direct toxic effects ranging from carcinogenesis to neurotoxicity [4,7,8].

Long range transport of pollution originating in urban areas has resulted in the expansion of many environmental problems to the regional and global level, where they are responsible for several forms of environmental degradation. The phenomenon of photochemical smog can be found far from the point of source of precursor emissions, the photochemical oxidants, mentioned in the previous section, cause significant detrimental effects, ranging from negative health effects such as eye irritation and impairment of respiratory function to widespread crop and materials damage, to reduced visibility in affected regions. Also at the regional level the pollution phenomenon known as acid rain, formed from the hydrated forms of NOx and SOx, has been found to be responsible for forest destruction and the acidification of lakes and streams [4,7,8].

Motor vehicles are found to contribute to the global build up of greenhouse gases in the atmosphere, CO_2 , N_2O , CH_4 and O_3 are involved in the process. These gases have the property of absorbing the IR radiation re-radiated back by the earth, thus heating the troposphere resulting in global warming. Also on the global scale, chloroflurocarbons from

air conditioning units in motor cars have been found to contribute to stratospheric ozone depletion [4,7].

Concern for the effect of these pollutants on health and the environment has led to the development and introduction of stringent motor vehicle emissions legislation, designed to improve air quality by reducing the impact of automobile exhaust gases [1-3]. Legislation has been adopted by most industrialised nations and is constantly increasing in stringency as governments and authorities are setting lower allowable exhaust gas emission limits. Current exhaust gas emission limits for passenger cars in the European Union is depicted below in table 1.1 [9].

Engine Type	CO (g km ⁻¹)	HC + NOx	Particulate
		(g km ⁻¹)	(g km ⁻¹)
Gasoline	2.2	0.5	-
spark ignition engine			
Direct injection	1.0	0.9	0.1
diesel engine			
Indirect injection	1.0	0.7	0.08
diesel engine			

Table 1.1 Current exhaust gas emission limits for passenger cars in the European Union.

Since the research work described in this thesis concentrates primarily on NOx abatement catalyst technology, we therefore confine our attention to the emission and elimination of NOx pollution from exhaust gas streams.

1.3 Air Pollution from NOx

NOx consists primarily of NO and NO_2 which are produced in all combustion processes by the oxidation of nitrogen in the air and fuel bound nitrogen. Predominantly, automotive NOx emissions are formed during the high temperature combustion of fuel in the engine, in a reaction between the nitrogen and oxygen in the air. One of the best known mechanisms for NO formation was first described by Zeldovich, which involves a chain reaction of O and N atoms as presented below.

$$0 + N_2 \leftrightarrow NO + O$$

 $N + O_2 \leftrightarrow NO + O$

The rate of NO formation increases rapidly with temperature. Although the primary oxide of nitrogen produced in combustion processes is NO, the conversion to NO_2 readily occurs at lower temperatures, typical of when exhaust gases are vented to the atmosphere. NO_2 is linked to the development of bronchitis, pneumonia, susceptibility to viral infections and alterations to the immune system. It also contributes to acid rain, urban smog and tropospheric ozone formation as mentioned previously. Thus if NO is prevented from entering the atmosphere, most of the downstream effects of NOx pollution can be eliminated [10,11].

1.4 NOx Emission Control

Several control strategies have been proposed to reduce the environmental impacts of NOx emissions [12]. The most desirable solution is to reduce or eliminate emissions at source rather than adopt "end of pipe" methods. The use of alternative, cleaner fuels and the development of new ultra low emission or non-polluting automotive technologies such as hybrid vehicles, battery powered electric vehicles, and vehicles powered by onboard fuel cells are the most attractive long term solution. The lack of infrastructure for the introduction of alternative fuels prohibits their widespread introduction and use. Furthermore, battery and fuel cell technology is still not yet advanced enough to compete with the internal combustion engine for widespread commercial use. Another approach to reducing NOx emissions from automobiles has involved the alteration of engine operation. Lower combustion temperatures within the internal combustion chamber and the inclusion of exhaust gas recirculation have both resulted in lower NOx emissions. Nothing however

has proved to be as efficient as the cleansing of exhaust gases prior to their release into the atmosphere via catalytic methods [9].

The three way automotive catalytic converter is the only effective measure currently available for atmospheric protection from automotive exhaust emissions. The three way catalyst is able to simultaneously remove HC, CO and NOx, provided that the fuel combustion process is carefully stoichiometrically balanced [13].

The desire for improved fuel economy and lower emissions of CO_2 is projected to increase the demands for fuel efficient lean burn gasoline and diesel engines. The three way catalytic converter, unfortunately, is ineffective for NOx removal under exhaust gases where excess oxygen is present. It is therefore of great environmental importance to develop a catalytic technology that will allow NOx removal in lean environments. Among the catalytic approaches, NOx storage-reduction (NSR) catalysts have shown tremendous promise as alternative systems capable of operating under net oxidising conditions, these systems have already found commercial application as NOx abatement catalysts for lean burn gasoline engine exhausts [14]. The reduction of NOx with a selective reducing agent in an oxidising atmosphere (SCR) is also the subject of intense research for mobile engine applications [10,11]. SCR is a more desirable route to the elimination of NOx emissions from net oxidising exhaust gases than NSR, as SCR technology could be applicable to diesel exhaust applications in addition to lean burn gasoline exhaust emissions.

1.4.1 The Three Way Catalytic Converter.

The three way catalytic converter is so called because of its ability to simultaneously remove NOx, CO and hydrocarbons over a single catalyst. The hydrocarbons and CO undergo oxidation, and the NOx reduction, as illustrated below.

$$CO + O_2 \rightarrow CO_2$$
$$HC + O_2 \rightarrow CO_2 + H_2O$$
$$NO + CO \rightarrow CO_2 + N_2$$

For efficient removal of all three pollutants the catalytic converter must operate at an air to fuel ratio close to the stoichiometric value. This is maintained by the use of an electronically controlled engine management system in which the concentration of oxygen passing into the engine is continuously monitored by an oxygen sensor. Under more oxidising conditions, such as those found in modern lean burn or diesel engines, the efficiency of the catalyst for the oxidation of hydrocarbons and CO is high, but the reduction capability of the catalyst declines rapidly. A schematic illustration of the effective operation of the three way catalysts is depicted below in Figure 1.1 [2].



Figure 1.1. The effect of exhaust gas stoichiometry on the conversion efficiency of a 3 way catalyst [2]

The conventional 3 way catalytic converter consists of combination of noble metals Pt, Pd and Rh, and additives such as ceria, zirconia and lanthana, amongst others, on a stabilised alumina support. The alumina support is coated upon a ceramic monolith structure as a washcoat upon which the active components, i.e. noble metals and additives, are dispersed. Pt and Pd components are effective oxidation catalysts and promote the reduction of NOx but are less effective in this role than Rh, which is by far the superior ingredient for NOx reduction. The additives are believed to improve the catalyst performance by extending the conversion during air to fuel perturbations and stabilising the alumina support against thermal degradation [13].

1.4.2 NOx Storage and Reduction Catalyst

In this technology a three way catalyst technology is combined with a NOx adsorbing material that stores the NOx when the engine is operating in the lean burn range. When lowering the oxygen concentration to the stoichiometic point, or even to rich conditions, the NOx is released and reduced to N_2 in the combined three way catalyst [14].

1.4.3 Selective Catalytic Reduction

Selective catalytic reduction (SCR) is a potential alternative to three way catalysts for use in lean burn driving conditions. Many catalysts have been found to be effective for this reaction, employing a variety of different reductants. A reductant is termed selective if NOx is preferentially reduced in the presence of oxygen.

The selective catalytic reduction of NO by NH₃ using V_2O_5 -WO₃-TiO₂ catalysts is currently the most widespread method used for the clean up of effluent gases from stationary sources of NOx emissions, such as power plants and industrial boilers. Advantages of using NH₃ as the reductant is its high selectivity towards reduction of NO in the presence of oxygen. There are problems associated with this technology, however, such as the need for stoichiometric control of NH₃ in the SCR reaction, to avoid emissions of unreacted NH₃. The use of NH₃ based SCR technology is, unfortunately, not practical for transportation applications due to the variety of transient conditions encountered which could lead to slip of unreacted NH₃. Additional problems include the storage and transportation of NH₃.

Iwamoto *et al* [15] and Held *et al* [16] were the first to report on a new selective reduction reaction, in which it was found that the selective reduction of NO could be carried out by hydrocarbons in an oxidising atmosphere on copper ion exchanged zeolites. These findings dispelled the widely believed concept that NH_3 was the only selective reductant in the presence of oxygen. The use of hydrocarbons as selective reductants presents a much more attractive proposal than using NH_3 . Hydrocarbon fragments from incomplete combustion are found in typical exhaust gas streams, making the addition of a reductant unnecessary [10,11].

As this research is concerned only with the selective reduction of NOx by hydrocarbons under net oxidising conditions, the remainder of this chapter concentrates purely on this subject and focuses on the different catalysts which have been reported to show activity for the reaction and the mechanisms invoked therein. Comprehensive review articles covering the vast literature published over the years on the SCR of NO using hydrocarbons are available [17,18,19,20]

1.5 Selective Catalytic Reduction by Non Zeolitic Catalysts

1.5.1 Oxide Catalysts

In 1990, the activity of some metal oxides for the selective catalytic reduction of NO using propane as a reducing agent in an oxidising atmosphere was demonstrated by Kintaichi *et al* [21]. Metal oxide catalysts examined were silica, alumina, silica-alumina, titania and zirconia. Silica alone was found to show no activity at all for the SCR reaction, however when silica/alumina and alumina catalysts were tested for the reaction, both exhibited activity, with activity increasing with alumina content for the silica/alumina catalyst. Titania and zirconia catalysts both showed activity for the selective reduction, although the activities were not so high as pure alumina. The most active catalyst tested in this series was found to be pure alumina, which exhibited peak activity at 773 K. The presence of water vapour was shown to inhibit NO reduction by propane over alumina [22], but it was shown that alumina exhibited excellent performance in the presence of high concentrations of oxygen and water vapour, using methanol as a reducing agent [22,23].

The catalytic behaviour of rare earth metal oxides have also been investigated for the SCR reaction with propane [24]. These authors report an inverse relationship between hydrocarbon oxidation activity and NO reduction activity for a series or rare earth oxide catalysts. It was found that CeO_2 and Pr_6O_{11} , on which propane was almost completely oxidised to CO_2 , were hardly effective at all for NO reduction. The activity of pure and Sr promoted rare earth oxides, for NO reduction by methane in the presence of oxygen, has been demonstrated by Zhang *et al* [25,26]; they report that La_2O_3 and Sr/La_2O_3 were the most active catalysts, while CeO_2 was much less active than all the other rare earth oxides tested.

The catalytic behaviour of sulphated metal oxides has also been examined for the lean SCR of NOx [27]. The activity for NO reduction by propane in 10% oxygen was examined on TiO₂ and SO₄/TiO₂. The extent of NO reduction was found to be much higher on the sulphated sample, almost identical results were obtained for ZrO_2 and SO_4/ZrO_2 . The difference in NO reduction activity was attributed to increased catalyst acidity. A Fe₂O₃ catalyst was found to exhibit no activity for NO reduction, the SO₄/Fe₂O₃ catalyst however demonstrated activity for NO reduction around 573 K. It has also been reported that Ga/SO₄-ZrO_x catalysts were found to be effective for the reduction of NO in a lean environment with hydrocarbons [28]. The authors report that Ga/SO₄-ZrO_x was much more

active than SO_4 -ZrOx or Ga/ZrOx and was more effective when using propane as the reductant.

Perovskite oxides have also been shown to exhibit some activity for the SCR of NO under lean oxidising conditions [29,30].

1.5.2 Supported Noble Metal Catalysts

Studies into the selective catalytic reduction of NO by propane [31,32] and propene [33,34] over Pt supported alumina catalysts have been performed.

Hamada *et al* [31] and Saski *et al* [32] have reported that Pt/Al_2O_3 catalysts containing 0.5 wt% Pt exhibited activity for the SCR of NO with propane as a reductant, peak activity was reached at 673 K, a temperature lower than the activity of alumina alone. Hamada also examined Rh and Pd supported alumina catalysts in this work and found them to be less active than the Pt alumina supported catalyst system.

Burch *et al* [33] conducted a detailed study of Pt/Al_2O_3 catalysts. They specifically examined the effect of Pt loading and dispersion on the activity of Pt/Al_2O_3 catalysts for the selective catalytic reduction of NO, using propene as a reductant. They demonstrated that catalytic activity was a function of metal loading, the temperature maximum of NO conversion was found to decrease from 620 K to 500 K when Pt loading was increased from 0.1 wt% to 2 wt%. The increase in Pt loading was also found to enhance maximum NO conversion. Pt dispersion was also found to affect the NO reduction activity, the degree of Pt dispersion was varied by changing the Pt precursor used during the preparation stage. Catalysts with high Pt dispersions prepared from hexachloroplatinic acid proved to be less active than catalysts with less well dispersed Pt, prepared from other Pt precursors.

Pt/SiO₂ catalysts have been examined for the SCR of NO by Tanaka *et al* [34]. They state that Pt/SiO₂ catalysts demonstrate activity for the SCR reaction with propene as a reductant at temperatures as low as 423 K, but also mentioned that N₂O formation could account for up to 75% of the total NO conversion. This was contrary to findings published by Hamada *et al* [31] where Pt/SiO₂ catalysts were found to be inactive for the SCR of NO by propane. Zhang *et al* [35] have reported that Pt loaded onto a coprecipitated B₂O₃-SiO₂-Al₂O₃ supported catalyst is active for the SCR reaction using propene as a reductant, at temperatures as low as 423 K. Noble metals other than Pt have also been assessed for the SCR reaction with hydrocarbons. Hamada et al [31] also examined supported Rh and Pd systems on alumina and silica. Pd and Rh alumina were found to exhibit activity for the SCR of NO with propane. Activity was found to peak at the lower temperature of 573 K for both Rh and Pd alumina, compared with the peak activity temperature of 673 K for Pt alumina, both however were found to be significantly less active than Pt alumina, with Pd exhibiting lower activity than Rh alumina. Rh/Al₂O₃ catalysts were also shown to exhibit activity for the SCR reaction using propene as a reductant [36]. Obuchi et al [37] examined the performance of Ir, Pd, Rh and Ru alumina supported catalysts, as well as Pt alumina for the SCR of NO with propene. Pt, Rh and Ru catalysts exhibited high activity. Pt and Rh on alumina exhibited the best activities for the SCR reaction. In the case of the supported Rh system, however, more than 90% of the NO consumed was converted to nitrogen. With Pt alumina catalysts only approximately a third of the total NO converted was converted to nitrogen, the remainder was converted to nitrous oxide. Bamwenda [38] reported that, in the case of Rh catalysts, the use of alumina as a support significantly enhanced the activity of the catalyst, Rh demonstrated superior performance when supported on alumina compared to Rh supported on TiO₂, ZnO and ZrO₂. In all cases in the literature, during the screening of supported noble metal catalysts. Pt has been found to be the most active catalyst and the most resistant to the presence of water and SO₂.

1.5.3 Other Supported Metal Catalysts

A number of papers describe the use of other supported metal catalysts for the SCR reaction under lean burn conditions.

Hamada *et al* [31] found that the addition of certain transition metals promoted the activity of alumina for the SCR of NO with propane at lower temperatures. The temperature of peak NO conversion activity was lower for Mn, Fe, Co, Ni, Cu and Pt (Al_2O_3) than that of alumina with no metal additive. The highest NO conversion at 673 K was obtained over Co/ Al_2O_3 , prepared from an acetate precursor. At 573 K, Fe/ Al_2O_3 prepared from a nitrate precursor was the most active. The catalytic behaviour of Co/ Al_2O_3 was found to change quite dramatically depending on the cobalt precursor used in the catalyst preparation stage. Co/ Al_2O_3 prepared from the nitrate precursor was found to be almost inactive for NO reduction by propane in an oxygen containing atmosphere, however Co/Al_2O_3 prepared from the acetate precursor catalysed NO reduction extremely effectively.

Torikai et al [39] independently examined the activity of a series of metal/Al₂O₃ catalysts for the SCR of NO using ethene as the reductant. They demonstrated the catalytic activity of Al_2O_3 could be greatly influenced by the addition of only 0.2 wt% metal. The activity of Al₂O₃ was found to be enhanced at temperatures 573-773 K by adding Cu, Fe, Co or Cr. Addition of Ni, Mn, Zn and V made little difference, while the addition of Ag, Ca and K had a detrimental effect upon activity. Therefore it was demonstrated that the most active temperatures depend on the cations supported. The order of active temperature regions was Fe (673 K) = Cr (673 K) < Cu (723 K) < Co (773 K) \leq (773-823 K) \leq Mn (823 K) = V $(823 \text{ K}) = \text{Zn} (823 \text{ K}) = \text{K} (823 \text{ K}) = \text{none} (\text{Al}_2\text{O}_3 \text{ only}, 823 \text{ K}) < \text{Ag} (873 \text{ K}) = \text{Ca} (873 \text{ K}).$ Torikai also reported that the addition of Cu promoted the activity of a SiO₂-Al₂O₃ support for the SCR of NO by ethene. The addition of Cu was found to produce a 3-5 fold increase in overall conversion. Similar results have also been published by Hosose et al [40]. They reported that the addition of Cu had a prominent effect in promoting the activity of SiO₂/Al₂O₃. The presence of Cs with Cu on an alumina support has also been found to extend the active temperature range for the SCR reaction, but slightly reduces peak NO conversions achieved when using propene as a reductant [41].

Ag supported alumina catalysts have been shown to exhibit high activity for the SCR reaction, by propene and oxygen containing organic compounds, even in the presence of water [42,43]. It was reported that, when using propene as a reductant, the addition of Ag lowers the temperature of peak activity to 673 K and increases the peak conversion achieved by alumina alone. Miyadera *et al* also reported that Ag/Al_2O_3 had excellent activity for the SCR of NO using ethanol and acetone, however methanol was a poor reducing agent. These results differ with those presented earlier by Torikai *et al* [39], who reported that the SCR of NO using ethene decreased upon the addition of silver. Miyadera *et al* attribute this to differences in Ag content. More recently, Ag/Al_2O_3 catalysts have been tested for the removal of NO from a real diesel exhaust gas. Three reducing agents were tested, in contrast to the above reports, methanol was reported to be the most suitable reductant when compared with propene and (CH₃)₂O [44]. Oxidised and reduced Ag/Al_2O_3 catalysts have been and the source of NO and the propene and (CH₃)₂O [44].

ethanol as reductants. It was found that the oxidised Ag/Al_2O_3 was far more active for the SCR reaction than reduced Ag/Al_2O_3 .

Mirayeda and Yoshida [43] examined other supported metal catalysts for the SCR of NO by propene, including In, Ga, Sn and Zn. They reported that all of these catalysts exhibited NO reduction activity. Ga and In were found to have greater activities than Ag/Al_2O_3 over the same temperature range. Sn/Al_2O_3 was found to exhibit lower peak activity. Zn/Al_2O_3 was active only in the higher temperature region above 673 K and exhibited similar peak conversions to Ag/Al_2O_3 . In their study, Miyaderea and Yoshida examined the effect of the presence of water and SO₂ on catalytic activity, and demonstrated that a detrimental effect was observed for all catalysts tested apart from Ag/Al_2O_3 , with Ga/Al_2O_3 suffering the largest reduction in activity.

The promotional effect of Sn on the catalytic activity of Al_2O_3 for the SCR of NO by methanol has been examined by Tabata *et al* [46]. The addition of Sn enhanced the activity of alumina for NO reduction especially in the low temperature region below 623 K. They also reported that Sn/Al₂O₃ maintained its high activity in the presence of SO₂ and water.

Recently Au supported on alumina has been shown to exhibit activity for the SCR reaction with propene even in the presence of excess oxygen and moisture. It has also been found the addition of Mn_2O_3 to Au/Al_2O_3 increased the overall NO conversions well as to extend peak conversions to a lower temperature range [47].

1.6 Selective Catalytic Reduction Using Zeolitic Catalysts

1.6.1 Protonated Zeolites

It has been demonstrated that zeolites in the protonic form are active catalysts for the SCR reaction [48,49,50]. Hamada et al [48] reported that the proton form of zeolites mordenite, ZSM-5 and Y are active catalysts for the selective catalytic reduction of NO utilising propane and propene as reductants. The most active of the three catalysts was H-mordenite followed by H-ZSM-5 and H-Y. The authors state that the active centres of protonic zeolite catalysts for the SCR reaction could be their acid sites. In a later study, Hamada et al [49] reported their findings concerning the SCR of NO with propane over alumina and H-ZSM-5 catalysts. They demonstrated that the presence of oxygen was essential for the reaction to occur and that the reduction of NO_2 proceeded to a much greater extent than for NO under the same conditions. These results drew them to the conclusion that the oxidation of NO to NO₂ is an important step in the SCR reaction. They postulated that, in the SCR reaction, NO is primarily oxidised into NO₂, which is then subsequently transformed into N_2 by reduction. Yogo et al [50] reported that the proton forms of zeolites ZSM-5, ferrierite, and mordenite demonstrate activity for the SCR of NO by methane in an oxygen rich atmosphere. They found, in agreement with Hamada et al [49], that the reduction of NO2 was greater than the reduction of NO under otherwise identical conditions.

1.6.2 Noble Metal Zeolite Catalysts

Supported noble metal catalysts have also attracted attention for lean burn SCR applications, as mentioned in the previous sections above. They have been reported to maintain high activity in the presence of water vapour and SO_2 , making them a viable contender for real exhaust gas applications.

Pt/ZSM-5 has been reported, by Hirabayashi *et al* [51], to exhibit activity for the SCR of NO using ethene as a reductant, at temperatures as low as 450 K. The reduction of NO was not selective to dinitrogen, since nitrous oxide also made up a considerable proportion of the conversion products. The most active temperature of Pt-ZSM-5 was 485 K. In this work, the conversion of NO to N_2 over the Pt-ZSM-5 catalyst was little changed upon the introduction of water vapour at 423-673 K. This was in contrast to the observation that the activities of Cu-ZSM-5 and Fe-mordenite were reduced to nearly 0% at 485 K on the addition of water vapour.

The activity of noble metal (Ru, Rh, Pd, Ir and Pt) ion-exchanged ZSM-5 catalysts for the SCR of NO by ethene in the presence of excess oxygen was also examined by Shin *et al* [52]. Of the catalysts tested, Pt-ZSM-5 showed the highest conversion of NO into N₂ at a temperature as low as 485 K. Rh-ZSM-5 showed the second highest conversion, but the active temperature (673 K) was much higher than that on Pt. Nitrous oxide was produced as a by product of all the catalysts tested. The activity of Pt-ZSM-5 did not decrease with water vapour or SO₂ in the reactant stream, in fact the selectivity into N₂ was slightly enhanced. The activity of Pt-ZSM-5 exhibited a long lifetime, the activity hardly changed even after 1000 hours of service.

In a study primarily aimed at probing the reaction mechanism, the SCR of NO by propane and propene in an excess of oxygen was examined by Rottlander *et al* [53]. Pt-ZSM-5 was found to be active for NO reduction with propene, with a maximum conversion at 535 K. The onset of NO reduction was observed at the beginning of propene combustion to CO_2 (440 K). With propane as the reductant NO conversion reached a maximum at 640 K. Therefore propene is found to be the most efficient reductant at T<600 K.

Burch and Scire [54] studied the activity of Pt-ZSM-5 catalysts for the reduction of NO with ethane and methane as reductants. They reported that the Pt-ZSM-5 was completely inactive towards NO reduction in the presence of oxygen with either methane or ethane.

Nishizaka and Misono [55] also report the inactivity of Pt-ZSM-5 for the SCR reaction using methane as a reductant, however, that Pd ion exchanged H-ZSM-5 demonstrated high activity for the removal of NO at 350-550 K, selectivity was high towards dinitrogen. Pd-ZSM-5, however, was found to be ineffective for the reduction of NO by propene under the same conditions. In the same study, Ru-ZSM-5 was demonstrated to exhibit moderate activity for the reduction of NO by methane.

More recent studies, suggesting that Pt-ZSM-5 is a commercially viable catalyst, have been reported by Iwamoto *et al* [56]. High catalytic activity and stability of Pt-ZSM-5, at temperatures between 423-773 K and 10000-150000 h^{-1} GHSV, was demonstrated, under real exhaust gas conditions; unfortunately the formation of nitrous oxide was still a problem on these systems.

1.6.3 Copper Zeolite Catalysts

Iwamoto *et al* [15] and Held *et al* [16] independently reported that NO could be selectively reduced in an oxidising environment over a Cu-ZSM-5 catalyst using hydrocarbons as reducing agents. In the aftermath following these publications Cu ZSM-5 became the focus of immense research interest into the selective catalytic reduction of NO with hydrocarbons, and was shown to exhibit exceptional activity for the SCR reaction. Within the published literature, a wide spectrum of reductants has been shown to demonstrate activity for the lean SCR reaction, such as paraffins, olefins and oxygen containing organic compounds [15-17,57-68]. Cu-ZSM-5 was found to exhibit almost complete selectivity in conversion of NO to dinitrogen. Some researchers, however, have reported that some minor products may also be produced, at selectivities below some analytical detectability limits [109-110].

Iwamoto *et al* [17,57,59] classified the hydrocarbon reductants for NO reduction over Cu-ZSM-5 as selective (C_2H_4 , C_3H_6 , C_3H_8 and C_4H_8) and non-selective (CH_4 and C_2H_6). It has generally been accepted that in most cases unsaturated reductants exhibit superior activity for the SCR reaction compared to saturated reductants [18]. The type of hydrocarbon employed for the reduction has been shown to be an important factor.

Iwamoto et al [17,57,59] demonstrated that over Cu-ZSM-5 the maximum activity for the reduction of NO was attained at 523, 598, 548-673 and 573 K for C₂H₄, C₃H₆, C₃H₈ and C₄H₈ respectively. Truex et al [60], reported similar findings, they found that the use of C_3H_8 instead of C_3H_6 as a reductant resulted in an increase in the temperature of maximum NO conversion, of approximately 100 K. An increase in hydrocarbon concentration has generally been found to result in an increase in the rate of NO reduction. Iwamoto et al [17,57,59] showed that increasing the concentration of propene from 166 ppm to 1000 ppm increased catalytic activity for reduction of NO to nitrogen. In early publications examining the SCR of NO with hydrocarbons over Cu-ZSM-5 catalysts, ethylene was reported to be more reactive than propene, which in turn was more reactive than propane [15,17,57,59]. In a study by Cho [62], differences in the activity of ethene and propene as reductants for the SCR of NO over a monolith supported Cu-ZSM-5 catalyst were reported. Cu-ZSM-5 exhibited NO conversions several times higher when ethene was used compared with propene. They also show that the activity of propene for NO reduction was greatly suppressed in the presence of ethene. In another study, of the activity of Cu-ZSM-5, Kharas [67] demonstrated that superior activity was achieved for the SCR reaction when using

propene as opposed to propane as the reductant. Montreuil and Shelef [63] examined oxygenated organic compounds for the selective reduction of NO in the presence of excess oxygen over Cu-ZSM-5; they were found to be effective reductants, yet propanol was found to be less efficient than propene. In contrast to the above, d'Itri *et al* [66] reported that propane is more effective than propene for the SCR reaction over an excessively ion-exchanged Cu-ZSM-5 catalyst. In a publication by Petunchi *et al* [64], the activity of isobutane as a reductant for the SCR reaction over Cu-ZSM-5 was examined, and was reported to exhibit superior activity compared to propene. Unlike some other transition metal exchanged zeolites [69-70], Cu-ZSM-5 was found to be ineffective for the reduction of NO by methane in the presence of oxygen [17,57,59].

A promoting effect by the presence of oxygen on the rate of NO reduction by hydrocarbons was first reported by Iwamoto and Hamada [59]. They stated that over Cu-ZSM-5, the rate of NO reduction by propene at temperatures below 673 K increased with the addition of oxygen up to concentrations of 1-2%, while at higher concentrations the activity decreased slightly.

Under laboratory conditions Cu-ZSM-5 was found to be a highly effective catalyst, however, various studies have shown that the presence of water vapour and SO₂ reduces the catalyst effectiveness [58]. Irreversible deactivation of Cu-ZSM-5 has been reported to occur due to prolonged exposure to high temperature, wet, exhaust gas [71].

The overall activity of Cu-ZSM-5 was found to depend on the exchange level of Cu. Sato *et al* [57] found that the activity of Cu-ZSM-5 for the selective reduction of NO with ethene passed through a maximum with Cu exchange. They proposed that the occurrence of maximum activity at copper exchange levels of around 80-100% could mean that isolated Cu ions were the active species. Kharas [67] reported that the maximum catalytic activity was obtained for a 207% exchanged Cu-ZSM-5 catalyst. It was suggested that the most active species for the NO reduction by propene would be small clusters of copper oxide, hydroxide or mixed species, which are found to be present at levels of exchange exceeding stoichiometry.

Teraoka *et al* [72] reported that the presence of alkaline earth (Ca and Sr) and transition metal (Fe, Co and Ni) cations in Cu-ZSM-5 enhanced the activity for the SCR of NO by ethene. Incorporation of these cocations resulted in conversions of NO to nitrogen greater than for Cu-ZSM-5 alone and an expansion of the active temperature range. In a more

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recent publication by Budi *et al* [73], the stabilisation of Cu-ZSM-5 against steam deactivation by pre-exchanging the zeolite with lanthanum was demonstrated. The presence of the La cations was suggested to inhibit dealumination.

Cu zeolites other than ZSM-5 have also been found to be active for the SCR reaction. In addition to ZSM-5, Iwamoto et al [17,57,59] examined Cu ion exchanged ferrierite, mordenite, L and Y zeolites for the selective reduction of NO using ethene as a reductant. Differences were observed in the maximum activity of these catalysts, with Cu-ZSM-5 found to be the most active catalyst and Cu-Y the least. Similarly Truex et al [60] have also reported a higher maximum NO conversion over Cu-ZSM-5 than over Cu-mordenite. Gopalakrishnan et al [61] have compared the effect of introducing Cu by ion exchange into zeolites including ZSM-5, mordenite, X and Y on the activity for the SCR reaction with propane. Cu-ZSM-5 catalyst was found to be the most active at 673 K, followed by Cumordenite with a maximum conversion at 703 K. The activities of Cu-X and Cu-Y were reported to be negligible over the entire temperature range. The selective reduction of NO by various hydrocarbons including C₂H₄, C₂H₆, C₃H₆ and C₃H₈ over Cu exchanged mordenite and "natural zeolite" was examined [74]. All reductants exhibited moderate NO reduction activity, in both cases the use of propene and ethane as the reducing agent produced the highest and lowest activities for NO reduction respectively. In this particular study, the Cu exchanged natural zeolite exhibited the superior activity of those tested and demonstrated strong water tolerance with C_3H_6 as the reductant.

In a study by Coq *et al* [75], Cu ion exchanged mordenite catalysts were found to exhibit activity for the selective catalytic reduction of NO by decane. The activity for NO reduction was proportional to the number of Cu²⁺ ions present up to a Cu exchange level of 53% then decreased, from which it was concluded that isolated ions were more active than Cu aggregates/clusters or protons for the selective reduction reaction under the present conditions. During the SCR reaction, the selectivities for nitrogen formation from NO conversion was always 100%. In a complementary study, the selective reduction of NO by decane over Cu exchanged β zeolites was examined and compared to Cu-ZSM-5 [76], again selectivities for nitrogen formation was 100%. For Cu-Na- β catalysts, activity was found to increase with Cu content and passed through a maximum at an exchange level of 113% Cu. In contrast, Cu containing catalysts prepared from H- β were found to be less active for the SCR reaction under the same conditions. Only CuO aggregates were formed

on Cu-H- β whatever the copper content. By contrast, isolated Cu²⁺ are the main species occurring on Cu-Na- β when copper exchange level is lower than 120%. It was again postulated that isolated Cu²⁺ ions were more reactive than CuO species for NO reduction. Cu-Na- β was found to be less active than Cu-ZSM-5 at high temperature, but much more active at low temperature.

The influence of the presence of cocations (H, Na, Mg and Ba) upon the activity of Cumordenite catalysts for the selective reduction of NO by propene has been investigated [77]. The presence of cocations was found to promote the activity for the SCR reaction especially at low temperatures.

Inui et al [78] revealed that Cu-Na-A zeolite exhibited activity for the reduction of NO using saturated n-C8, n-C10 and n-C16 hydrocarbons in the presence of oxygen, activity for the SCR reaction was observed within the temperature range 473-773 K.

The catalytic activity of Cu-ion-exchanged SAPO materials for the selective reduction of NO using propene as a reductant under oxidising atmospheres was first studied by Isihara *et al* [79-81]. They reported that Cu-SAPO-34 exhibited higher activity than a Cu-ZSM-5 and maintained activity to much greater temperatures. Cu-SAPO-34 was found to be active over the temperature range 623-873 K, other types of SAPO studied included SAPO-11 and SAPO-5, which were found to be less effective. It was also demonstrated that Cu-SAPO-34 had a high thermal stability and was more resistant to poisoning by water and SO₂ than Cu-ZSM-5. The activity of Cu-SAPO-34 for the selective reduction of NO by propene was also examined by Diwell *et al* [82]. They too reported that Cu-SAPO-34 was more active than Cu-ZSM-5, but in contrast, they found that Cu-SAPO-34 is subject to water and SO₂ poisoning under real lean burn conditions. They state that to take full advantage of the hydrothermal stability of Cu-SAPO-34, more effective stabilisation of copper ions in the SAPO framework may be necessary.

1.6.4 Other Transition Metal Zeolites

Several Fe-exchanged zeolites, including mordenite, ferrierite, ZSM-5, Y and L have been tested for the selective reduction of NO by ethene in the presence of oxygen [83]. Catalytic activity was found to be dependent on the zeolite structure. The order of activity at 473 K was found to be (mordenite > ferrierite > ZSM-5 > Y > L). Fe-mordenite was demonstrated to be one of the most active catalysts tested at such low temperatures. The activity of the

Fe-mordenite zeolite was found to increase almost linearly with the Fe-exchange level up to 60% and became constant at higher exchange levels.

Co-ZSM-5 was demonstrated to exhibit comparable activity to Cu-ZSM-5, albeit at a higher temperature, for the selective reduction of NO in an oxygen rich environment using ethene as the reductant [17,57,83]. The activities of Ni and Mn-ZSM-5 zeolites were also examined, however, their activities were lower than Co-ZSM-5. Li and Armor [69,70] were the first to report that NO could be selectively reduced by methane in the presence of O_2 over a Co exchanged ZSM-5 zeolite. This finding was tremendously significant as it represented a potential NOx control method for use with lean burn natural gas fuelled vehicles. Complete conversion of NO to nitrogen was obtained on Co-ZSM-5 at 673 K. The catalytic activity was found to be significantly enhanced in the presence of excess oxygen and with increasing methane level, although a relatively small amount of methane was needed for complete NO reduction because of the high selectivity of methane towards the NO reduction reaction. The presence of water was found to reversibly suppress the conversion of NO to nitrogen, particularly at lower temperatures [84]. Examination of Ni and Mn exchanged ZSM-5 zeolites revealed that they too were also active for this reaction. The order of activity being Co-ZSM-5 > Mn-ZSM-5 > Ni-ZSM-5. The effects of zeolite structure was also studied by Li and Armor [69-70]. Using methane as the reducing agent, Co-exchanged mordenite, ZSM-5 and Y were compared; Co-mordenite exhibited only slightly lower activity for the reduction of NO than Co-ZSM-5 and Co-Y demonstrated very low activity. This same group later reported [85] that Co-ferrierite showed a two-fold increase in activity compared to Co-ZSM-5, at temperatures > 723 K.

Ga exchanged zeolites were also found to be active in the selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen. A comprehensive review has been published by Armor [86]. Yogo *et al* [87,88] first reported NO reduction over Ga exchanged zeolites utilising propane as the reducing agent. The zeolite structure was found to be an important factor, with Ga-ZSM-5 and Ga-Y being the most and least active catalysts, respectively, at temperatures < 773 K. Ga-ferrierite exhibited the highest activity at temperatures > 773 K. In a later study, it was reported that methane and ethane were also effective reducing agents for the NO reduction over Ga-ZSM-5 [89], as with Co-ZSM-5 the presence of excess oxygen was required. Similar results were observed by Li and Armor [90], using methane as a reductant with a Ga-ZSM-5 catalyst, Ga-Y once again exhibited

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little activity for the NO reduction reaction. Higher selectivity of methane for NO reduction was observed with Ga-ZSM-5 than with Co-ZSM-5 under the same reaction conditions. The activity of Ga-ZSM-5, however was more influenced by the presence of water vapour than that of Co-ZSM-5.

In addition to the catalysts reviewed in detail above, several other cation exchanged zeolites have been also tested for the reduction of NO by hydrocarbons in the presence of oxygen, i.e. Ag, Al, Cr, In, Pb, Sn and Zn. The activity of these catalysts for the selective reduction of NO has been studied with a variety of reducing agents. Ag ZSM-5 has been reported to exhibit high activity for the SCR reaction using ethene at high temperatures, within the range 600-1000 K [17,57,59]. In a study by Yogo et al [87] the activity of a series of transition metal ion exchanged ZSM-5 catalysts were examined using propane as a reductant. The activities of Al, Sn, Zn, Ga and In catalysts were examined and compared with Cu-ZSM-5. Al-ZSM-5 demonstrated high activity for the SCR reaction at between 573 and 873 K, it was claimed that the activity surpassed that of a Cu-ZSM-5 catalysts tested under the same conditions. Sn-ZSM-5 also showed activity, with the maximum occurring at 573 K, in this instance the activity was generally lower than Cu-ZSM-5. Zn-ZSM-5 was also reported to exhibit activity in this study, with a peak activity temperature occurring at 773 K, at this temperature activity of the Zn-ZSM-5 was higher than that of Cu-ZSM-5. Zn-ZSM-5 has also been reported to exhibit activity for the SCR reaction, utilising ethene as a reductant [17]. In-ZSM-5 was tested and shown to display activity for the SCR reaction within the temperature range 573-873 K. The performance of this catalyst was reported to be superior to Cu-ZSM-5 examined under the same reaction conditions. In a separate study, In-ZSM-5 was reported to exhibit comparable activity to Cu-ZSM-5 when using propene as a reductant [91], however, the peak activity was observed at lower temperatures. In-ZSM-5 has also been shown to be active in the SCR reaction using methane as a reductant. High conversions were reported over the temperature range 573-873 K. Pb-ZSM-5 has been seen to exhibit high activity for the reduction of NO by propene, in the temperature range 623-823 K [91]. Cr-ZSM-5 has been found to demonstrate low activity for the SCR reaction, for all reductants tested [69]. These results are general agreement with other literature reports, indicating that Cu-exchanged zeolites are the most active catalysts in the low temperature range (≤ 623 K).

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1.6.5 Rare Earth Zeolites

Rare earth ion-exchanged Y zeolites have been examined by Misono and Kondo [92] for the reduction of NO by propene. Tests showed that Ce and Pr-Y zeolites exhibit significant activity for the reaction. The observed maximum NO conversion levels with these catalysts, however, were found to be significantly lower than levels obtained with transition metal (Cu, Co and Zn) ZSM-5 zeolites. The temperature of maximum NO conversion were reported to be 673 and 723 K for the Ce and Pr-Y zeolites respectively. Misono and Kondo [92] also tested a Ce-ZSM-5 zeolite which was found to be more active than the Ce-Y, and showed a maximum conversion of NO at 673 K. Ce-ZSM-5 proved more active than Cu-ZSM-5 at 573 K. The addition of alkaline earth metal ions such as Mg, Ca, Sr and Ba has been found to enhance the activity of Ce-ZSM-5 catalyst, particularly at temperatures above 623 K [91]. A mechanical mixture of Ce-ZSM-5 and Mn₂O₃ was found to be more active than Ce-ZSM-5 alone, by employing Mn_2O_3 as an oxidising agent for NO [93,94,95]. Misono and co-workers were able to propose a mechanism whereby Mn_2O_3 oxidises NO to NO₂ and Ce-ZSM-5 subsequently reduces NO₂ to nitrogen. A similar mechanism was presented for Ce-ZSM-5 alone. The first step remained the oxidation of NO into NO2, the latter then reacted with the hydrocarbon to form compounds of a nitro type which decompose into nitrogen or N₂O, via several intermediates.

1.6.6 Metallosilicates

Certain metallosilicates have also been reported as potential catalysts for the reduction of NO by hydrocarbons. Inui *et al* [96] examined a series of metallosilicate catalysts with the ZSM-5 structure for the selective reduction of NO. The metallosilicates studied can be divided into three main groups. The first set included metal cations in the framework of the metallosilicates, which were not easily reducible but generated strong acidity (Al and Ga), the second set contained metal cations which were partially reducible (Fe, Mn and Cr), and the third set consisted of a cation which was easily reducible (Cu). Protonated Fe-silicate had strong acidity, while protonated Mn and Cr silicate showed only limited acidity and protonated Cu-silicate showed essentially no acidity. Using cetane as a model hydrocarbon, they reported that the catalysts containing Fe-Mn and Cr were the most active for the reduction of NO, with the Fe-silicate system being the most active catalyst of the group.

These results suggest that the presence of both acidity and reducible cation are important factors in a catalyst effective for the reduction of NO.

Kikuchi *et al* [97] studied Fe, B and Ga silicates, which have similar structures to ZSM-5, for the reduction of NO using propene as the reductant. They demonstrated that HB and HGa-silicate underwent initial deactivation at 573 K. Steady state activities were approximately 20% of the activity of HFe-silicate, which on the contrary underwent an initial activation period. The activity of the HFe-silicate catalyst was found to compare favourably with an H-ZSM-5 zeolite tested under identical conditions. It was also reported that the catalytic activity of Fe-silicate was not affected by the presence of SO₂.

1.7 Mechanisms for the SCR Reaction

The mechanism of NOx reduction, by hydrocarbons, under lean oxidising conditions has attracted much attention. The different reaction mechanisms that have been proposed can be roughly classified into decomposition mechanisms and reduction mechanisms [98]. In the former mechanisms NO, is catalytically decomposed to nitrogen and surface oxygen, the added hydrocarbon are present to regenerate the active site. A reductive mechanism involves a direct interaction between an activated hydrocarbon, a partially oxidised hydrocarbon or a carbonaceous species and NOx. The reaction may then proceed by a series of reaction steps via adsorbed nitrogen containing compounds such as nitriles [99], isocyanates [100,101] or organic nitro, nitrite or nitroso compounds [34,67,94,102] which all have been suggested to be key intermediates towards N_2 formation.

1.7.1 Decomposition Mechanisms

Burch *et al* [33,103,104] and Inui *et al* [78] have both published evidence in support of a decomposition mechanism. They both suggest that no direct interaction between the hydrocarbon and the nitric oxide is required. In this view, the purpose of the hydrocarbon is to remove oxygen and to regenerate the active site for the NO decomposition reaction, which occurs by a redox mechanism.

Based upon their studies of NO decomposition over a Cu-Na-A zeolite catalyst in the presence of excess oxygen and cetane, Inui *et al* [78] proposed that the reaction proceeds by a mechanism in which NO is adsorbed on a catalytically active site and decomposed into nitrogen and oxygen. The presence of hydrocarbon serves to reduce the surface oxygen to regenerate the active site. The promoting effect of oxygen was rationalised by formation of a partially oxidised hydrocarbon intermediate which was suggested to be responsible for the faster removal of surface oxygen.

Burch *et al* have examined the catalytic activity of metal exchanged zeolites [103,104] and Pt/Al_2O_3 [33] for the catalytic reduction of NO. Burch and Millington [103] carried out a study of the selective reduction of NO by propene in excess oxygen over Cu-ZSM-5. Gas switching experiments, in which propene was switched in and out of the reaction, were performed in order to probe the mechanism of reaction. Upon the introduction of propene, rapid attainment of steady state activity was achieved but in the absence of propene no sustained activity was noted. These results led Burch and Millington to the conclusion that a

carbonaceous deposit was not responsible for the reduction of NO, instead the mechanism they proposed involved the direct decomposition of NO. They reported that if the active site for NO reaction was an isolated Cu ion within the zeolite, then in the presence of excess oxygen this site would normally be associated with adsorbed oxygen. To generate the active site it was necessary to remove the adsorbed oxygen, this could be achieved by reaction with a suitable reductant. It was found that the chances of NO adsorption are significantly enhanced if the reductant is able to remove more oxygen molecules from the surrounding area in addition to the adsorbed oxygen atom. Propene was suggested to be more active as a reductant than H₂ and CO, as it could consume more oxygen atoms. In the reaction mechanism, adsorption of NO upon the active site(s) results in the formation of a dinitrosyl species, which converts into gaseous N₂O and adsorbed O. The N₂O is then decomposed to N₂ at another active Cu site and the catalytic cycle is complete. The presence of excess oxygen in the reaction mixture was found to enhance the rate of NO conversion to N₂, it was stated that the role of the oxygen was to prevent over reduction of the active Cu⁺ site to the inactive Cu⁰.

Burch and Scire [104] studied the activity of several other metal exchanged ZSM-5 zeolites for the reduction of NO, utilising hydrogen in the absence of oxygen. The purpose of using hydrogen as a reductant was to probe the complex reaction mechanism of NO reduction on zeolite based catalysts. Reduction readily took place under these conditions, and the results were consistent with a simple redox mechanism in which NO adsorption and decomposition on reduced metallic or metal ion sites lead to the formation of gaseous N_2 and adsorbed oxygen; and excluded the participation of carbonaceous deposits or carbon containing species in the reaction mechanism.

Burch *et al* [33] have examined the SCR of NO by propene on 1% Pt/Al_2O_3 using the temporal analysis of products (TAP). They demonstrate that the predominant mechanism for selective NO reduction involves the decomposition of NO on reduced Pt metal sites, followed by regeneration of the active Pt sites by the reductant. The process is initiated by the hydrocarbon reducing a small region of surface Pt-O into metallic Pt. On these activated sites, the adsorption and dissociation of NO takes place. The rate of NO dissociation was found to be temperature dependent. At lower temperatures NO is adsorbed molecularly and only a fraction of it dissociates, some NO will recombine with a N atom which explains the formation of N₂O. As the temperature increases, the complete dissociation into N and O

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atoms occurs and the formation of N_2O is decreased, the most favoured reaction then is the recombination of two adsorbed N atoms to give molecular N_2 . The key step of the mechanism is the competition between NO and O_2 for the reduced sites. Under typical operating conditions, propene was found to be a far more efficient reductant than either CO or H_2 . The greater efficiency is explained on the basis of the additional reducing power of the propene molecule ensuring that patches of reduced Pt are available for NO adsorption reaction. A small additional activity of reduced Pt in the presence of propene has been explained on the basis of a second mechanism involving the carbon assisted decomposition of NO at sites on the reduced Pt adjacent, to give adsorbed carbon containing moieties believed to be fragments from adsorbed propene molecules. For example C(ads) and NO(ads) could combine to give NCO(ads) or CNO(ads) as intermediates on the way to the dissociation of NO(ads).

1.7.2 Reductive Mechanisms

There are many variants on the reductive mechanisms, as highlighted above.

One school of thought suggests the importance of carbonaceous deposits which are reasonably stable on the catalyst in the reaction environment. Kikuchi *et al* [97], Bennet *et al* [105] and Ansell *et al* [106] have all provided evidence that the catalytic activity continues for some time after the hydrocarbon is removed from the reaction mixture, under conditions where a hydrocarbon deposit has been laid down.

Kikuchi *et al* [97] proposed that a long lived carbonaceous species formed on the surface of metallosilicate catalysts was responsible for the reduction of NO by propene. They based their conclusions on the following observations. When propene was removed from the reactant stream, the conversion of NO decreased only gradually to zero, yet when propene was reintroduced the conversion of NO rapidly returned to its original level. They also state that oxygen was a necessary component for the reaction, to activate the carbonaceous species for the reduction of NO.

A temperature programmed reaction study of the activity of Cu-ZSM-5 under an oxidising exhaust gas was performed by Bennet *et al* [105]. Their data shows a first order dependence of NO conversion on propene concentration. They state that these results are in support of a mechanism in which a reactive intermediate capable of reducing NO is generated by the hydrocarbon. The kinetic data are not consistent with this intermediate being CO, but they do not exclude either a partially oxidised species or some form of active coke.

The involvement of a carbonaceous deposit in the reduction of NO is also proposed by Ansell et al [106]. Based on their transient kinetic studies utilising propene as the reducing agent over Cu-ZSM-5, they proposed that the hydrocarbon is converted to a carbonaceous species on the zeolite regardless of whether oxygen is present or not. They suggested that it is this deposited coke species which acts as the reductant for NO and that its reducing ability is greatly enhanced by the presence of oxygen. They demonstrate that over a precoked catalyst, high conversions of NO can be achieved in the presence of oxygen but absence of propene. In the absence of oxygen there is a much lower level of conversion. They state that the role of oxygen is to induce generation of an adsorbed state of NOx (i.e. NO₂ species) on the Cu sites. The results of Montreuil and Shelef [63], indicating that oxygenated organic compounds are also efficient reducing agents, were alternatively explained by Ansell et al [106] in favour of their proposed mechanism. According to their explanation, coke would be formed from cracking of alcohol, aldehydes and ketones, as well as from alkanes and alkenes, on the acidic zeolites and subsequently act as the reactive intermediate. The capability of a reducing agent would thus be determined by the degree of cracking efficiency.

Certain authors suggest that partially oxidised hydrocarbons may be important reaction intermediates. In a report by Kintaichi *et al* [21] it was shown that the selective reduction is closely related to the extent of propane oxidation. The existence of a partially oxidised hydrocarbon intermediate, which is directly involved in the reduction mechanism, was inferred.

It was shown by Sasaki *et al* [32] that NO or NO₂ was reduced to N₂ over Cu-ZSM-5 and Pt/Al_2O_3 , under reaction conditions where the oxidation of propane proceeded. They proposed that the first step of NO reduction over these catalysts was the oxidation of propane to partially oxidised hydrocarbons of the general form (CxHyOz), which then could react with NO or NO₂ to form N₂.

Montreuil and Shelef [68] have shown that some oxygenated organic compounds may be used for the reduction of NO in the presence and absence of oxygen over Cu-ZSM-5. They observe that propanol is a better reducing agent than propene in the absence of oxygen. These results could support the premise that an oxygenated intermediate is formed when using hydrocarbon reductants. They add, however, that the formation of the oxygenated intermediate may not be rate determining for the selective reduction reaction over Cu-ZSM-5 catalysts under the conditions studied, as they observe that the activity of propene is higher than that of propanol in the presence of oxygen.

In a publication by Iwamoto and Mizuno [17], the mechanism of the SCR reaction over Cu-ZSM-5 was discussed. By taking into account that the presence of oxygen was essential to promote the selective catalytic reduction, the formation of a partially oxidised reaction intermediate of the general form (CxHy(O,N)) was suggested to be favoured over a decomposition mechanism or a mechanism involving the transformation of NO to NO₂. A partially oxidised intermediate was favoured on the basis of the following facts:hydrocarbons such as olefins and paraffins with the carbon numbers more than two and three respectively are effective for the SCR reaction and the coexistence of O₂ is essential. They state that the intermediate would have ability to reduce NO selectively at lower reaction temperatures, and that the drop in NO conversion to N₂ at high temperatures is probably due to the severe complete oxidation of the intermediate or the hydrocarbon by oxygen. They also speculate on the structure of the partially oxidised intermediate, and from the work of Ukisu *et al* [100,101], suggest that it may possibly be an isocyanate entity.

d'Itri and Sachtler [65] have demonstrated that on Cu-ZSM-5 catalysts prepared by impregnation, NO reduction is most effective under conditions where propane oxidation was incomplete. They propose that an intermediate of propane oxidation other than CO reacts strongly with NO.

Kharas [67] has suggested that the reaction mechanism for the reduction of NO by propane over Cu-ZSM-5 proceeds initially via the oxidative abstraction of hydrogen from a hydrocarbon to yield a metal alkyl species. The following stage involves the insertion of NO into the metal alkyl bond resulting in the formation of N-nitroso-N-alkylhydroxylamine or oximate ligands which may decompose to nitrogen or nitrous oxide.

Many groups propose that the formation of NO_2 , as reaction intermediate, is a fundamental stage of the overall reaction mechanism. It has been suggested that NO_2 formed during the homogeneous oxidation of NO then proceeds to oxidise the hydrocarbon. Evidence shows that the NO_2 is readily reduced to N_2 by hydrocarbons in the absence of oxygen, whereas anaerobic reduction of NO is very slow. Support for this mechanistic step is found in studies in which NO is replaced by NO_2 in the gas phase over several catalysts, including alumina,

H-ZSM-5 and Cu-ZSM-5. The formation of NO₂ as the first step in the reduction of NO has been suggested by Hamada *et al* [49] and Sasaki *et al* [32] over alumina and H-ZSM-5 and by Petunchi *et al* [107] over Cu-ZSM-5. Shelef *et al* [108] also speculated that the oxidation of NO to NO₂ was an important step in the mechanism, however, they report that the oxidation of NO to NO₂ occurred on Cu sites in Cu-ZSM-5, thereby explaining the much greater over Cu-ZSM-5 than H-ZSM-5.

Several variations of the mechanisms reviewed above have also been proposed. In particular many of them still involve the initial formation of NO_2 in the reaction mechanism, but not necessarily in the gas phase.

A reaction scheme has been proposed by Yokoyama and Misono [94] for the reduction of NO by propene over Ce exchanged zeolites. In this proposal NO₂ is not formed by the gas phase reaction of NO with oxygen, but is the product of a heterogeneous reaction catalysed by Ce ions in the zeolite. In a subsequent step, adsorbed NOx species react with propene to form a nitrogen containing organic intermediate, possibly a nitro or nitrite compound which then decomposes to N₂ upon reaction with NO and or O₂. Experimental support for this scheme is derived from comparison between the rates of NO oxidation to NO₂ and NO reduction to N₂ for the catalysts tested. The authors also detected presence of small amounts of C₂N₂ and HCN in the product and speculate that isocyanate species may be involved also. Therefore they suggest that the mechanism of reduction of NO by propene in excess oxygen may consist of several parallel and consecutive reactions and proceed via several intermediates. Radtke *et al* [109,110] also reported the formation of HCNO during the reduction of NO by propene and ethene over Cu-ZSM-5.

During the reaction of NO/(NO₂) with propene and oxygen on Pt/SiO₂, Tanaka *et al* [34] carried out mechanistic studies using FTIR spectroscopy. They reported the presence of organic species of nitro, nitrite and carbonyl upon the surface. They stated that these species could react rapidly with oxygen and NO₂ to give N₂, N₂O and CO₂, but it is thought that they are inactive towards NO and propene. This mechanism was explained; initially the hydrocarbon reacts with the NO₂, resulting from NO oxidation to generate the nitro and nitrite species, a part of which are transformed further into carbonyl species and the reaction between oxygen and the species containing one nitrogen atom, i.e. adsorbed nitro or nitrite species.

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The reduction of NOx with propene or propane in the presence of oxygen was studied at low concentrations over a 7.4 wt% Cu-ZrO2 and a 3.2 wt% Cu-ZSM-5 catalyst by Bethke et al [111]. The rates of N₂ production were compared in experiments using only NO or a mixture of NO and NO₂ in the feed. They also compared the rates of NO₂ reduction to NO under the same conditions, and of NO oxidation to NO2 in the absence of hydrocarbons. A mechanistic scheme in which adsorbed NO₂ reacted with adsorbed hydrocarbon through two pathways was proposed. The path responsible for N₂ formation results in the generation of an N-containing surface intermediate. This N containing intermediate is further oxidised by NO₂ and or O₂ to form other intermediates which eventually react with NO to produce N2. The data in this study did not provide any indication regarding the nature of this surface species. In a separate report [112] it was shown, with *in situ* isotope labelling experiments, that adsorbed CN and NCO species are formed that react with NO to form N2. A mechanism involving the initial formation of NO₂ is also supported by Shelef [18], for the SCR reaction over copper exchanged and metal-free ZSM-5 zeolite in the presence of oxygen. The formation of NO₂ takes place in the first stage, NO₂ however is not formed via a gas phase reaction but is the product of NO and surface oxygen. This step is followed by gaseous NO₂ desorption. Activation of the hydrocarbon is then thought to take place on Bronsted acid sites by the formation of carbenium ions, which oligomerise. The formation of nitroxy-carbon species occurs by reaction of the oligomers with NO_2 . Finally the surface nitroxy-carbon species then react with NO₂ to form dinitrogen.

It has been demonstrated by Hayes *et al* [113] that when a Cu-ZSM-5 catalyst is exposed to the full SCR gas mixture, features are observed which suggest the presence of organic nitro species. It is stated that no FTIR features are observed of the type seen when these materials are exposed only to NO, thereby demonstrating that the selective NOx reduction by propene follows a different reaction pathway from NO decomposition reactions in the absence of hydrocarbons. At the temperatures of interest, > 570 K, the unsaturated hydrocarbon is more strongly adsorbed than NOx and so its reaction products dominate the spectra. The formation of nitro species was noted to occur also in the absence of gas phase oxygen by interaction with the extra lattice oxygen of the zeolite. The nitro species was presumed to be formed by a simple radical recombination between adsorbed allyl and NO₂ species. In support of this it is noted that the surface concentration of allyl is much reduced when NO₂ or NO oxygen are present. In common with other work, the role of NO₂ rather than NO in the SCR reaction was deemed to be predominant. Decomposition experiments, utilising model compounds such as nitromethane provide support for the inclusion of nitro species in the reaction pathway since they react rapidly in oxygen at the reaction temperature and show the desired selectivity to nitrogen. It therefore seems reasonable to propose that reduction of nitro groups by adsorbed hydrocarbon fragments provides the route to the formation of nitrogen nitrogen bonds band hence the liberation of dinitrogen. In addition Hayes *et al* [99] reported that cyanide species, nitriles, formed upon Cu-ZSM-5 catalysts, at 550 K, under lean SCR reaction conditions. In the absence of oxygen these were retained without decomposition by the catalyst up to temperatures > 750 K. In the presence of oxygen they were selectively oxidised to dinitrogen and carbon dioxide at the same temperature as the selective catalytic reduction of NO. Consequently Hayes *et al* [99] proposed that the nitrile was an important intermediate in the selective reduction of nitrogen oxides to dinitrogen in the presence of hydrocarbons and excess oxygen.

Adelman *et al* [114] have speculated on the mechanism of selective NOx reduction with alkanes over Cu-ZSM-5, in their study utilising propane as the hydrocarbon reductant. They suggest that an adsorbed NOy complex, not gaseous NO₂, plays an important role in the catalytic mechanism. In this work, it is suggested that initially NO reacts with oxygen to form an adsorbed NOy group where $y\geq 2$. A propane molecule then reacts with the NOy(ads) group, undergoing H abstraction to form a sec propyl radical. This radical then reacts with a gas phase NO molecule to form 2-nitrosopropane which is unstable and spontaneously isomerises to acetone oxime which then reacts swiftly to form N₂ and N₂O. Isotopic labelling shows that the nitrogen-nitrogen bands are formed between two nitrogen atoms with different histories, one from a NO molecule and one from an adsorbed oxime complex.

1.8 Catalyst Characterisation

An immense number of characterisation studies have been performed, pertaining to the catalysts described in section 1.6, and also related to the mechanisms discussed above, in section 1.7. Characterisation material, relevant to this particular research work, will be mentioned and discussed at relevant points in this thesis.

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Chapter 2 Experimental

2.1 Catalyst Preparation

2.1.1 Zeolite ZSM-5 Starting Materials

Three separate batches of NH_4^+ -ZSM-5 zeolite were obtained from CATAL (Sheffield). The zeolites were supplied as D411 Si:Al = 25, C411 Si:Al = 25, (in this sample the presence of extraframework aluminium was detected from the infrared spectrum, this was quantified by solid state NMR to afford a framework Si:Al = 34) and C405 Si:Al = 15, (this sample also contained a significant amount of extraframework aluminium, visible from the infrared spectrum, this has been quantified by solid state NMR to afford a framework Si:Al = 31). NH_4^+-ZSM-5 was calcined in static air at 773 K for 4 hours to produce H-ZSM-5, which was used in the preparation of metal loaded zeolite catalysts.

2.1.2 Preparation of Copper ZSM-5 Catalysts

Cu-ZSM-5 catalysts were prepared via a conventional multiple ion exchange procedure from H-ZSM-5 zeolites, prepared as described above. 3 g of the parent zeolite H-ZSM-5 was added to 150ml of a 0.01M solution of copper (II) acetate (BDH, 99%) in distilled water or ethanol. The solution was stirred at room temperature overnight. The catalyst was then separated by filtration, washed with either distilled water or ethanol and then dried in air, for 24 hours 298 K. This exchange procedure was then repeated, in some cases up to 5 times, to achieve the desired level of exchange. The extent of copper loading in the zeolite was determined via ICP analysis kindly conducted by Johnson Matthey Plc.

2.2 Catalytic Microreactor Testing

2.2.1 Catalytic Microreactor



Figure 2.1 Catalytic microreactor design

A schematic illustration of the catalytic microreactor, designed to provide a model automotive exhaust, is depicted in Figure 2.1. The microreactor was fed by four independent pressure regulated gas lines, gas flow rates were accurately controlled by Brooks thermal mass flow controllers, model 5850TR. The gases used to create the simulated exhaust gas were 5% nitric oxide in helium, 1% propene in helium, 20% oxygen in helium and helium alone (functioning as a diluent). All the gases used were supplied by Air Products Ltd. The four gas lines merged into a single line to enable mixing of components. The simulated exhaust gas could then be directed through the catalyst bed or via a bypass route. The catalyst bed was situated in the centre of a 1/2 inch stainless steel reactor tube between two plugs of silica wool. The reactor tube was contained within a Carbolite tube furnace, the temperature of which was regulated via a 91E Eurotherm temperature controller. The products of reaction were monitored by on-line gas chromatography and an on-line chemiluminescence NOx analyser run in series. A back pressure regulator positioned between the GC and the NOx analyser was used to maintain atmospheric pressure in the reactor and the GC sample loop whilst the NOx analyser operated under vacuum. The NOx content in the feed could also be monitored by the chemiluminescence NOx analyser.

2.2.2 Gas Chromatographic Analysis

The underlying principle of chromatography in general is the variation in the rate at which different components of a mixture migrate through a stationary phase under the influence of a mobile phase [1,2].

Gas samples from the microreactor exhaust were analysed by means of gas solid chromatography (GSC), so called because the mobile phase is a gas and the stationary phase is a solid. The apparatus used was a Pye Unicam PU4550 gas chromatograph equipped with Molecular Sieve 5A and Porapak QS columns and fitted with a thermal conductivity detector (TCD) and coupled to a Chromjet electronic integrator. The gas chromatograph operating conditions employed were a column oven temperature of 308 K, detector temperature of 493 K and TCD filament temperature of 593 K.

Samples of the product gas were introduced into the gas chromatograph via the 6 port gas sampling valve depicted in Figure 2.2 A, using a 1.25ml sample loop. Diagrams illustrating the configuration of the gas sampling valve, column switching valve and columns are given in Figure 2.2. A and B. Once injected, the sample could elute through both columns in series or through the Poropak alone. Sampling and column selection for each injection was controlled via the electronic integrator. An oxygen trap was used between the molecular sieve and the TCD to improve nitrogen resolution (on the molecular sieve column) and protects the TCD filaments. The flow rate of helium carrier gas through the column assembly was set at 20ml min⁻¹ and was balanced by an identical flow through the TCD reference channel. Changes in carrier gas flow rate when the molecular sieve column was bypassed were prevented by the use of a restricter valve which provided an equivalent pressure drop.

Analysis of the microreactor exhaust gases by the gas chromatograph was limited to nitrogen, nitrous oxide_and carbon dioxide. The electronic integrator was used to interpret the output from the TCD, Figure 2.3 shows a typical gas chromatograph trace for product analysis.



A



Figure 2.2 Gas chromatograph valve and column configuration



Figure 2.3 A typical GC trace for product analysis

In order to analyse for all the products, two separate sample injections were required. The first injection passes through the Porapak column only and analyses for carbon dioxide and nitrous oxide. The second injection was made with both columns in series, once oxygen and nitrogen had entered the Molecular Sieve column it was isolated by switching until the carbon dioxide and nitrous oxide passed over the detector The Molecular Sieve column was then switched back in and the nitrogen was allowed to elute. Residual propene and water trapped on the Porapak column were removed by raising the column oven temperature to 423 K with the Molecular Sieve column isolated. The detector was calibrated for various concentrations of nitrogen, carbon dioxide and nitrous oxide using a mixed calibration gas obtained from ARGO consisting of 1000ppm carbon dioxide, 1000ppm nitrogen, 1000ppm nitrous oxide.

2.2.3 Thermal Conductivity Detector



Figure 2.4 A schematic illustration of a thermal conductivity detector (TCD)

The thermal conductivity detector (TCD) or as it is also known the Katharometer is depicted in Figure 2.4. The TCD is based on the principle that a hot body loses heat at a rate which is dependent on the thermal conductivity, and therefore the composition, of the surrounding gas [1]. The TCD consists of two heated filaments of a metal which has a high coefficient of resistance, and which forms two arms of a Wheatstone bridge circuit. The two separate filaments are situated in a separate channels on a heated metal block. Pure carrier gas flows through one channel (reference channel) and the effluent from the column through the other. A change in thermal conductivity of the gas flowing through the sample channel, arising from elution of a sample component, alters the temperature and hence the resistance of the filament in that channel. This produces an out of balance signal in the bridge circuit which manifests itself as a peak on the integrator trace, as in Figure 2.3.

2.2.4 Chemiluminescent NOx Analysis

In addition to analysis for carbon dioxide, nitrous oxide and nitrogen via gas chromatography, the microreactor exhaust was also analysed for oxides of nitrogen NOx $(NO + NO_2)$ by an on line chemiluminescent NOx analyser (Signal Instruments Model 4000). Operation is based upon the chemiluminescent gas phase reaction between ozone and nitric oxide, to give nitrogen dioxide and oxygen [3,4]. Approximately 10% of the nitrogen dioxide produced is in an electronically excited state and during the transition from this state to the ground state, molecules lose energy, giving rise to the emission of visible light.

$NO + O_3 \rightarrow NO_2 + O_2 + hv$

The intensity of the emission is proportional to the mass flowrate of nitrogen dioxide into the reaction chamber, and is measured by means of a photomultiplier tube. From this the exact amount of nitrogen dioxide present in the sample can be calculated. The instrument was calibrated using the mixed calibration gas supplied by ARGO, already. The calibration of the instrument was linear, at least, up to 10000ppm nitric oxide. As only a small proportion of the excited nitrogen dioxide molecules lose energy by emitting light, the analyser operates at low pressure, in order to maximise the light output from the chemiluminescent reaction. Low pressure operation also minimises the effects of interference from other gases which are known to deactivate excited nitrogen dioxide, such as carbon dioxide and water vapour.

As only nitric oxide can be detected by chemiluminescence, a converter is incorporated within the analyser, to convert any nitrogen dioxide to nitric oxide, which can then be quantified as above. Conversion of nitrogen dioxide to nitric oxide is carried out by passing the gas through a heated tube containing a carbon material. Part of the conversion is accomplished thermally.

$2NO_2 + Heat \rightarrow 2NO + O_2$

The remainder of the conversion is carried out by carbon chemically reducing nitrogen dioxide.

$$NO_2 + C \rightarrow NO + CO$$

 $2NO_2 + C \rightarrow 2NO + CO_2$

When the gas is passing through the converter the analyser is said to be in NOx mode, when the gas is by-passing the converter the instrument is said to be in NO mode.

2.2.5 Catalytic Testing

Catalytic evaluation experiments were carried out using the fixed bed microreactor described earlier.

All catalysts were pelleted and sieved to particle diameter of 0.6-1.0 mm before being loaded into the reactor tube. Generally 0.25 g, 0.6 cm³, of material was used.

Prior to catalytic testing, all catalysts were calcined at 773 K for 1 hour in flowing $2\%O_2$ in helium.

The performance of the catalysts for the selective reduction of NOx was expressed in terms of conversion of NO or NOx to NO₂, N₂, N₂O and of C_3H_6 to CO₂. Catalyst performance was determined using both the output from the gas chromatograph and the chemiluminescent NOx analyser.

The chemiluminescent NOx analyser can analyse for NO and NOx (NO+NO₂). Under some conditions it is useful to be able to operate the chemiluminescent analyser in either NO or NOx mode. For example under conditions when some NO may be converted to NO_2 . Information derived from the NOx analyser output is outlined in below,

% NOx Conversion = $(1 - (\text{Residual NOx ppm}) \times 100)$ = % Conversion $\rightarrow N_2O+N_2$ (Feed NOx ppm)

% NO Conversion = $(1 - (\text{Residual NO ppm}) \times 100)$ = % Conversion $\rightarrow \text{NO}_2 + \text{N}_2\text{O} + \text{N}_2$ (Feed NO ppm)

Feed gas analysis demonstrated the presence of a small quantity of NO_2 . Therefore conversions could be described as either NO conversion or NOx conversion, dependent on the difference between residual NO_2 values compared with the initial value present.

From the GC, the following further information was obtained.

%Conversion of NOx \rightarrow N ₂	_	$\frac{2 \text{ x ppm } N_2 \text{ produced}}{\text{ ppm of NOx in feed}} \qquad x 1$	00
%Conversion of NOx \rightarrow N ₂ O	=	$\frac{2 \text{ x ppm N}_2\text{O produced}}{\text{ppm of NOx in Feed}} \times 10^{-10}$	00
%Conversion of $C_3H_6 \rightarrow CO_2$	=	$\frac{\text{ppm CO}_2 \text{ produced}}{3 \text{ x ppm of C}_3 \text{H}_6 \text{ in Feed}} \times 1$	00

Steady state rates of reaction were measured, Starting at 773 K and cooling in 25 degree increments to 473 K, using a reactant gas mixture of 2000ppm NO, 1200ppm C_3H_6 , 2%O₂

in a balance of helium, typical GHSV 30,000 h^{-1} . Turnover numbers for the Cu-ZSM-5 catalysts were expressed as molecules of NOx (NO+NO₂) converted to dinitrogen per copper site per second.

The activity of a carbonaceous residue deliberately deposited on Cu-ZSM-5 catalysts for the selective reduction of NOx was investigated. Before studying the reactivity, carbonaceous deposits were laid down by passing the reactant mixture over the catalyst at 473 K or 573 K, a procedure known to form hydrocarbon or coke deposits [5]. The catalyst was then heated to 923 K at 10 K per minute in a mixture of NO 2000ppm and 2% O_2 (balance helium), the extent of NOx conversion was monitored continuously using the chemiluminescent NOx analyser.

2.3 Catalyst Characterisation

2.3.1 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy can be used to study an adsorbed phase at a surface [6,7,8]. Absorption of electromagnetic radiation in the IR region (5000-200cm⁻¹) leads to transitions between both vibrational and rotational energy levels of molecules. The rotational modes of the adsorbed molecules are restricted and only vibrational modes are observed. Only the vibrations which lead to a change in dipole moment are infrared active. The position of bands in an IR spectrum is dependent on the strength of the vibrating bond, the nature of the vibration and the masses of the atoms in the vibrating group.

For many years infrared spectroscopy was performed using dispersive spectrometers. In a dispersive instrument radiation of only a single wavelength is incident on the sample at any time and the spectrum is obtained by measuring the absorption as the wavelength is scanned. The technique of infrared spectroscopy has been revolutionised by application of Fourier transform methods. The heart of a FTIR spectrometer is an interferometer, operating on a principle developed by Michelson in ca 1890, and is shown schematically below in Figure 2.5.



Figure 2.5 A schematic illustration of the Michelson interferometer

The essential components are an infrared source, two mirrors (one stationary and one moving), a beamsplitter and a detector. The primary output from the spectrometer is the interferogram which plots the intensity of radiation at the detector as a function of the

moving mirror's position. When the interferogram is subjected to a mathematical manipulation called Fourier transformation, the result reflects the intensity of the source. Placing a sample in the path of the radiation modifies the interferogram and the resulting Fourier transform is the complete infrared spectrum.

There are several ways in which the quality of the IR spectrum is improved by Fourier transform methods over traditional dispersive instruments and these are referred to as advantages.

(I) Fellget's advantage is the ability to sample all wavelengths of interest simultaneously, leading to an increased speed of analysis and also leads to a significant improvement in signal to noise compared to dispersive instruments.

(II) Jacquinot's advantage results from the fact in a Fourier transform instrument there are no slits and fewer optical elements, and so the energy used and the sample size may both be bigger than in dispersive instruments leading to improved sensitivity.

(III) Conne's advantage relates to the accuracy with which the frequency can be defined in the spectrometer. FTIR spectrometers use a laser of accurately known, constant frequency, to calibrate the interferogram. As a result, frequencies are very accurately defined.

In this work, IR experiments were carried out using an ATI RS1 Fourier transform spectrometer in transmission mode. The sample was pressed into a self supporting wafer and placed in a specially constructed in situ cell which could be heated to > 800 K. Once in the cell, the sample was then exposed to the desired chemical environment while an IR beam was passed through the sample.

Transmission FTIR was used to examine the copper exchanged zeolite samples. Samples were calcined ex situ in static air at 773 K for 4 hours. Once the samples were installed in the cell, the samples were activated in 10mbar O_2 at 423 K. Deposition of carbonaceous residue on Cu-ZSM-5 samples was also examined. Coke was deposited on Cu-ZSM-5 samples by exposing the catalyst of interest to a reaction mixture consisting typically of 2 mbar NO, 1 mbar propene and 7 mbar oxygen at 473 K or 573 K.

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2.3.2 X-ray Photoelectron Spectroscopy & X-ray Auger Electron Spectroscopy



Figure 2.6 The principle of X-ray photoelectron spectroscopy and X-ray excited Auger electron spectroscopy

The principle of X-ray photoelectron spectroscopy (XPS) is illustrated on the left hand side of Figure 2.6 [8,9,10]. During XPS the surface of the catalyst under examination is irradiated with a beam of soft monoenergetic X-rays. They interact with atoms in the surface region causing the emission of photoelectrons. Typical X-ray sources are MgK α (1253.6ev) or AlK α (1486.6 ev). The kinetic energy of the emitted photoelectrons is given by the equation.

$$KE = hv - [BE + \phi]$$

BE is the binding energy of the core hole involved, hv is the photon energy which is fixed and ϕ is the work function of the spectrometer. In addition to the photoelectrons emitted by the photoelectric process, Auger electrons are emitted due to relaxation of the energetic ions left after photoemission. In the Auger process, an outer electron falls into the inner orbital vacancy and a second electron is emitted, removing the excess energy. The principle of X-ray excited Auger electron spectroscopy (XAES), is depicted on the right hand side of Figure 2.6.

XPS is a surface sensitive technique, only probing about the top 2nm of the solid sample. It is sensitive to the chemical environment being studied, in particular peak positions are dependent on oxidation states. A typical photoelectron spectrum is shown in Figure 2.7.



Figure 2.7 A typical Mg Ka X-ray photoelectron spectrum of a Cu-ZSM-5 catalyst

In this thesis XPS and AES have been used to probe the nature of the metal cations at the catalyst surface. Experiments were carried out on a VG ESCA 3 spectrometer. This consisted of three main parts, the X-ray source (a magnesium or aluminium anode), the analyser, and the detector, and is depicted schematically in Figure 2.8. The analysis chamber houses the analyser, the magnesium and aluminium anodes and a photomultipler detector. This section was separated from a preparation chamber by a gate valve. The zeolite samples, examined as either as-prepared or calcined ex situ, were deposited onto the sample holder as a powder. The sample holder was mounted on a retractable screw, this enabled simple transfer of the sample between the preparation chamber and the analyser chamber, and was aligned at 45° to the impinging beam of X-rays. Once the preparation chamber was evacuated, the sample holder was wound through the gate valve into the analysis chamber,

then evacuated to approximately 10^{-7} mbar and the sample cooled by liquid nitrogen before any spectra were recorded.

Spectra were measured at an X-ray anode potential of 10kV and an electron bombardment current of 20mA, using an analyser pass energy of 20eV. A wide scan from 0-1000 eV at 0.5 eV steps was performed initially, after which regions of interest were selected and narrower scans performed.



Figure 2.8 A schematic illustration of the VG ESCA 3 spectrometer

2.3.3 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy examines the detail contained in the absorption spectra near to an absorption edge [8,11,12].

Absorption of X-rays by a solid material increases substantially when the photon energy becomes equal to the binding energy of any shell of electrons in an atom in the sample under study. When photon energy is sufficient to promote an electron from the core level to a vacant orbital at the Fermi level, an increase in absorption occurs and the spectrum is said to exhibit an absorption edge. Figure 2.9 indicates that as well as an absorption edge, there are oscillations or fine structure in the absorption.



Figure 2.9 A typical X-ray absorption spectrum of a Cu-ZSM-5 catalyst

The spectrum is divided into two main regions, the near edge structure, (NEXAFS or XANES) which includes the edge and up to ca 50 eV above, while the extended fine structure (EXAFS) may extend up to 2000 eV above the edge.

The sharp absorption edge provides a fingerprint of the local environment of the absorbing species. The shape of the near edge depends on the coordination environment and on the identity of the ligands or nearest neighbours. The position of the absorption edge depends on the oxidation states present within the sample

The EXAFS region provides a method of examining the local structure surrounding an element of interest in a catalyst, and is most useful when there is insufficient long range order for XRD to be useful.

In this thesis, information derivable from the XANES region of the spectrum was not utilised, only the data obtained from the EXAFS region was used here. EXAFS, in transmission mode, was used to investigate the local environment of the metal ions in the zeolite, to obtain coordination numbers and interatomic distances.

Experiments were conducted at the CCRL Daresbury Laboratory, on beamline 9.3. An outline of the experimental apparatus used is shown in Figure 2.10.



Figure 2.10 Schematic illustration of experimental apparatus used in an EXAFS experiment

Station 9.3 provides a source of white X-rays which, by means of a Si 220 monochromator, provides a suitable range of X-ray energies. The required experimental parameters were set up around the Cu K absorption edge. The ionisation detectors used to measure X-ray absorption were filled with the appropriate mixtures of inert gases, and a standard sample, in this case Cu foil, was placed in the X-ray beam. A Cu K edge spectrum in the range 3-12 Å, consisting of three scans, was then collected using EXAFS data collection software.

Catalyst samples were prepared by pressing self supporting discs with thickness dependent on the content of the element under study. A Cu K edge spectrum in the range 3-12 Å, consisting of three scans, was collected. The spectra were analysed using the following data interpretation software packages EXCALIB, EXBACK and EXCURV 92.

2.3.4. X-ray Powder Diffraction

X-ray diffraction (XRD) is the method of choice for the elucidation of the structure of crystalline solids. In catalyst characterisation, XRD is applied to the identification of crystalline phases, for the determination of the structures of catalysts [8,13].

XRD is based on the principle that when a beam of X-rays is incident on a crystalline solid, diffraction occurs when the angle of incidence on planes of atoms in the structure satisfies the Bragg equation.

$n\lambda = 2d. \sin \theta$

where n is a small integer, λ is the wavelength of the monochromatic X-ray beam (1.542 Å for a copper target), d is the separation between planes in the crystal and θ is the angle of incidence of the X-rays. For a single crystal the Bragg condition will not be satisfied at any arbitrary angle of incidence, only at specific orientations of the crystal with respect to the source and detector are X-rays reflected from planes. If the sample is a finely ground crystalline powder containing many randomly orientated crystallites some will always satisfy the Bragg equation and diffraction will occur. This is the basis for powder diffraction, which is illustrated schematically in Figure 2.11. XRD is most effective when performed on single crystals, however as single crystals are rarely available for catalyst samples, powder diffraction is the characterisation method commonly used.



Figure 2.11 A schematic illustration of an X-ray power diffractometer

A powder diffraction pattern is shown in Figure 2.12. A refection is observed corresponding to a plane of atoms in the structure which satisfies the Bragg equation, with an intensity relating to the electron density within the plane and the local arrangement of atoms in the unit cell. The X-ray powder pattern is a characteristic fingerprint of the phase coexisting in a catalyst. In this work, X-ray powder diffraction was used to examine the various phases present in the zeolite samples.

Diffraction experiments were carried out on a Hiltonbrooks modified Philips 1050 powder diffarctometer, with CuK α radiation, operating the generator at 42.5 kV and 18 mA.



Figure 2.12 A typical powder XRD pattern of a Cu-ZSM-5 catalyst

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Chapter 3 Influence of Copper Ion Exchange Level on the Activity of Cu-ZSM-5 Catalysts for the Lean SCR Reaction

3.1 Background

The exceptional activity exhibited by copper ion exchanged ZSM-5 zeolite catalysts for NO decomposition and for the selective catalytic reduction of NOx by hydrocarbons in the presence of excess oxygen is well documented [1-10]. The nature of the active copper species in the SCR reaction however still remains uncertain.

The coordination environment of Cu^{2+} cations in the ZSM-5 zeolite matrix has been studied by the electron spin resonance (ESR) technique. Kucherov and Slinkin showed that a calcined Cu-ZSM-5 catalyst contained two discrete types of isolated coordinatively unsaturated Cu(II) cations, with square planar and square pyramidal coordination [11]. The same authors also demonstrated that the catalytic activity of Cu-ZSM-5 in hydrocarbon oxidation reactions could be correlated with the concentration of copper cations in discrete ion exchangeable sites [12,13]. Activity was shown to depend on the Cu²⁺ site topography. The sample of Cu-ZSM-5 which contained the most coordinatively unsaturated square planar Cu(II) cations by far exceeded the activity of the samples containing five coordinate square pyramidal Cu(II) ions.

Information about the Cu^{2+} environment has also been obtained by electron spin echo envelope modulation (ESEEM) spectroscopy. This technique provides information about the proximity of Cu^{2+} cations to framework aluminium atoms. Kevan *et al* [14] have studied the location and mobility of copper ions by the interaction of adsorbates on Cu-ZSM-5 using ESR and ESEEM spectroscopy. It was suggested that the adsorption of molecules such as water, alcohol, pyridine and ammonia causes the migration of Cu^{2+} to the main channel. Masai *et al* [15] have studied the redox behaviour and mobility of the Cu ions in Cu-Na-ZSM-5 during benzyl alcohol oxidation by recording IR bands of CO adsorbed on cuprous ions. The Cu ions have been suggested to migrate from a recessed site to a more open space, such as a channel intersection, by the adsorption of benzyl alcohol. The oxidation activity of benzyl alcohol was dependent on the location of the Cu ions.

Anpo *et al* [16] employed Cu^+ luminescence spectra to characterise the copper sites present in Cu-ZSM-5 and found two bands at 450 and 540 nm, which they ascribed to monomeric

and dimeric Cu^+ species respectively, analogously to the assignment of Barrie *et al* [17] for Cu^+ supported on alumina.

Wichterlova et al [18-21] also demonstrated that the coordination of copper in Cu-ZSM-5 zeolite catalysts can be characterised by Cu⁺ luminescence spectra. In their publications, they claimed that after Cu(II) reduction to Cu(I), Cu-ZSM-5 contains two dominant types of copper site differing in location and coordination. One copper site is expected to be close to two aluminium framework atoms where Cu^{2+} ions are coordinated without an extralattice ligand. This site is reflected in the blue (480 nm) Cu⁺ photoluminescence band. The second site adjacent to one aluminium atom most likely involves Cu^{2+} with an extraframework oxygen or hydroxyl ligand, for example di or polymeric (-Cu-O-)n species, which originate from the $(Cu^{2+}-OH)^+$ exchanged cations, which bear an extraframework oxygen. This second site is characterised by a yellow/green Cu⁺ photoluminescence band at (540 nm). The distribution of Cu between sites has been found to depend on the number of copper ions exchanged. The species characterised by the emission at 540 nm was present in Cu-ZSM-5 regardless of copper concentration but was found to prevail in zeolites with a high Si/Al and with copper content approaching and exceeding an ion exchange level of 100%. These authors also state that exchange of copper using the copper (II) acetate precursor leads to a higher number of these sites than the copper (I) chloride precursor. A significant observation made in these studies was that the activity for NO decomposition of these catalysts, expressed as a turnover frequency was proportional to the number of Cu sites exhibiting luminescence at 540 nm. These authors state however that a final conclusion cannot be drawn as to whether the active site characterised by the Cu⁺ photoluminescence band at 540 nm is represented by some long range Cu⁺...Cu⁺ dimer, as previously suggested for Cu-ZSM-5 [16] and for Cu⁺ ions supported on alumina [17] or by a Cu⁺ monomer. They do state however that the active species are sites originating from the $(Cu^{2+}-OH)^+$ cations present in the salt solution; which enter the cationic sites balanced by one framework Al, and which transform upon zeolite dehydration probably into charged species bearing extra lattice oxygen (ELO). In a later study [21] these authors suggest that the copper complex associated with the Cu⁺ photoluminescence band at 540 nm exhibits an open coordination. This was supported by a semi quantitative correlation between the intensity of the Cu⁺ photoluminescence band at 540 nm and the intensity of the ESR signal ascribed to Cu²⁺ in a planar environment. They also suggest that the copper complex attributed to the Cu⁺

photoluminescence band at 480 nm reflects a more packed environment, corresponding to an ESR signal attributed to a square pyramidal coordination.

The results of Wichterlova *et al* would therefore appear to imply that NO activation can proceed on single Cu cations; however, the (Cu-O-)n species bearing an extralattice oxygen and possessing close Cu ions are believed to contribute substantially to the high and stable activity of the Cu ZSM-5 zeolites [18-21].

A number of researchers have suggested the presence of an entity where copper is associated with ELO (e.g. the bridged $[Cu-O-Cu]^{2+}$ species) in over exchanged Cu-ZSM-5 zeolites, and have considered them to be important active species in the NO decomposition and the selective catalytic reduction reaction.

Iwamoto *et al* [22] state that during the preparation of ion exchanged Cu-ZSM-5 catalysts the formation of $[Cu(OH)]^+$ takes place, it is believed that attainment of loadings in excess of 100% is achieved via this species. Thermal decomposition of this complex was proposed to result in the formation of $[Cu-O-Cu]^{2^+}$, thought to be an active species for NO decomposition. The appearance of Cu⁺ at elevated temperatures was suggested to be due to the dimerisation or polymerisation of $[Cu(OH)]^+$ species by a dehydration mechanism to form $[Cu-O-Cu]^{2^+}$ species and subsequent reduction of Cu²⁺ by $\frac{1}{2}$ O₂ evolution.

Sarakany *et al* [23] used TPR, TPD and FTIR to characterise excessively ion exchanged Cu/Na-ZSM-5 catalysts, after calcination in oxygen at 773 K at least two types of copper oxygen species are present in addition to Cu^{2+} ions, these have been identified as CuO and $[Cu-O-Cu]^{2+}$. They also propose that the $[Cu-O-Cu]^{2+}$ species is auto-reduced to Cu^{+} during outgasing in helium or argon.

According to Valyon and Hall [24,25] and later to Jang, Hall and D'Itri [26], the maintenance of charge balance in excessively ion exchanged Cu-ZSM-5 catalysts requires the incorporation of extralattice anionic ligands, for example an oxygen atom or a hydroxyl group. Their studies led to the conclusion that (ELO) is carried into the zeolite during the exchange process. A portion of the Cu²⁺ is known to exchange into the zeolites as [CuOH]⁺. It is well known that within these zeolites the copper species readily exhibit interconversion between Cu(II) and Cu(I), depending on the environment present [4,5]. Valyon and Hall have proposed an explanation for this facile reduction of Cu(II) to Cu(I), the reduction has been associated with oxygen removal. They propose that in systems where Cu(II) cations are linked to extralattice oxygen (ELO) the ELO can be much more easily removed than

framework oxygen. In essence the catalyst is an oxygen carrier which can be reduced by CO, hydrocarbons or by desorption of oxygen at elevated temperatures to afford Cu^+ species. ELO cationic species such as CuOH⁺ or [Cu-O-Cu]²⁺ may exist in the zeolite depending upon the environmental conditions. In sum they suggest that a reversible reaction is present in which the CuOH species may be dehydroxylated and rehydroxylated, as follows.

$2[Cu^{2+}OH^{-}]^{+} \leftrightarrow [Cu-O-Cu]^{2+} + H_2O$

This suggests that the often postulated bridged copper/oxygen can be formed from two hydroxylated cations by this simple condensation reaction. They do not specify the location of these ions nor how the charge is spread out to neutralise that on the zeolite framework.

EPR spectroscopy was utilised by Larsen *et al* [27] to probe the oxidation state and coordination environment of Cu in ion exchanged Cu-ZSM-5. It was suggested that $Cu^{2+}O^{-}$ moieties were formed by dehydration of $(Cu^{2+}-OH)^{+}$ ions and that the $Cu^{2+}O^{-}$ and Cu^{+} ions were responsible for the activity in NO decomposition reaction. A mechanism for autoreduction of Cu^{2+} in Cu-ZSM-5 was advanced in which Cu^{2+} is auto-reduced to Cu^{+} and $Cu^{2+}O^{-}$ that was consistent with the EPR data. Based on the assumption that Cu is substituted in zeolite as $(Cu^{2+}-OH)^{+}$ the following mechanism for is suggested.

 $[Cu^{2+}-OH]^{+} \leftrightarrow Cu^{+} + OH$ $[Cu^{2+}-OH^{-}]^{+} + OH \leftrightarrow Cu^{2+}O^{-} + H_{2}O$

This mechanism however contrasts with previously reported mechanisms involve the presence of Cu pairs and spontaneous desorption of oxygen.

Cu-ZSM-5 catalysts have been characterised, by X-ray photoelectron spectroscopy and in situ X-ray absorption spectroscopy, by Joyner *et al* [28,29]. The combination of structural and surface analysis allowed the local structure, chemistry of copper ions and the nature of the active sites in NOx reduction to be examined. The external surfaces of the as prepared zeolites were found to be highly enriched in copper species. X-ray absorption (EXAFS and XANES) results, and the observation of anomalously high XPS binding energies and unexpectedly low Auger kinetic energy, indicated that copper became well dispersed in the zeolite channels upon pretreatment, in the form of both isolated ions and small clusters containing extralattice oxygen. The catalysts were reported to show varying activity for the reduction of NOx by hydrocarbons in the presence of oxygen, which correlated with the dispersion of the copper within the zeolite. In the active catalysts, both electron

spectroscopy and X-ray spectroscopic measurements indicate that there is ready conversion between Cu(I) and Cu(II), and possibly between clusters and ions, depending the atmosphere present. The Cu(II) state predominates under conditions relevant to lean burn exhaust gas purification. Therefore the equilibrium between Cu(II) and Cu(I) appeared to be significant in maintaining the catalytically active sites. Interconversion between Cu(I) and Cu(II) is facile for both isolated copper sites and clustered species, and the oxidation state depends on the environment. It was also suggested that the bridging oxygen atoms between copper ions may be more active than molecular oxygen for NO oxidation and hydrocarbon activation. Impediment of Cu(II) reduction is observed for exchanged Cu-ZSM-5 catalysts following activation and may indicate higher stability of [Cu-O-Cu]²⁺ species. Additionally interaction between Cu(II) and framework oxygen may also stabilise the copper in the higher oxidation state. Joyner et al [28,29] concluded that both copper clusters and isolated ions may be necessary to provide the optimum catalytic performance. It seemed likely that low coordinated Cu ions along with Bronsted acid sites are responsible for hydrocarbon activation, while multinuclear clusters can provide reactive oxygen and also promote NO activation. The combination of ions and clusters seems likely to be important in maintaining a proper balance between Cu(II) and Cu(I) states under reaction conditions, since the two copper oxidation states were observed together with the most active ion exchanged catalysts, under both reducing and oxidising atmospheres.

Therefore it has been identified by Joyner *et al* that there are two different types of copper species within the ZSM-5 zeolite channels [28,29]. Isolated copper ions and small clusters where the copper atoms are linked by extra lattice oxygen species such as $[Cu-O-Cu]^{2+}$ dimers are also present. It has also been suggested that the isolated copper ions in ZSM-5 occupy two types of sites, which may have different SCR activity [30,31]

As it is likely that the relative concentration of different isolated copper sites and dimers vary with copper content of the zeolite, this work examines the relationship between the copper content of a series of catalysts and the turnover number for the SCR reaction. Dimeric and other copper clusters are likely to be formed preferentially at higher copper loadings so if they are catalytically important we expect to see turnover number increasing with copper content. Morreti *et al* [32-34] have shown that for NO decomposition the turnover number versus copper loading curve has an S shape, with a very rapid increase above 2 wt % copper.

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As mentioned above a unique and stable activity in NOx abatement has been found for Cu-ZSM-5 zeolites, especially those with a high degree of ion exchange and over exchange of copper. Repeated ion exchange of the ZSM-5 zeolite using aqueous copper (II) acetate solution was found to bring about excess loading of copper ions above nominal exchange capacity [7]. Iwamoto et al [22] stated that it was impossible to prepare excessively ion exchanged ZSM-5 zeolites with copper (II) nitrate or sulphate solutions. His findings suggested that excess loadings of copper ZSM-5 zeolites commonly took place in the presence of an acetate buffer. It was found however that increasing the pH of the solution by the addition of basic compounds readily achieved overexchange copper in the ZSM-5 zeolite [35]. It has been suggested that all the copper may not be active in the Cu-ZSM-5 catalysts overexchanged using this method [36]. Characterisation of these catalysts revealed aggregated copper species on the surface of the catalyst, formed by deposited copper on the ZSM-5 crystals, which are labile and upon calcination can form CuO particles on the zeolite. In this study the authors report that this surface deposited copper is inactive for NO decomposition and stated that the catalytic activity of the ZSM-5 catalysts depends on the copper exchanged in the zeolite channels. Therefore it was concluded that the reported multistep ion-exchange process from dilute cupric solution at pH 5.5-5.6, even if more tedious, is presently the only way one can guarantee the active over exchanged Cu-ZSM-5 state [36].

Much attention has been devoted to the identification of copper species in these overexchanged Cu-ZSM-5 zeolite systems due to their high activity as has been outlined above. If one considers the conclusions reached by authors who studied the state of the copper species in overexchanged Cu-ZSM-5 catalysts; the species that represents the overexchanged portion is thought to consist of dimeric entities or clusters containing two close copper atoms [28,29]. If we consider that conclusion together with the statement made by Iwamoto *et al* [22] i.e. that " It is impossible to prepare excessively copper ion exchanged ZSM-5 zeolites with copper (II) nitrate or sulphate solutions.....The findings suggest that the excess loading of copper ions on zeolites commonly takes place in the presence of an acetate buffer". These two conclusions pose an important question, what is the significance in using copper (II) acetate to prepare excessively ion exchanged Cu-ZSM-5 catalysts, that are more active for the NO decomposition reaction and the SCR reaction? It is therefore an additional aim of this chapter to examine whether or not the fact that

copper (II) acetate exists in the crystal phase as a dimeric entity may be responsible for the formation of dimeric or cluster entities in overexchange Cu-ZSM-5 catalysts. It is desirable to consider copper (II) acetate and to investigate the dimerisation of copper (II) acetate in solution.

In 1953 van Niekerk and Schoenning determined the crystal structure of copper (II) acetate monohydrate [37]. It consists of a binuclear molecule $Cu_2(CH_3COO)_{4.}2H_2O$ in which copper (II) ions are bridged by four acetate groups with two water molecules occupying the terminal positions, as illustrated in Figure 3.1. The striking feature of this six-fold coordinated copper complex is the close approach of 2.64 Å between the two copper ions which is only slightly greater than 2.56 Å, the interatomic distance in copper metal. Following the determination of the crystal structure showing the presence of dimeric species, there has been widespread interest in the chemical form of Cu(II) acetate in solution [38-40].



Figure 3.1. The molecular structure of dimeric copper(II) acetate monohydrate.

The dimeric structure of cupric acetate is found to persist in many non aqueous solvents yet is destroyed in water, forming monomeric hydrated ions. In organic solvents such as alcohols the coordinating power of the ligands are much weaker than the water molecule. Protic solvents such as water promote dissociation. It has been established that a stronger axial ligand coordination tends to weaken the Cu-Cu interaction, i.e. the more basic the axial ligands the more they lengthen the Cu-Cu bond distance. Therefore a general relationship has been established between the donor ability of the axial ligands and the length of the Cu-Cu bond. In weaker donor solvents like ethanol the dimeric structure of copper acetate is preserved while in strong donor solvents like water the solvent molecules are capable of breaking the bridging carboxylate group by displacing the metal carboxylate oxygen bond. The dimeric structure in particular is maintained as a result of the bond competition between the carboxylate ions and the solvent molecules

Copper (II) acetate is characterised by an abnormally low magnetic moment, attributed to a spin exchange mechanism which results from the close proximity of copper atoms in the dimer [38,39]. The magnetic susceptibility of copper (II) acetate in various solvents was examined by Kondo and Kubo by means of a Gouy magnetic balance at room temperature [39]. The investigation was undertaken in order to determine whether or not the dimeric structure persists in solutions of copper (II) acetate in various solvents. It was shown that the structure of copper (II) acetate depends to a considerable extent upon the kind of solvent in which it is dissolved. The value of the effective magnetic moment in ethanol is practically identical with that in the solid state, indicating the presence of the solute in dimer molecule as in the crystal. On the other hand the moments in aqueous solutions are slightly greater than the spin only value 1.73 BM for a single odd electron, leading to the conclusion that copper (II) acetate dissociates into single molecules in these solvents. From the normal moments one can conclude that copper (II) acetate dissociates into single molecules in water. The molecules of water capable of being readily coordinated on metal atoms as ligand are considered to occupy appropriate positions about the Cu atoms thereby breaking the weak Cu-Cu bond in the dimer molecules.

Using absorption spectroscopy in the UV/Vis region, Tsuchida and Yamada [40] found that copper (II) acetate in ethanol showed a new absorption band at 3750 Å, in addition to that observed at 7000 Å commonly observed for copper salts. They attributed the new band to the presence of a dimeric Cu-Cu link in such entities. In contrast aqueous solution of copper acetate show only one broad absorption band at 7000 Å. The absorption of this new band is greatly polarised along the Cu-Cu axis which is the reverse of the polarisation property of the band at 7000 Å.

In addition to the magnetic and spectroscopic behaviour of copper (II) acetate, it has also been demonstrated that if the copper(II) acetate retains the binuclear configuration the solution will exhibit a blue/green colour. A colour change from blue/green to blue will be observed if the dimeric structure is destroyed in solution [38-40].

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In the present study Cu-ZSM-5 catalysts with varying levels of copper loading were prepared via a conventional multiple ion exchange procedure, using dilute aqueous solutions of copper (II) acetate. In addition Cu-ZSM-5 catalysts have also been prepared, via multiple ion exchange, using solutions of copper (II) acetate in ethanol. We examine Cu-ZSM-5 catalysts prepared in ethanol and compare them with Cu-ZSM-5 catalysts prepared from the same parent zeolite through aqueous ion

As mentioned earlier this work examines the relationship between the copper content of a series of catalysts and the turnover number for the SCR reaction. Turnover numbers are calculated for a series of Cu-ZSM-5 catalysts prepared from an ethanol ion exchange media and compared with Cu-ZSM-5 prepared in an aqueous ion exchange media, in order to determine whether the maintenance of copper(II) acetate in its dimeric in the ion exchange solution improves the activity of the resulting Cu-ZSM-5 catalysts. This may support suggestions that the most reactive entities in the SCR reaction consist of dimeric or clustered species comprising of two close Cu sites [32-34].

3.2 Results and Discussion.

The ion exchanged Cu-ZSM-5 zeolite catalysts whose performance in the SCR reaction has been examined in this investigation are listed below in Table 3.1.

Cu-ZSM-5	Parent	Framework	wt% Copper	% Exchange	Preparation
Catalyst	Zeolite *	Si:Al Ratio	loading	Level **	media***
1	D411	25	1.09	54.4	Aqueous
2	D411	25	1.42	70.8	Aqueous
3	D411	25	1.81	90.3	Aqueous
4	D411	25	2.02	100.8	Aqueous
5	D411	25	3.18	158.7	Aqueous
6	D411	25	3.26	164.2	Aqueous
7	C405	31	0.96	60.6	Aqueous
8	C405	31	1.22	77.0	Aqueous
• 9	C405	31	1.63	103.0	Aqueous
10	C405	31	1.71	108.0	Aqueous
11	C405	31	1.86	117.5	Aqueous
12	C405	31	1.94	122.5	Aqueous
13	C411	34	1.21	81.0	Ethanol
14	C411	34	1.47	98.4	Ethanol
15	C411	34	2.18	146.3	Ethanol
16	C411	34	2.36	158.0	Ethanol
17	C411	34	2.66	178.4	Ethanol
18	C411	34	3.74	250.4	Ethanol
19	C411	34	3.90	261.0	Ethanol
20	C411	34	0.93	62.2	Aqueous
21	C411	34	1.47	98.4	Aqueous
22	C411	34	2.23	149.2	Aqueous
23	C411	34	2.66	178.4	Aqueous

Table 3.1. Cu-ZSM-5 catalysts investigated in the SCR reaction in a mix of 2000ppm NO, 1200ppm C_3H_6 , 2% O₂, balance helium, at a GHSV of 30,000h⁻¹

Hereafter when referring to a particular catalyst, the following notation will be used: Cu-ZSM-5 (Exchange level %) (Si:Al) (Preparation Medium).

* All parent zeolites were originally obtained in the NH_4^+ -ZSM-5 form, then subjected to a calcination stage to transform the zeolite into H-ZSM-5 before ion exchange

** Degrees of exchange were calculated on the assumption that 1Cu²⁺ exchanges for 2Al

*** Preparation media, shorthand notation is used in some Figures; (Aq)=Aqueous (Et) and/or (EtOH)=Ethanol.


Figure 3.2. Effect of reaction temperature, during the SCR reaction, on steady state conversion of NOx to N_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=25)(Aq), Cu-ZSM-5 164.2%, (circles); Cu-ZSM-5 158.7%, (open circles); Cu-ZSM-5 100.8%, (triangles); Cu-ZSM-5 90.3%, (open triangles); Cu-ZSM-5 70.8%, (squares); Cu-ZSM-5 54.4%, (open squares).



Figure 3.3. Effect of reaction temperature, during the SCR reaction, on steady state conversion of C_3H_6 to CO_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=25)(Aq), Cu-ZSM-5 164.2%, (circles); Cu-ZSM-5 158.7%, (open circles); Cu-ZSM-5 100.8%, (triangles); Cu-ZSM-5 90.3%, (open triangles); Cu-ZSM-5 70.8%, (squares); Cu-ZSM-5 54.4%, (open squares).



Figure 3.4. Effect of reaction temperature, during the SCR reaction, on steady state conversion of NOx to N_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=31)(Aq), Cu-ZSM-5 122.5%, (circles); Cu-ZSM-5 117.5%, (open circles); Cu-ZSM-5 108.0%, (triangles); Cu-ZSM-5 103.0%, (open triangles); Cu-ZSM-5 77.0%, (squares); Cu-ZSM-5 60.6%, (open squares).



Figure 3.5. Effect of reaction temperature, during the SCR reaction, on steady state conversion of C_3H_6 to CO_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=31)(Aq), Cu-ZSM-5 122.5%, (circles); Cu-ZSM-5 117.5%, (open circles); Cu-ZSM-5 108.0%, (triangles); Cu-ZSM-5 103.0%, (open triangles); Cu-ZSM-5 77.0%, (squares); Cu-ZSM-5 60.6%, (open squares).



Figure 3.6. Effect of reaction temperature, during the SCR reaction, on steady state conversion of NOx to N_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=34)(EtOH), Cu-ZSM-5 261.0%, (circles); Cu-ZSM-5 250.4%, (open circles); Cu-ZSM-5 178.4%. (triangles); Cu-ZSM-5 146.3%, (open triangles); Cu-ZSM-5 98.4%, (squares); Cu-ZSM-5 83.7%, (open squares); Cu-ZSM-5 81.0%, (diamonds).



Figure 3.7. Effect of reaction temperature, during the SCR reaction, on steady state conversion of C_3H_6 to CO_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=34)(EtOH), Cu-ZSM-5 261.0%, (circles); Cu-ZSM-5 250.4%, (open circles); Cu-ZSM-5 178.4%. (triangles); Cu-ZSM-5 146.3%, (open triangles); Cu-ZSM-5 98.4%, (squares); Cu-ZSM-5 83.7%, (open squares); Cu-ZSM-5 81.0%, (diamonds).



Figure 3.8. Effect of reaction temperature, during the SCR reaction, on steady state conversion of NOx to N₂ exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=34)(Aq), Cu-ZSM-5 178.4%, (Circles); Cu-ZSM-5 149.2%, (triangles); Cu-ZSM-5 98.4%, (squares); Cu-ZSM-5 62.2%, (diamonds).



Figure 3.9. Effect of reaction temperature, during the SCR reaction, on steady state conversion of C_3H_6 to CO_2 exhibited by: Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=34)(EtOH), Cu-ZSM-5 178.4%, (Circles); Cu-ZSM-5 149.2%, (triangles); Cu-ZSM-5 98.4%, (squares); Cu-ZSM-5 62.2%, (diamonds)



Figure 3.10. Turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) as a function of copper content for Cu-ZSM-5(54.4-164.2%)(25)(Aq) catalysts, at 573 K, (triangles); 598 K (squares); and 623 K, (diamonds).



Figure 3.11. Turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) as a function of copper content for Cu-ZSM-5(60.6-122.5%)(Si:Al=31)(Aq) catalysts, at 623 K, (triangles); 648 K (squares); and 673 K, (diamonds).



Figure 3.12. Turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) as a function of copper content for Cu-ZSM-5(81.0-261.0%)(Si:Al=34)(EtOH) catalysts, at 598 K, (triangles); 623 K (squares); and 648 K, (diamonds).



Figure 3.13. Turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) as a function of copper content for Cu-ZSM-5(62.2-178.4%)(Si:Al=34)(Aq) catalysts, at 598 K, (triangles); 628 K (squares); and 648 K, (diamonds).





Figure 3.14. Comparison of turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) for catalysts with similar copper content prepared in different media; Cu-ZSM-5(98.4%)(Si:Al=34)(EtOH) and Cu-ZSM-5(98.4%)(Si:Al=34)(Aq), at 598 K, (white); 623 K (grey); and 648 K, (black).



Cu-ZSM5

Figure 3.15. Comparison of turnover numbers (NOx molecules converted to dinitrogen per Cu atom per second) for catalysts with similar copper content prepared in different media; Cu-ZSM-5(146.3%)(Si:Al=34)(EtOH) and Cu-ZSM-5(149.3%)(Si:Al=34)(Aq), at 598 K, (white); 623 K (grey); and 648 K, (black).







Cu-ZSM-5 catalysts studied exhibit the expected performance in the lean SCR reaction of NO with propene as the reductant. The catalytic activity of Cu-ZSM-5 zeolites expressed as conversion of NOx into dinitrogen and of C_3H_6 to CO₂ as a function of temperature are depicted in Figures 3.2-3.9. Selectivity in NOx conversion is entirely to dinitrogen with no nitrous oxide observed at the sensitivity of our GC analysis. In all catalysts examined the activity for NOx reduction to nitrogen rose with increasing levels of copper ion exchange, and continued to rise at loadings in excess of 100%. The maximum of NO reduction activity shifts to a lower temperature with increasing copper content. It is well documented, that higher activity is achieved with higher loadings of copper within the zeolite; in particular at levels of exchange exceeding the nominal exchange capacity of the zeolite. Many authors have reported that for the selective reduction of NO by hydrocarbons, activity to nitrogen formation increases with Cu²⁺ exchange levels for Cu-ZSM-5 catalysts [3,10,41-43]. It was also observed in these studies that the temperature of maximum conversion of NO shifted to a lower temperature with increased levels of copper exchange in Cu-ZSM-5.

The activity of each of the catalysts tested for the oxidation reaction of propene to CO_2 , during the SCR reaction, also followed a general trend as described in the literature. During the SCR of NOx under lean conditions, it has been reported that propene oxidation also increases continuously with increasing temperature [44-46]. The temperature at which the NO conversion reaches a maximum corresponds to the temperature where complete hydrocarbon conversion is achieved. This coincidence of the onset of NO reduction with hydrocarbon oxidation has led authors to suggest that selective reduction is closely related to the extent of hydrocarbon oxidation [44]. It is also significant to note that for all catalysts tested here the activity for NO reduction reaches a peak at higher temperatures; this suppression in activity is due to the total oxidation of the hydrocarbon reductant molecule by oxygen, known to be favoured at high temperature [32-34, 44-46].

The NOx abatement activity of Cu-ZSM-5 is known to vary with the Si:Al ratio of the zeolite, but this is a contentious issue in the literature. Moretti *et al* [32-34] have proposed that turnover frequency for NO decomposition over Cu-ZSM-5 increases with the number of framework aluminium atoms present, i.e. decreasing Si:Al ratio. They propose that the most active sites present in Cu-ZSM-5 consist of two close copper ions, the [Cu-O-Cu]²⁺ species for instance. Contrary views have been advanced by Iwamoto *et al* [3,21] and Wichterlova *et al* [18-21]. They propose that activity for NO decomposition improves with

increasing Si:Al ratio. These authors suggest that isolated copper species are the sites with superior NO decomposition activity.

In this study, differences in activity for the SCR of NOx are observed for Cu-ZSM-5 catalysts prepared from parent zeolites with different framework Si:Al ratios. A direct comparison however cannot be made regarding the effect of Si:Al ratio on SCR activity. An additional structural variable (other than framework Si:Al ratio) is present in this system which precludes us from attempting such a comparison. It is known, from MAS NMR, that out of the three parent zeolites used in the preparation of catalysts tested, two have a significant proportion of extraframework aluminium species, namely parent zeolite C405 and C411. The presence of extraframework aluminium may introduce complications into such a direct comparison. It has been reported that activity of dealuminated H-mordenite catalyst for the selective reduction of NO with methane is suppressed due to the presence of nonlattice aluminium species that hinder the access of reactant molecules to the active sites. The authors also state that in both fresh and used catalysts, only sites associated with lattice aluminium are active in the SCR reaction [47].

The main aim of this work is to probe the relationship between copper content and turnover number for the SCR reaction for a series of Cu-ZSM-5 catalysts. In particular we are concerned with whether or not the portion of copper exchanged into ZSM-5 above the nominal exchange capacity is responsible for special activity observed for excessively ion exchanged catalysts, in the SCR reaction. Dimeric and clustered species are likely to be formed preferentially at higher copper loadings, so if they are catalytically important we expect to see turnover numbers increasing with copper content.

Turnover numbers (molecules of NOx converted to dinitrogen per Cu site per second) have been calculated for Cu-ZSM-5 catalysts. This procedure normalises the activity for variations in copper loading, allowing us to examine and compare the activity of each copper site present. Turnover numbers have been calculated for Cu-ZSM-5 catalysts using conversions to dinitrogen, taken from the increasing part of the activity versus temperature curve.

Turnover numbers have been determined for the series of Cu-ZSM-5 catalysts originating from the parent zeolite characterised by a Si:Al ratio of 25 with different copper contents. Catalysts were prepared via a conventional multiple ion exchange technique, from an aqueous solution of copper (II) acetate. Turnover numbers have been calculated at 573, 598

and 623 K, and the results are shown in Figure 3.10. Nitric oxide conversions ranged from 3% for the lowest copper content at the lowest temperature at which turnover numbers are shown, to 45% observed with the highest copper loading at the highest temperature shown. Despite the considerable range of conversion, a consistent picture emerges, indicating two turnover regimes. At each of the three temperatures studied, the turnover number is approximately constant up to about 90% copper exchange. Above this degree of exchange the turnover increases, approximately doubling at the two higher temperatures reported, and then remains constant as the copper content increases further. The decline observed at high degrees of exchange and 623 K is considered to be due to the onset of excessive propene oxidation.

Turnover numbers have also been calculated for the series of Cu-ZSM-5 catalysts originating from the parent zeolite characterised by a framework Si:Al ratio of 31, and the results are depicted in Figure 3.11. These catalysts were also prepared by ion exchange from an aqueous solution of copper (II) acetate. Turnover numbers were calculated at 623, 648 and 673 K. They correspond to a range in activity for nitric oxide conversion to dinitrogen of 3% for the lowest copper content at the lowest temperature at which turnover numbers are shown, to 34% observed with the highest copper loading at the highest temperature shown. Two turnover regimes were also noted with this set of catalysts. At each of the three temperatures examined the turnover number is approximately constant up to about 100% copper exchange. Above this degree of exchange, turnover number increases further. This set of catalysts demonstrate comparable behaviour, with respect to the variation of turnover number with copper content, to the Cu-ZSM-5 catalysts with a Si:Al ratio of 25.

The simplest interpretation of these results is that two copper species, isolated ions and small clusters, are both active in the SCR reaction. Although more complicated explanations can be envisaged, the approximate doubling of the turnover number between 90% and 100% copper exchange suggests that in this range of copper loading new types of copper entity are created, with greater unit activity than is found in the zeolite at lower copper loading.

The constancy of the turnover number at low copper contents suggests that the active species are isolated copper ions, which EXAFS and other techniques show to be present

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[28,29]. A recent study by Lamberti *et al* [30] suggested that introduction of Cu(I) into a ZSM-5 with a very low aluminium content, from vapour phase copper (I) chloride, generates isolated copper ions in two different sites, as also suggested by others [31]. The present results suggest that these different isolated sites are probably of similar activity in the SCR reaction.

As the copper content is increased, the turnover number doubles, and then becomes constant in the exchange range 100-165% and 100-122% for the catalysts prepared from the parent zeolites characterised by a framework Si:Al ratio of 25 and 31 respectively. This constancy is very significant, as it suggests that there are only two types of active copper entity, and that these continue to increase in concentration up to the maximum copper content studied. Since the catalysts are prepared by exchange and not by impregnation, this indicates that the second type of active species is a dimer or other small metal/oxygen cluster, and not simply isolated copper ions in a different type of site. Stoichiometry dictates that degrees of exchange above 100% cannot be achieved by isolated Cu (II) ions (irrespective of the nature of the site occupied), but must involve the formation of metal oxygen clusters such as [Cu-O-Cu]²⁺ containing two close Cu atoms. The entities which are introduced into the catalysts by copper overexchange are thus dimers or other small clusters, and these must therefore be the species with the highest turnover number. It is interesting to note that, since the turnover number is calculated per copper ion, the doubling indicates that the activity of a dimer cluster is about four times that of an isolated ion.

These results for the SCR reaction are similar to but less dramatic than those reported by Moretti *et al* [32-34] for the NO decomposition reaction. These authors observed an S shaped relationship between activity and copper content. It was found that the very first addition of copper species to ZSM-5 is inactive, then increasing the exchange level up to about 80% leads to catalysts with rather low activity. Conversely the activity of Cu-ZSM-5 catalysts increases by roughly 100 fold when the extent of copper exchange increases from 80 to 100%. It was concluded that not all the copper sites were equivalent in their NO decomposition activity and that 20% is an upper limit for the fraction of Cu which is the most active. It was also stated that the Cu active sites with the highest turnover frequency should have a very special configuration. Moretti stated that the most active catalysts, those with copper loadings close to 100% of exchange level or higher, have the lowest Si:Al ratios and contain the most active sites for NO decomposition, believed to be two close

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copper ions. Li and Hall [4] had earlier reported a two fold increase in activity for NO decomposition as the copper exchange level was increased from 76-166%.

Turnover numbers have also been calculated for a series of Cu-ZSM-5 catalysts prepared by ion exchange in ethanol. In order to determine whether or not the maintenance of copper(II) acetate in its dimeric form, which is present in an ethanol ion exchange solution, improves the activity of the resulting Cu-ZSM-5 catalysts. This would be significant as we have already demonstrated within this study that the most active sites for the SCR reaction are present in overexchanged Cu-ZSM-5 and are believed to consist of dimeric or clustered species comprising of two close Cu ions [28-29,32-34].

Turnover numbers were calculated for Cu-ZSM-5 catalysts prepared from the parent zeolite characterised by a framework Si:Al ratio of 34, in both aqueous and ethanol ion exchange media, the results of which are shown in Figures 3.13 and 3.12 respectively. Much higher exchange levels were obtained for the catalysts prepared in ethanol. In both series of catalysts, those prepared in an aqueous medium and those prepared in an ethanol medium, turnover numbers do not rise at 100%. This behaviour is contrary to that observed for Cu-ZSM-5 catalysts prepared in an aqueous ion exchange media from parent zeolites characterised by a framework Si:Al ratio of 25 and 31, where turnover numbers are seen to approximately double upon achieving an ion exchange level of 100%. Two distinct turnover regimes are still noted, however the highest turnover numbers are achieved at much higher copper loadings. There are various possible explanations for this lag in activity with increasing copper content. The first one is concerned mainly with the fact that these zeolites are prepared from the parent zeolite with the highest Si:Al ratio in this study. As the framework aluminium ion concentration is decreased; the charge compensating Cu^{2+} ions must move further apart. The $CuOH^+$ species is more stable when these OH groups are remote from each other and it therefore becomes difficult to convert CuOH⁺ groups into [Cu-O-Cu]²⁺, i.e. those that have been suggested to possess superior activity for the SCR reaction. The second possibility is related to the fact that the level of exchange is calculated on the basis that Cu²⁺ is exchanged for 2H⁺, associated with 2 negatively charged framework aluminium entities. The possibility of copper locating in sites unassociated with negatively charged framework aluminium entities, which may be inactive for the SCR reaction, is not taken into account. In catalysts prepared with high Si:Al ratio it has been reported that copper may be exchanged not only at protonic sites associated with framework aluminium sites but also at defect sites such as the nested silanols at silicon vacancy defects [43]. In addition it is noted that this catalyst is prepared from a parent zeolite which contains a substantial proportion of extraframework aluminium species. The formation of a copper deposit, i.e. copper aluminate has been proposed for catalysts which have undergone dealumination, therefore contain a substantial fraction of non lattice aluminium species [48]. Copper loading in these alternative sites is ignored in the calculation of exchange level, and which may well be inactive for the SCR reaction. It has also been mentioned that the presence extraframework aluminium was responsible for suppressing the activity of a H-mordenite SCR catalysts, due to active site blockage [47].

A direct comparison can be made between the activity for the SCR reaction and copper loading of these catalysts on the basis of ion exchange in an aqueous solution or ethanol, providing the comparison is made between Cu-ZSM-5 catalysts with similar levels of copper exchange. Turnover numbers for Cu-ZSM-5 catalysts prepared in ethanol were compared with those for Cu-ZSM-5 catalysts prepared from an aqueous solution. Figure 3.14 compares the turnover numbers for catalysts with 98.4% Cu exchange. The turnover numbers calculated at 623 and 648 K are significantly higher for the sample prepared in ethanol. Similar behaviour is found in Figure 3.15 where turnover numbers have been calculated and compared for Cu-ZSM-5 catalysts with 146.3% Cu and 149.3% Cu, prepared from an ethanol ion exchange medium and an aqueous ion exchange media respectively. In this representation however it can be seen that significantly higher turnover numbers are obtained for the Cu-ZSM-5 catalysts prepared in an ethanol ion exchange medium at all temperatures shown. Interestingly however, as can be seen from Figure 3.16, turnover numbers for Cu-ZSM-5 catalysts with ion exchange level of 178.4% prepared from both an ethanol and aqueous ion exchange medium are comparable at all temperatures examined.

These results may be interpreted quite simply. They appear to indicate that Cu-ZSM-5 catalysts with lower levels of copper exchange, prepared via an ethanol ion exchange solution of copper (II) acetate are more active than Cu-ZSM-5 catalysts prepared from an aqueous copper (II) acetate ion exchange solution. There however seems to be no apparent benefit in using an ethanol ion exchange solution when Cu-ZSM-5 catalysts with higher copper loadings are compared. It would seem that species with greater unit activity are forming at lower Cu loadings in the ethanol solution than in the aqueous solution. These

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results indicate that the retention of copper (II) acetate in the dimeric form in an ethanol ion exchange solution introduces copper into the catalysts with greater unit activity per copper ion than catalysts prepared from an aqueous ion exchange solution of copper (II) acetate. At higher levels of copper loading turnover numbers calculated for excessively ion exchanged Cu-ZSM-5 catalysts prepared from ethanol or aqueous ion exchange media and are found to be comparable. This is not really surprising, in fact it is in line with conclusions already drawn in this study. The proportion of copper present above the nominal ion exchange capacity, at excessively high copper loadings, in Cu-ZSM-5 catalysts prepared via an aqueous ion exchange solution is known to be present as dimeric or clustered entities comprising two close copper ions. In this study it has also been shown that they demonstrate greater unit activity than copper present at lower levels of ion exchange. This comparison would seem to provide additional evidence in support of the conclusions reached in this study. That the most active sites in Cu-ZSM-5 SCR catalysts consist of dimeric or clustered copper species consisting of two close copper ions [49].

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Chapter 4 Reactivity of Carbonaceous Deposits on Cu-ZSM-5 Catalysts for the SCR of NOx

4.1 Background

In studies probing the reaction mechanism of the selective catalytic reduction of NOx by hydrocarbons under lean oxidising conditions, much interest now centres on the nitrogen – nitrogen bond forming step. Spectroscopic evidence has been presented for oxidised nitrogenous species such as organic nitro, nitrite or nitroso compounds [1-7] and also for reduced species such as nitriles, cyanides [2,8-12] and isocyanates [7,12-14]. All of these have been suggested to be key intermediates towards N_2 formation. Less attention has been paid to the characterisation of hydrocarbon moieties which must also be involved, although it has long been recognised that long lived carbonaceous species can be formed, with possible mechanistic importance [15-17].

In this chapter the reactivities of hydrocarbon species deliberately deposited on Cu-ZSM-5 catalysts, with different copper contents, have been examined. It has previously been shown that nitrogen is released from these deposits [2]. In this work it was demonstrated that these deposits are also able to activate NO and oxygen directly.

The importance of carbonaceous deposits, which are reasonably stable on the catalyst surface under lean SCR reaction conditions, in the mechanism of the selective catalytic reduction of NOx has been discussed by various authors. Kikuchi *et al* [15], Bennet *et al* [16] and Ansell *et al* [17] all provide evidence that the catalytic activity for NOx reduction continues for some time after the hydrocarbon is removed from the reaction mixture, under conditions where it is assumed that hydrocarbon deposit has been laid down upon the catalyst surface.

Kikuchi *et al* [15] proposed that a long lived carbonaceous species formed on the surface of metallosilicate catalysts under SCR reaction conditions; and was responsible for the reduction of NO by propene. Their assumptions were based on the following observations. When propene was removed form the reactant stream, the conversion of NO decreased only gradually to zero, yet when propene was reintroduced the conversion of NO rapidly returned to its original level. They also stated that oxygen was a necessary component for the reaction, to activate the carbonaceous species for the reduction of NO.

The mechanistic importance of carbonaceous deposits formed on Cu-ZSM-5 catalysts under SCR reaction conditions has also been discussed by Bennet *et al* [16] and Ansell *et al* [17]. A temperature programmed reaction study of the activity of Cu-ZSM-5 under an oxidising exhaust gas was performed by Bennet *et al* [16]. Temperature programmed reaction results indicate that under transient conditions an important role of Cu-ZSM-5 is to store the reactants at low temperature, before catalysing nitrogen formation during excursions to higher reaction temperatures. Their data reveals that the hydrocarbon does not directly reduce NO. Also reported within this study, steady state kinetic measurements reveal a near first order dependence of NO conversion on propene partial pressure. The authors state that their results are in support of a mechanism in which a reactive intermediate capable of reducing NO is generated by the hydrocarbon. Their kinetic data are not consistent with this intermediate being CO, but do not exclude either a partially oxidised species or some form of active coke.

The involvement of a carbonaceous deposit in the reduction of NO is also proposed by Ansell *et al* [17]. Based on their transient kinetic studies utilising propene as the reducing agent over Cu-ZSM-5, they propose that the hydrocarbon is converted to a carbonaceous species on the zeolite regardless of whether oxygen is present or not. They go on to suggest that it is this deposited coke species which acts as the reductant for NO and its reducing ability is greatly enhanced by the presence of oxygen. They demonstrate that over precoked catalysts high conversions of NO may be achieved in the presence of oxygen but absence of propene; in the absence of oxygen however there is a much lower level of conversion. They state that the role of oxygen is to induce generation of an adsorbed state of NOx (i.e. NO_2 species) on the Cu sites. The mechanism proposed by Ansell *et al* [17] comprises two processes, NO activation and coke deposition, and they state that an efficient catalyst should perform both functions effectively.

Adsorbed species, described by the blanket term "carbonaceous deposit" or "coke", known to form upon the surface of catalysts under some SCR reaction conditions, are not necessarily solely carbonaceous in nature. Various surface species containing carbon and nitrogen have been observed on different lean NOx catalysts; under conditions where significant amounts of carbonaceous or coke species are known to deposit, i.e. low temperature or reducing SCR conditions. These species have been shown also to be comprised of nitriles, cyanides and isocyanate species as well as carbonaceous / coke

deposits. Various authors have documented the presence of these species and some have reported their activity in NOx reduction and their possible roles as reaction intermediates [2,7-14].

Infra-red spectroscopic studies of the SCR of NOx over an alumina supported Cu/Cs oxide catalyst were carried out by Ukisu et al [13,14]. They suggest that the IR band observed at 2234 cm⁻¹, was ascribable to an adsorbed isocyanate species. This band formed and grew in intensity when the catalyst was exposed to a typical lean NOx mixture of NO, O₂ and C₃H₆ at room temperature and was subsequently heated to 673 K in vacuum. It was suggested that this surface isocyanate species arose from the thermal decomposition of a precursor complex such as NOx.CyHz. The isocyanate species was stable upon the surface of the catalyst up to temperatures of 673 K under vacuum, yet it was demonstrated that this adsorbed species exhibited high activity for NOx reduction when exposed to NO. When the surface isocyanate species was exposed to NO at 623 K the band at 2234 cm⁻¹ completely disappeared. Analysis of the reaction products indicated that the formation of N₂, CO₂ and CO had taken place. Exposure of the deposit to O₂ at 623 K also resulted in the elimination of the 2234 cm⁻¹ band, in this case, however, CO₂ was the main reaction product with only a small amount of N_2 observed. Ukisu et al [13,14] concluded that the formation of an isocyanate intermediate at low reaction temperatures and its reaction with NO was a key step in the mechanism for efficient NO reduction with hydrocarbon reductants in the presence of excess oxygen.

Bell *et al* [7] utilised high temperature in situ FTIR to study adsorbed species present during the SCR of NOx with C_3H_6 in excess oxygen over Cu-ZSM-5. The presence of adsorbed species was characterised as a function of copper loading and reaction temperature.

IR spectra for 1.5 wt% and 3 wt% Cu-ZSM-5 catalysts were collected under typical SCR reaction conditions at 673 K; and compared with spectra for obtained under similar reaction conditions for H-ZSM-5. On H-ZSM-5, adsorbed species detected were CO₂, isocyanates and carbonaceous deposits. In the spectra observed for 1.5 wt% Cu-ZSM-5, CO₂ was detected along with Cu⁺-CO and carbonaceous deposits (which formed at a lower rate than on H-ZSM-5). The IR spectrum collected for a 3 wt% Cu-ZSM-5 catalyst exhibited evidence for CO₂, but no Cu⁺-CO and little carbonaceous species; instead Cu(NxOy)z was detected, indicating that adsorbed surface species on samples with higher copper loading

were more oxidised. The authors state that one of the reasons for why samples with higher copper loadings exhibit superior activity for lean NOx reduction may be that they contain less carbonaceous deposits and less Cu^+ -CO.

The effect of variations in temperature on the formation of adsorbed surface species upon a 3 wt% Cu-ZSM-5 catalyst was also investigated. At low temperatures where hydrocarbon and NOx conversion was negligible, IR detected the presence of carbonaceous deposits, Cu^+ -CO and isocyanates. At 473 K an isocyanate band was present, bands due to CO_2 were weak, indicating the absence of hydrocarbon oxidation, and carbonaceous deposits covered the catalyst surface rapidly. At 573 K, CO_2 , $Cu-N_2$ and Cu^+ -CO were present along with slowly forming carbonaceous deposits. Cu-ZSM-5 exhibited maximum NOx conversion between 653 and 723 K. In general, IR spectra demonstrated a shift from carbonaceous deposits, Cu^+ -CO and isocyanate species at low temperature (< 653 K) to CO_2 , N_2 and Cu(NxOy)z species at 653-723 K, indicating that the surface of catalysts were more oxidised at higher reaction temperatures, characteristic of higher NOx reduction activity.

Bell et al [7] reported that under conditions where carbon containing species predominated in the IR spectrum, catalysts had poor hydrocarbon oxidation and NOx reduction activity; these species appeared to occupy sites for which NOx reduction intermediates could not effectively compete. Oxidised nitrogen containing species were mainly observed on Cu-ZSM-5 catalysts with greater numbers of copper sites. Bell et al [7] proposed that these Cu(NxOy)z species could be reaction intermediates for the lean NOx reaction with hydrocarbons over Cu-ZSM-5. As the reaction temperature increased, the detected NOx species were also increasingly oxidised. This also suggested that NOx reduction occurs via an oxidised intermediate. At low temperatures where NOx reduction activity was low, IR detected mainly carbonaceous deposits, Cu⁺-CO, and isocyanates. The effects of increasing temperature on the surface species were similar to those observed as a consequence of increasing copper concentration; generally when carbon containing species were no longer detected on the surface NOx reduction activity improved. Bell et al [7] concluded that IR studies conducted at low temperature could not fully explain the surface species present during the lean NOx reduction reaction; which is favoured at higher reaction temperatures. Hayes et al [2] reported that organic cyanide species (nitriles) formed upon Cu-ZSM-5 catalysts under typical lean SCR reaction conditions. In the absence of oxygen these were retained without decomposition by the catalyst up to temperatures >750 K. In the presence

of oxygen they were selectively oxidised to dinitrogen and carbon dioxide at the same temperature as the selective catalytic reduction of NO. Consequently Hayes et al [2] suggested that they may be important reaction intermediates. The formation and storage of such a stable organonitrogen compound inside the zeolite matrix was achieved by passing a mixture of O₂, C₃H₆ and NO in helium over the catalysts at 550 K for 1 hour; at which temperature the Cu-ZSM-5 catalyst was almost inactive for the selective reduction of NO. There was however some reaction between the NO and the propene, since analysis of the catalysts showed the presence of an organonitrogen deposit. When a catalyst with a deposit laid down in this way was heated to 623 K in the reaction mixture specified above, rapid N2 evolution was observed initially, corresponding to >100% conversion of NO. Gradually the rate of reaction fell to a steady state value, the rate which was observed when no organic material had been prestored. The anomalous rate, corresponding to an apparent conversion of > 100%, was said to be due to the release of nitrogen present in the stored deposit. The stability of the stored species was demonstrated by heating the catalysts in NO/propene for 1 hour at 549 K and then raising the temperature to 623 K in helium. No decomposition or N_2 evolution was observed during heating, even after 20 min at 623 K. As soon as oxygen was admitted, however, a large pulse of nitrogen was evolved. The identity of the stored species was established by IR spectroscopy. Bands which could result from either CN or NCO species were observed at 2260-2270 cm⁻¹. To differentiate between nitrile and isocyanate species, the stored material was exposed to water at room temperature and the IR spectrum was found to be unaffected. This was not consistent with isocyanates, which rapidly decompose in water yielding primary amines. By exposing the catalysts to MeCN at room temperature it was established that nitriles have similar spectroscopic and reactivity properties to the stored species. Hayes et al [2] propose that the nitrile produced in the storage process is an important intermediate in the selective reduction of nitrogen oxides to dinitrogen in the presence of hydrocarbons and excess oxygen.

Li *et al* [12] observed surface intermediates with in situ IR spectroscopy when 1000ppm NO, 1000ppm C_3H_6 and 4% O_2 was flowed over a Cu-ZrO₂ catalyst at 498 K. IR bands were detected at 2140 and 2190 cm⁻¹ and attributed to -CN and -NCO adsorbed species respectively. These two IR bands were also present when ethanol, another effective reductant, was used in place of propene. When an ineffective reductant was used in the SCR reaction they were not observed. The authors state that these observations support

suggestions that these surface species are reaction intermediates in the SCR of NO by C_3H_6 or ethanol. The surface CN and NCO species were observed under a wide range of lean NOx reaction conditions, however their intensity decreased with increasing oxygen concentration. They were observable up to 573 K, although at that temperature, their intensities were significantly diminished, probably due to the enhanced reactivity of these species at higher temperature. Further confirmation of the role of these species in the SCR reaction was demonstrated by the production of nitrogen upon their reaction with NOx. Known quantities of NO or NO₂ were pulsed over the catalysts and nitrogen production was monitored. The nitrogen formed from the first few pulses was greater than the amount of nitrogen in the NO pulse, suggesting that N₂ was formed from both NO in the pulse and some N-containing species adsorbed on the surface. The total amount of nitrogen formed from the NO pulses at 543 K was substantially lower than that from the 498 K experiment; in agreement with IR results which showed that the intensities of the bands due to CN and NCO were lower at higher temperatures. The authors also examined a Cu-ZrO₂ catalyst which had been subjected to a pretreatment in a flow of C3H6 and O2, and helium but without NO. The level of nitrogen produced was much reduced and the amount produced probably reflected the reaction of NO with surface carbonaceous deposits. In conclusion these authors state that their work extended earlier reports by Hayes et al [2], of organic nitrile species as possible reaction intermediates.

The aim of this chapter is to investigate the reactivity of "carbonaceous" deposits deliberately deposited on a series of Cu-ZSM-5 catalysts with different copper loadings; for the SCR of NOx. It is thought that the reactivity of these coke deposits formed upon Cu-ZSM-5 catalysts may provide deeper insight into the controversial mechanism of the SCR reaction.

4.2 Results and Discussion

The reactivity of carbonaceous material deliberately deposited on Cu-ZSM-5 zeolite catalysts under lean NOx reaction conditions is examined [20]. Cu-ZSM-5 catalysts studied have been prepared with varying degrees of copper ion exchange, from two different parent zeolites, and are listed in Table 4.1. These carbonaceous deposits, referred to often for simplicity as coke, may be laid down on the Cu-ZSM-5 catalysts by exposure to a typical SCR reaction mixture at low temperatures, as previously demonstrated by Hayes *et al* [2]. Before studying the behaviour of the deposited coke, the reactant gas mixture of 1000ppm NO, 1200ppm C₃H₆ and 2% O₂, (balance helium) was passed over the catalysts at 473 K, a procedure known to form hydrocarbon or coke deposits. Under these conditions there was no steady state conversion of NO to N₂ observed at the sensitivity of our GC analysis. The reactivity of the carbonaceous material deposited was then examined by exposing the catalysts at 473 K to the same concentration of NO and oxygen as present in the reaction mixture, (but no propene), and then heating to approximately 873-973 K at 10 K min⁻¹. The conversion of NOx was monitored continuously by the chemiluminescent detector.

Cu-ZSM-5 Catalyst	Parent Zeolite *	Framework Si:Al Ratio	wt% Copper loading	% Exchange Level **	Preparation medium
1	D411	25	1.09	54.4	Aqueous
2	D411	25	1.42	70.8	Aqueous
3	D411	25	1.81	90.3	Aqueous
4	D411	25	2.02	100.8	Aqueous
5	D411	25	3.18	158.7	Aqueous
6	D411	25	3.26	164.2	Aqueous
7	C405	31	0.96	60.6	Aqueous
8	C405	31	1.22	77.0	Aqueous
9	C405	31	1.63	103.0	Aqueous
10	C405	31	1.71	108.0	Aqueous
11	C405	31	1.86	117.5	Aqueous
12	C405	31	1.94	122.5	Aqueous

Table 4.1 Cu-ZSM-5 catalysts subjected to coke deposition.

Hereafter when referring to a particular catalyst, the following notation will be used: Cu-ZSM-5 (Exchange level %) (Si:Al).

* All parent zeolites were originally obtained in the NH_4^+ -ZSM-5 form, then subjected to a calcination stage to transform the zeolite into H-ZSM-5 before ion exchange

** Degrees of exchange were calculated on the assumption that 1Cu²⁺ exchanges for 2Al⁻



Figure 4.1 Exit NOx concentration observed during heating at 10 K min⁻¹ in NO-oxygen, after the formation of hydrocarbon deposits at 473 K on Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=25), Cu-ZSM-5 164.2%, (circles); Cu-ZSM-5 158.7%, (open circles); Cu-ZSM-5 100.8%, (triangles); Cu-ZSM-5 90.3%, (open triangles); Cu-ZSM-5 70.8%, (squares); Cu-ZSM-5 54.4%, (open squares).



Figure 4.2 Exit NOx concentration observed during heating at 10 K min⁻¹ in NO-oxygen, after the formation of hydrocarbon deposits at 473 K on Cu-ZSM-5 catalysts (Exchange Level %)(Si:Al=31), Cu-ZSM-5 122.5%, (circles); Cu-ZSM-5 117.5%, (open circles); Cu-ZSM-5 108.0%, (triangles); Cu-ZSM-5 103.0%, (open triangles); Cu-ZSM-5 77.0%, (squares); Cu-ZSM-5 60.6%, (open squares).



Figure 4.3 Observed and calculated NOx concentration observed during heating at 10 K min⁻¹ in NO-oxygen, after the formation of hydrocarbon deposits at 473 K on a 54% Cu-ZSM-5 catalyst as described in the text. Experimental, (squares); calculated, (open circles).











Figure 4.6 Comparison of steady state and transient % NOx conversion, for a 100% exchanged Cu-ZSM-5 catalyst. Steady state (squares); Transient (circles).

Catalyst	Amount of	NO	NO	Total NO
Cu-ZSM-5 (exchange level%)(Si:Al)	NO fed	Converted	Converted	Converted
	during	(mg)	$(mg) g^{-1}$	(%)
	experiment		catalyst	
	(mg)			
Cu-ZSM-5 (54.4%)(Si:Al=25)	33.3	6.3	25.0	18.8
Cu-ZSM-5 (70.8%)(Si:Al=25)	33.0	5.9	23.7	18.0
Cu-ZSM-5 (90.3%)(Si:Al=25)	34.0	5.3	21.2	15.6
Cu-ZSM-5 (100.8%)(Si:Al=25)	33.8	5.4	21.6	16.0
Cu-ZSM-5 (158.7%)(Si:Al=25)	32.8	5.2	20.8	15.8
Cu-ZSM-5 (164.2%)(Si:Al=25)	34.2	5.3	21.0	15.4
Cu-ZSM-5 (60.6%)(Si:Al=31)	39.4	7.8	31.0	19.7
Cu-ZSM-5 (77.0%)(Si:Al=31)	40.0	8.2	32.7	20.4
Cu-ZSM-5 (103.0%)(Si:Al=31)	39.4	6.9	27.8	17.6
Cu-ZSM-5 (108.0%)(Si:Al=31)	39.4	7.2	29.0	18.4
Cu-ZSM-5 (117.5%)(Si:Al=31)	40.1	7.4	29.7	18.5
Cu-ZSM-5 (122.5%)(Si:Al=31)	39.8	6.8	27.1	17.1

2 . . x 10

Table 4.2 Reactivity of pre-deposited coke, upon Cu-ZSM-5 catalysts, for the selective catalytic reduction of NO.

Catalyst Cu-ZSM-5 (exchange level%)(Si:Al)	NOx converted (mg) g ⁻¹ catalyst	*Carbon (mg) g ⁻¹ catalyst	*Hydrogen (mg) g ⁻¹ catalyst	*Nitrogen (mg) g ⁻¹ catalyst
Cu-ZSM-5 (54.4%)(Si:Al=25)	25.0	28,6	6.1	3.9
Cu-ZSM-5 (164.2%)(Si:Al=25)	21.0	16.9	3.4	0.7

Table 4.3 Cu-ZSM-5 catalysts investigated in the reactivity of coke deposit. * carbon, hydrogen, and nitrogen values from elemental microanalysis.

Catalyst	Activation Energy kJ/mol ⁻¹		
Cu-ZSM-5 (exchange level%)(Si:Al)			
Cu-ZSM-5 (54.4%)(Si:Al=25)	92		
Cu-ZSM-5 (70.8%)(Si:Al=25)	88		
Cu-ZSM-5 (90.3%)(Si:Al=25)	84		
Cu-ZSM-5 (100.8%)(Si:Al=25)	82		
Cu-ZSM-5 (158.7%)(Si:Al=25)	75		
Cu-ZSM-5 (164.2%)(Si:Al=25)	75		
Cu-ZSM-5 (60.6%)(Si:Al=31)	103		
Cu-ZSM-5 (77.0%)(Si:Al=31)	97		
Cu-ZSM-5 (103.0%)(Si:Al=31)	92		
Cu-ZSM-5 (108.0%)(Si:Al=31)	91		
Cu-ZSM-5 (117.5%)(Si:Al=31)	89		
Cu-ZSM-5 (122.5%)(Si:Al=31)	88		

Table 4.4 Activation energy (kJ mol⁻¹), of pre-deposited coke, upon Cu-ZSM-5 catalysts, for the selective catalytic reduction of NO.

The results of experiments for Cu-ZSM-5 catalysts with varying degrees of copper ion exchange; prepared from parent zeolites characterised by framework Si:Al ratios of 25 and 31 are shown in Figure 4.1 and 4.2 respectively. These figures show the instantaneous concentration of NOx (NO + NO₂/N₂O₄) at the reactor exit. In all cases the deposit on the catalysts show significant activity in NOx reduction. It is generally observed that the maximum of activity for catalysts with higher degrees of copper exchange occurs at lower reaction temperatures than for catalysts with lower levels of copper ion exchange. The amount of NOx converted in each case is similar, however a discrete but significant trend is observed and is presented in Table 4.2. Generally catalysts with higher levels of copper ion exchange and lower levels of residual Bronsted acidity convert less NOx than catalysts with lower levels of copper ion exchange and higher levels of residual Bronsted acidity. The amount of NO converted ranged from 25 mg g⁻¹ catalyst to 21 mg g⁻¹ catalyst for Cu-ZSM-5 catalysts with 54% and 164% copper ion exchange respectively, prepared from the parent zeolite with a framework Si:Al ratio of 25. It is found that the total amount of NOx converted however is of the same order of magnitude as the amount of deposited coke upon the catalyst surface. Hayes et al [2] previously reported that coke, approximately 30 mg g⁻¹ of catalyst, was formed on an overexchanged Cu-ZSM-5 catalyst tested at 10,000h⁻¹ GHSV. Coke deposition on Cu-ZSM-5 catalysts with 54% and 164% copper ion exchange has been quantified and characterised, by elemental microanalysis, in this work. Details regarding the amount of carbonaceous deposit formed upon these catalysts and its nature can be seen clearly from Table 4.3. Greater NOx conversion and the formation of a larger amount of coke deposit was observed for the Cu-ZSM-5 catalyst with an ion exchange level of 54%; than the catalyst with an ion exchange level of 164%. The higher levels of NOx conversion, observed for catalysts with lower levels of copper ion exchange may be directly attributed to the presence of a greater concentration of reductant, present as coke. The larger coke deposition capacity of catalysts with lower levels of copper ion exchange is believed to result from the higher number of residual Bronsted acid sites, which are expected to have high effectiveness for hydrocarbon activation.

It is worth discussing the reactivity of coke deposits formed upon Cu-ZSM-5 catalysts prepared from the parent zeolite characterised with a framework Si:Al ratio of 31 for NO conversion. The amount of NO converted ranged from 31 mg g⁻¹ to 27 mg g⁻¹ catalyst, for Cu-ZSM-5 catalysts with 60% and 122% copper ion exchange respectively. Ion exchange levels quoted correspond to the lowest and highest extremes of copper loading observed for this series of catalysts. The amount of NOx converted by pre-coked catalysts prepared from this parent zeolite is greater than observed for precoked catalysts, with similar copper exchange levels, prepared from the parent zeolite with a framework Si:Al ratio of 25. This greater NOx reduction is thought to be due to the presence of larger amounts of coke deposit, suggesting that Cu-ZSM-5 catalysts, prepared from the parent zeolite with Si:Al ratio of 31 have a greater coke deposition capacity. To explain this phenomenon, as well as the influence of Bronsted acidity in coke formation on these catalysts, the participation of extra framework aluminium species known to be present, from MAS NMR characterisation, in these catalysts; may also be considered to promote coke formation. It has previously been reported that extraframework aluminium species were involved in the formation of coke upon HY and H-ZSM-5 zeolite catalysts, during hydrocarbon cracking reactions [18]. The reactivity of carbonaceous deposits for the SCR of NOx is significantly different for the catalysts studied, with maximum reactivity being observed at a much lower temperature at the higher degrees of copper ion exchange.

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A simple kinetic model has been formulated in an effort to understand the differences in reactivity between catalysts with different degrees of copper exchange and takes the form of this general expression,

Rate = k [NO] [HC]
$$exp^{(-Ea/RT)}$$

the model assumes:

1. That the rate of reaction is first order in the amount of hydrocarbon deposit remaining on the catalyst as the temperature is increased.

2. That the rate of reaction is first order in the NO concentration, taken to be the mean of the NO concentration on entering and leaving the catalyst bed.

3. That the reaction is zero order in oxygen, since this is present in substantial excess at all stages of the experiment.

4. That the reaction is described by a single activation energy.

5. That the rate of reaction is the same over a 5 K interval, and that the rate at any temperature is obtained by numerical integration over all of the 5 K intervals up to that temperature from the initial temperature of 473 K.

The model has 3 disposable parameters, the activation energy for reaction, and two constants which have the nature of pre-exponential factors. One of these normalises the calculated NO concentrations to those which are observed, while the other relates to the consumption of the hydrocarbon deposit.

Comparison between experimental and calculated NO conversions, observed and obtained for Cu-ZSM-5 catalysts, Si:Al 25, with copper ion exchange levels of 54, 100 and 164% are presented in Figures 4.3, 4.4 and 4.5 respectively. There is very good agreement between calculated and experimental values for such a simple model. In line with the changes in activity, the apparent activation energy of the reaction decreases as the copper content of the zeolite is increased. The model indicates that the greater activity of the coke on the catalyst with the 164% copper exchange is mainly due to a lower activation energy of 75 kJ mol⁻¹, compared with 92 kJ mol⁻¹ for activity of the coke on the catalyst with 54% copper exchange; intermediate activity exhibited by the coke on the catalyst with 100% exchange is therefore attributable to an activation energy of 82 kJ mol⁻¹. The activation energies for NO reduction exhibited by all the pre-coked catalysts examined in this study, deduced from the kinetic model, are presented in Table 4.4. The model also shows that all the hydrocarbon deposit is consumed during each of the ramping experiments, this is
supported by an XRD investigation, presented later in this thesis. As discussed earlier, Cu-ZSM-5 catalysts prepared from the parent zeolite with Si:Al ratio 31 convert more NOx during the reduction reaction than Cu-ZSM-5 catalysts with a Si:Al ratio of 25, with similar levels of copper ion exchange. This is speculated to be due to the presence of a greater amount of reducing species, coke on these catalysts. Also the activation energies calculated for pre-coked Cu-ZSM-5 catalysts, prepared from the parent ZSM-5 material with Si:Al ratio 31 are generally higher than those with a similar level of copper ion exchange, prepared from the parent ZSM-5 material with Si:Al ratio 31 are generally higher than those with a similar level of copper ion exchange, prepared from the parent ZSM-5 material with Si:Al ratio 25.

These results show a variation in the stability of the hydrocarbon deposit towards NO, which is inversely dependent on copper content. This suggests that the residual acidity of the zeolite could be a factor in determining how catalyst activity varies with copper loading. These results suggest that the presence of too many Bronsted zeolite acid sites, consequently higher levels of carbonaceous deposits, inhibits the NOx reduction reaction. It is has been shown that relatively few Bronsted acid sites remain in the so called overexchanged catalysts, which are the most active for NOx reduction [19], and which appear to form the most active coke. The present study compared catalysts with low levels of ion exchange with catalysts having little residual Bronsted acidity. These materials were pretreated under conditions which allowed the acid sites to have maximal influence in hydrocarbon activation, namely at low temperature, the result on the most acidic catalysts was a hydrocarbon deposit which was less active in NOx reduction at low temperatures than formed at steady state. Comparison of % NOx conversion during a transient experiment with a steady state reaction, for a 100% exchanged Cu-ZSM-5 catalyst, is shown in Figure 4.6. This shows that the steady state process occurs more quickly at lower temperatures. Equally the deposit produced on catalysts with lower copper content, and therefore higher residual Bronsted acidity, is even less active in NO reduction. There is thus an inverse correlation between Bronsted acidity and catalytic performance. It is still not clear however, whether the small amount of residual Bronsted acidity which remains on the most active Cu-ZSM-5 catalysts is necessary for the reaction to occur, since it is possible that Lewis acidity associated with the Cu(I) sites is sufficient to activate the hydrocarbon species.

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Chapter 5 Characterisation of Copper Species in Cu-ZSM-5

5.1 Background

Cu-ZSM-5 is one of the most promising catalytic systems for NO decomposition and for the SCR of NO by hydrocarbons in a lean oxidising environment. It is generally accepted that overexchanged materials are the most active in both reactions [1-10].

The so called "excess ion exchange" preparation procedure is believed to promote the formation of Cu-O species, where extralattice oxygen is coordinated to copper ions, such as $[Cu-O-Cu]^{2+}$ or $Cu^{2+}O^-$. The presence of an entity where copper is associated with an extraframework oxygen in overexchanged Cu-ZSM-5 catalysts has been proposed by several authors; and furthermore is considered to be an important active species in both the NO decomposition and the SCR reaction [11-22]. Cu-ZSM-5 catalysts prepared by excess ion exchange have a characteristic redox property, which is represented by the facile reduction of Cu(II) to Cu(I). This redox behaviour is rationalised by the presence of extraframework oxygen introduced during sample preparation. In contrast Shelef [23] proposed isolated irreducible Cu(II) ions as catalytically active sites in Cu-ZSM-5 with a low level of ion exchange. The facile interconversion of Cu(II) to Cu(I) however suggests that irreducible copper cations are only a minority species in overexchanged zeolites.

A comprehensive characterisation study was performed by Joyner *et al* [21,22]. Utilising electron and X-ray absorption spectroscopy they revealed that there are two different types of copper species within the zeolite channels of overexchanged Cu-ZSM-5 catalysts. Isolated copper ions and small metal / oxygen clusters where the copper atoms are linked by extra lattice oxygen species, such as $[Cu(II)-O-Cu(II)]^{2+}$ dimers.

Stoichiometry dictates that degrees of ion exchange above 100% cannot be achieved by isolated Cu(II) ions, but must instead involve the formation of the metal oxygen clusters such as [Cu-O-Cu]²⁺. The proportion of copper present above the nominal ion exchange capacity in Cu-ZSM-5 is therefore thought to consist of dimeric entities or clusters containing two close copper atoms.

The relationship between degree of ion exchange and turnover number (defined as the number of NOx molecules converted to nitrogen per copper site per second), for a series of Cu-ZSM-5 catalysts has been studied; the results have been presented in Chapter 3 of this thesis [24]. These experiments were conducted in order to assess whether the high activity for the SCR reaction displayed by overexchanged Cu-ZSM-5 catalysts was attributable to

the presence of small metal / oxygen clusters or was simply a function of an increasing total number of isolated copper ions.

Turnover numbers were determined for a series of otherwise identical Cu-ZSM-5 catalysts with different copper contents. Turnover number was found to be roughly constant at copper contents < about 90% exchange, then increased by a factor of two at 100% exchange then remained constant up to the highest nominal extent of exchange studied. These results suggested that both isolated copper ions and small metal / oxygen clusters, including dimers catalyse the SCR reaction, however the activity of the dimer cluster was found to be about four times that of an isolated copper ion. It was shown therefore that the most active sites consisted of these dimeric clustered copper species, that they demonstrate greater unit activity for the SCR reaction than copper present at lower levels of ion exchange.

The entities introduced into the catalyst by overexchange are thus dimers or small metal / oxygen clusters such as $[Cu-O-Cu]^{2+}$, and these are the species with the highest turnover number.

To complement and support the conclusions drawn from the turnover number study, this chapter aims to compare the copper species present in Cu-ZSM-5 catalysts with varying levels of copper ion exchange. A combination of electron spectroscopies: X-ray photoelectron spectroscopy (XPS), X-ray excited Auger electron spectroscopy (XAES) and X-ray absorption spectroscopy (EXAFS) was utilised to compare the nature, location, dispersion, aggregation and oxidation state of copper species in an overexchanged Cu-ZSM-5 zeolite catalyst, with the copper species present in a ZSM-5 zeolite catalysts with a lower level of ion exchange. The combination of structural and surface analysis permitted the identification of different copper species, differing in their environment, degree of aggregation and location.

The copper species present in an overexchanged Cu-ZSM-5 zeolite catalyst has already been characterised by Joyner *et al* [21,22]; using a combination of electron spectroscopy and X-ray absorption spectroscopy.

From electron spectroscopy the nature of the copper species were investigated using the Cu $2p_{3/2}$ binding energies and associated shake up satellites, the kinetic energy of the Cu L_3VV Auger transition and the Auger parameter, which is the sum of a photoelectron binding energy and the related Auger kinetic energy.

The external surfaces of the as prepared zeolites were found to be highly enriched in copper species, which however became more evenly distributed across the zeolite crystal upon calcination or on exposure to reducing conditions or reactive atmospheres. This decrease in surface copper concentration was attributed to migration of copper ions into the bulk zeolite channels.

XPS and XAES spectra exhibited distinctly higher XPS binding energies, lower Auger kinetic energies and lower Auger parameters compared to bulk copper oxides and other copper compounds [25,26]. It was stated that these unusual spectral parameters indicated the presence of isolated metal ions and / or small clusters dispersed within the zeolite matrix. This behaviour had been noted previously for metal cations dispersed in zeolites [26-35], and had been attributed to initial state changes such as charge transfer and changes in the Madelung energy and to final state effects particularly intraatomic and extraatomic relaxation energies.

EXAFS spectroscopy was used to probe the coordination environment of copper species in an overexchanged Cu-ZSM-5 catalyst, and showed the presence of isolated copper species and small copper / oxygen aggregates.

The main feature of the Cu-K edge EXAFS of an overexchanged material was a Cu-oxygen bond distance of approximately 1.96 Å, with a coordination number between five and six. The contribution of other shells was less significant, however a small peak was noted in the Fourier transform at 2.95-2.96 Å, due to a Cu-O-Cu bond, typical for both Cu(II) and Cu(I) oxides. In light of the evidence for Cu-Cu interatomic distances typical of those found in copper oxides; Joyner *et al* stated that EXAFS indicated the presence of small copper / oxygen clusters with low nuclearity. It seemed probable that in the as prepared material these small clusters contain hydroxyl groups which were converted into Cu-O-Cu entities on calcination. EXAFS results showed that there was a range of aggregation of copper ions in the catalysts studied.

Hamada *et al* [37] has also characterised copper species in Cu-ZSM-5 by EXAFS. The observation of Cu-Cu distances, similar to those observed in copper oxides, was also reported for Cu-ZSM-5 catalysts with a high copper loading; and was suggested to indicate the formation of aggregated copper species.

In the active catalysts both electron spectroscopy and X-ray spectroscopic measurements indicate that there is ready interconversion between Cu(I) and Cu(II) for both isolated

copper sites and clustered species, depending the atmosphere present. Joyner *et al* [21,22] state that the equilibrium between Cu(II) and Cu(I) appeared to be significant in maintaining the catalytically active sites. The Cu(II) state was found to predominate under conditions relevant to lean burn exhaust gas purification.

Therefore it was revealed that there are two different types of copper species within the ZSM-5 zeolite channels of an overexchanged ZSM-5 zeolite catalyst [21,22]. Isolated copper ions and small clusters where the copper atoms are linked by extra lattice oxygen species such as [Cu-O-Cu]²⁺ dimers are both contained within the zeolite channels. It was proposed that both copper clusters and isolated ions may be necessary to provide the optimum catalytic performance.

5.2 Results and Discussion

Ion exchanged Cu-ZSM-5 zeolite catalysts examined by XPS/XAES and EXAFS are listed below in Table 5.1

Cu-ZSM-5	Parent	Framework	wt% Copper	% Exchange	Preparation
Catalyst	Zeolite	Si:Al Ratio	loading	Level	medium
1	D411	25	1.32	65.9	Aqueous
2	D411	25	3.26	164.2	Aqueous

Table 5.1. Cu-ZSM-5 catalysts investigated by XPS, XAES and EXAFS.

Copper species present in both the overexchanged and low level exchanged Cu-ZSM-5 zeolite catalysts, listed in Table 5.1, are characterised by X-ray photoelectron spectroscopy (XPS), X-ray excited Auger spectroscopy (XAES) and X-ray absorption spectroscopy (EXAFS). The combination of structural and surface analysis techniques enables the identification of copper species differing in environment, degree of aggregation and location.

X-ray excited electron spectra were recorded with a VG ESCA 3 spectrometer using MgKa radiation, details of which are given in Chapter 2 of this thesis. Binding energies and kinetic energies were determined relative to C 1s, binding energy = 285.0 eV. Binding energies are accurate to 0.2eV and kinetic energies are accurate to 0.3 eV. Prior to use in the calculation of atomic concentrations, which are accurate to \pm /- 20%, the relevant relative integral peak intensities were corrected for photoionization cross sections [36], electron escape depths and analyser factors.

The main features of interest from the electron spectroscopy results are the Cu $2p_{3/2}$ photoelectron binding energy with the associated shake up satellites and the kinetic energy of the Cu L₃VV Auger transition.

Cu-ZSM-5 samples were investigated as prepared and calcined. Relevant spectral information is presented in Table 5.2. Results presented are the binding energy of the Cu $2p_{3/2}$ peak, the kinetic energy of the Cu L_3VV Auger peak, the Auger Parameter which is the sum of the binding energy and kinetic energy and the Cu/Si atomic ratio. Typical Cu $2p_{3/2}$ photoelectron and Cu L_3VV Auger peaks, for an as prepared and calcined Cu-ZSM-5 catalyst, are presented in Figure 5.1 and 5.2 respectively.

Sample	Treatment	Cu 2p _{3/2}	Cu L ₃ VV	copper	ΔΚΕ/	$\Delta \alpha^{b}$	Cu/Si
		BE/eV	KE/eV	Auger	eV ^b		atomic
				parameter			ratio
				/ eV ^a			
65.9%	As Prepared	935.8	912.9	1848.7	-4.8	-4.3	0.014
Cu-ZSM-5							
65.9%	Calcined	935.8	911.3	1847.1	-6.4	-5.9	0.018
Cu-ZSM-5							
164.2%	As Prepared	936.4	914.2	1850.6	-3.5	-2.4	0.121
Cu-ZSM-5							
164.2%	Calcined	936.8	912.8	1849.6	-4.9	-3.4	0.029
Cu-ZSM-5							
CuO	As Received	933.8	917.6	1851.4	-	-	-

a) Cu Auger parameter α -Cu = BE(Cu 2p_{3/2}) + KE(Cu L₃VV).

b) Auger parameter and KE shifts with respect to CuO.

Table 5.2 Electron spectroscopy (XPS/XAES) results for as prepared and calcined Cu-ZSM-5 catalysts.

Sample	Treatment	Cu-O	Cu-O	Cu-Cu ^a	Cu-Cu ^a
		CN^b	R/Ű	CN^{b}	R/Ű
65.9%	As Prepared	6.9	1.928	0.0	0.0
Cu-ZSM-5					
65.9%	Calcined	6.5	1.933	0.0	0.0
Cu-ZSM-5					
164.2%	As prepared	5.8	1.933	1.5	2.911
Cu-ZSM-5					
164.2%	Calcined	4.9	1.942	2.0	2.903
Cu-ZSM-5					

a) The Cu(-O-)Cu distance in the oxide structure.

b) Coordination number, accurate to $\pm 15\%$

c) Interatomic distance, accurate to ca ± 0.02 Å.

Table 5.3. X-ray absorption spectroscopy (EXAFS) results for as prepared and calcined Cu-ZSM-5 catalysts.





Figure 5.1 (A) Cu $2p_{3/2}$ photoelectron spectra and (B) Cu L_3VV Auger spectra as prepared overexchanged 164.2% Cu-ZSM-5



Figure 5.2 (A) Cu $2p_{3/2}$ photoelectron spectra and (B) Cu L_3VV Auger spectra calcined overexchanged 164.2% Cu-ZSM-5



Figure 5.3 Reciprocal and real space Cu K edge EXAFS for as prepared ion exchanged 65.9% Cu-ZSM-5



Figure 5.4 Reciprocal and real space Cu K edge EXAFS for calcined ion exchanged 65.9% Cu-ZSM-5



Figure 5.5 Reciprocal and real space Cu K edge EXAFS of as prepared overexchanged 164.2% Cu-ZSM-5



Figure 5.6 Reciprocal and real space Cu K edge EXAFS for calcined overexchanged 164.2% Cu-ZSM-5



Figure 5.7 Two dimensional chemical state plot of electron spectroscopy results obtained for Cu-ZSM-5 zeolite catalysts, as reported by Joyner *et al* [22].

Copper species present within the Cu-ZSM-5 zeolites may be distinguished from one another by the use of the Cu $2p_{3/2}$ photoelectron peaks and Cu L₃VV Auger lines. The Cu $2p_{3/2}$ photoelectron peaks, for the as prepared and calcined overexchanged and low level ion exchanged Cu-ZSM-5 catalysts, all had an associated shake up satellite slightly higher that the binding energy of the main peak diagnostic of the Cu(II) oxidation state. The presence of a shake up satellite at higher binding energy than the main core level is a characteristic feature of all Cu(II) compounds and is the best indicator of the presence of this oxidation state [25].

Distinctly higher XPS binding energies and lower Auger kinetic energies were observed for both catalysts studied, as prepared and calcined, compared to bulk CuO. The resulting Auger parameters were also observed to be lower in energy than bulk CuO. Calcination had no apparent influence on the Cu 2p_{3/2} binding energy position for either catalyst studied. Upon calcination there was however a decrease in both the kinetic energy of the Cu L₃VV Auger transition and resulting Auger parameter, for both the overexchanged and low level exchanged Cu-ZSM-5 catalysts. Cu/Si atomic ratios were calculated for as prepared and calcined materials. In the overexchanged Cu-ZSM-5 catalysts the Cu/Si atomic ratio is considerably reduced following calcination, for the low level ion exchanged sample however the Cu/Si atomic ratio is not significantly altered.

The photoelectron binding energy and Auger kinetic energy positions of the relative peaks are affected by the oxidation state and local environment of the element under consideration. Changes in both the X-ray photoelectron binding energy and the Auger electron kinetic energy result from initial state changes such as charge transfer and changes in Madelung energy; and also from final state effects, particularly intra and extraatomic relaxation. For a particular atomic species the changes in photoelectron binding energy (BE), Auger kinetic energy (KE) and the Auger parameter may be defined as follows [25,28].

 $\Delta BE = \Delta E(q) - \Delta ER$ $-\Delta KE = \Delta E(q) - 3\Delta ER$ $\Delta \alpha = 2\Delta ER$

Where $\Delta E(q)$ is the change in the initial state term and ΔER represents the change in relaxation energy which is normally dominated by the extraatomic component.

The term α is defined as the Auger parameter, which is the sum of the binding energy of the most prominent and sharp photoelectron peak and the kinetic energy of the most prominent and sharp Auger transition.

The Auger parameter is useful to characterise the chemical states of elements in cases where steady state charging of the sample or small shifts in core binding energy present analytical problems. With the use of the Auger parameter steady state charge corrections are unnecessary, these effects cancel each other out. Chemical shifts in XAES transitions are usually larger than photoelectron transitions, leading to higher sensitivity of Auger parameter for investigation of chemical states.

The change in the Auger parameter may be defined as the sum of the changes in the photoelectron binding energy and Auger kinetic energy. The change in Auger parameter was shown above to represent twice the relaxation energy change, of which the extra atomic portion is known to dominate. Therefore changes in the Auger parameter are proportional to the change in the extraatomic relaxation between different chemical states. The change in the Auger parameter is therefore a direct measure of the electronic interaction with the surrounding atoms. The Auger KE and resulting Auger parameter is sensitive to the chemical state and environment of copper species in zeolites [22,28-34].

It has been shown that by arranging the photoelectron binding energies and Auger electron kinetic energies on a 2-dimensional chemical state plot, different chemical states and locations of copper can be identified [28]. In such a chemical state plot the kinetic energy of the Auger line is on the ordinate, the binding energy of the photoelectron line in the negative direction is on the abscissa, and the Auger parameter is on a diagonal grid. A chemical state plot published by Joyner *et al* [22] is represented in Figure 5.7. This presents the spectral characteristics of copper species present in Cu-ZSM-5 catalysts subsequent to various pretreatments, and for comparison, in bulk Cu(I) and Cu(II) oxides and Cu metal.

As documented above the XPS and XAES spectra of both overexchanged and low level ion exchanged Cu-ZSM-5 catalysts studied, as prepared and calcined, have distinctly higher XPS binding energies, lower Auger kinetic energies and lower Auger parameters compared to bulk CuO and other copper (II) compounds [25,32]. These anomalous spectral parameters are suggested to reflect the presence of isolated metal ions and small clusters dispersed within the zeolite matrix. Similar behaviour has been noted previously for metal cations dispersed within zeolites (21,22,26-34). The anomalously low values obtained for

both the kinetic energy of the Cu L_3VV Auger transition and the Auger parameter, for both Cu-ZSM-5 zeolites studied; probably reflects the decrease of the extraatomic relaxation term, due to the high dispersion of the copper ions within the zeolite framework. Decreases in extraatomic relaxation energy are expected for highly dispersed phases [32-35]. The Auger kinetic energy and Auger parameter, taken together provide an efficient means to distinguish the location and aggregation of copper species dispersed within a zeolite matrix. The slight decrease in both the Auger kinetic energy and Auger parameter observed upon calcination is ascribed to an increase in copper dispersion caused by further migration of copper into the zeolite matrix.

An interesting feature of as prepared overexchanged Cu-ZSM-5 sample is the high surface concentration of copper species, indicated by the Cu/Si atomic ratio. Although initially concentrated at the external surface of the zeolite, copper becomes well dispersed throughout the bulk on calcination. The decrease in surface copper concentration upon calcination indicates further migration of copper species into the zeolite channels. Furthermore the negative shift of the kinetic energy of the Auger transition and the Auger parameter supports this. Cu/Si atomic ratios calculated for the low level ion exchanged Cu-ZSM-5 material, indicates that the Cu/Si atomic ratio is not significantly altered upon calcination. This result suggests that copper species present in the low level ion exchanged Cu-ZSM-5 catalysts is well dispersed upon preparation, unlike the overexchanged sample where a large proportion of the total copper species resides on the external surface of the zeolite crystal prior to calcination.

The 2-dimensional chemical state plot illustrated in Figure 5.7 shows that different combinations of chemical state, dispersion and location of copper species can be identified, using the combination of Cu $2p_{3/2}$ X-ray photoelectron binding energy, the Cu L₃VV Auger electron kinetic energy and the Auger parameter.

Therefore both the overexchanged and low level ion exchanged Cu-ZSM-5 catalysts studied exhibit higher XPS binding energies, lower Auger kinetic energies and lower Auger parameters in comparison to CuO and other bulk Cu(II) compounds. This is suggested to indicate that copper is dispersed within the zeolite matrix, as isolated ions or small clusters adopting the +2 oxidation state. In the low level ion exchanged Cu-ZSM-5 zeolite copper is evenly dispersed across the zeolite before and after calcination. In the as prepared overexchanged Cu-ZSM-5 catalyst the external surface of the catalysts is highly enriched in copper species, which do however become more evenly distributed across the zeolite crystal as a result of calcination.

X-ray absorption (EXAFS) spectroscopy was employed to compare the coordination environment of copper species in an overexchanged Cu-ZSM-5 catalyst with that in a catalyst prepared with a low level of copper ion exchange. Spectra were collected at the CCRL synchrotron radiation source in Daresbury. Spectra were analysed using standard techniques developed at Daresbury, in particular the program EXCURV 92. A fuller description of this technique and experimental detail is given in chapter 2 of this thesis.

EXAFS characterisation was carried out on, as prepared and calcined, overexchanged and low level ion exchanged, Cu-ZSM-5 catalysts. The results of the analysis for each sample are presented in table 5.3. EXAFS spectra were recorded and analysed in the range 3-12 Å. The main feature of the Cu K edge EXAFS spectra for both the overexchanged and low level ion exchanged, as synthesised and calcined, Cu-ZSM-5 catalysts, is a Cu-O bond distance of approximately 1.94 Å with an associated coordination number of 5-6. In addition there is also a weaker feature at 2.91 Å which is identified as the Cu-O-Cu bond present in the structures of both Cu(II) and Cu(I) oxides, this feature however is observed only for the as prepared and calcined overexchanged Cu-ZSM-5 catalyst. These features are illustrated in Figures 5.3-5.6, in the reciprocal and real space Cu-K edge EXAFS. The structure at 2.9 Å is present in bulk CuO, although the coordination number is somewhat lower in the overexchanged Cu-ZSM-5.

The presence of Cu-Cu interatomic distances typical of those found in copper oxides suggests the presence of small copper / oxygen clusters with low nuclearity in the overexchanged Cu-ZSM-5 catalysts [22]. Hamada *et al* [37] also observed Cu-Cu distances, similar to those observed in copper oxides, for Cu-ZSM-5 catalysts with a high copper loading, and also suggested the formation of aggregated copper species.

Therefore important results emerged from the X-ray absorption spectra. The EXAFS results for the low level ion exchanged Cu-ZSM-5 catalysts showed no evidence of Cu-Cu distances indicating the presence of highly dispersed isolated copper ions only within the zeolite matrix.

EXAFS investigations for the overexchanged Cu-ZSM-5 catalysts revealed evidence for Cu-Cu distances typical of Cu-O-Cu bonding at low coordination numbers. The observation

of Cu-Cu distances indicate the formation of small copper clusters. The small copper clusters are thought to be formed from the conversion of copper hydroxyls present in the as prepared material which decompose to form Cu-O-Cu species on calcination

The X-ray excited electron and X-ray absorption spectroscopy results provide complementary data for the investigation of the copper species present in Cu-ZSM-5 catalysts. XPS/XAES and EXAFS showed that copper is well dispersed within the zeolite channels of both the overexchanged and the low level ion exchanged Cu-ZSM-5 catalyst. Copper is suggested to be in the form of both isolated copper species and small Cu-O clusters in overexchanged Cu-ZSM-5 catalysts, but only in the form of isolated copper ions in the Cu-ZSM-5 catalysts with a low level of copper ion exchange.

The entities introduced into the catalyst by overexchange are thus dimers or small metal / oxygen clusters such as $[Cu-O-Cu]^{2^+}$, these species were not observed in the Cu-ZSM-5 catalysts with a low level of copper ion exchange, these species were shown to exhibit the highest turnover number for the SCR reaction. Therefore the presence of these dimeric clusters are suggested to explain the higher activity for the SCR of NOx exhibited by overexchanged Cu-ZSM-5 catalysts.

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Chapter 6 Characterisation of Carbonaceous Deposits Formed on Cu-ZSM-5 Catalysts

6.1 Background

In chapter 4 the reactivity of carbonaceous species deliberately deposited on Cu-ZSM-5 catalysts was examined. It was previously shown that nitrogen is released from these deposits [1]. In chapter 4 it was demonstrated that these deposits are also able to activate NO and oxygen directly [2,3].

It is well recognised that carbonaceous deposits can form on the surface of catalysts for the selective catalytic reduction of NOx under lean oxidising conditions, with possible mechanistic importance [4-6]. Various surface species containing carbon and nitrogen have also been observed under conditions where carbonaceous or coke species are known to deposit. These species have been shown to be comprised of cyanides and isocyanate species as well as hydrogen deficient carbonaceous / coke deposits [1,7,8,9,10].

Carbonaceous deposits, referred to for simplicity as "coke", were laid down on the Cu-ZSM-5 catalysts by exposure to a typical SCR reaction mixture at low temperatures. The reactivity of the carbonaceous deposits in NO reduction, in the absence of other hydrocarbons, was studied by exposing pre-coked catalysts to the same NO-oxygen concentration as was used for steady-state reaction; and heating from 473 K to ca 873-973 K at 10 K min⁻¹. The deposit on the catalysts demonstrated significant activity in NOx reduction. It was found that the total amount of NOx converted was of the same order of magnitude as the amount of deposited coke upon the catalysts surface, it was assumed therefore that all of the carbonaceous deposit was consumed during the reaction. The results showed a variation in the stability of the hydrocarbon deposit towards NO, which was inversely dependent on copper content; implying that the acidity of the zeolite remaining after exchange with copper could be a factor in determining how catalyst activity varies with copper loading. It is has been shown that relatively few Bronsted acid sites remain in the so called overexchanged catalysts, which are the most active for NOx reduction [11]. There is thus an inverse correlation between Bronsted acidity and catalytic performance, suggesting that the presence of too many Bronsted zeolite acid sites and consequently higher levels of carbonaceous deposits, inhibits the NOx reduction reaction.

It is pertinent to confirm the presence of such a carbonaceous / coke deposit upon the Cu-ZSM-5 catalyst, and also to explore its nature. It would also be informative to ascertain whether any structural change takes place within the zeolite framework upon coke deposition, and following the subsequent removal of the carbonaceous deposit upon reaction with NOx. In order to answer some of these questions in situ FTIR and powder XRD experiments were conducted. The merits of both techniques for the above purposes will now be discussed.

6.1.1 FTIR Studies of Coke Deposition on Zeolites

FTIR spectroscopy is a useful technique to investigate the nature of carbonaceous deposits laid down on zeolite catalysts during SCR reaction. FTIR spectroscopy has been used to obtain information about the nature of the species present in coke deposited on different zeolites during hydrocarbon conversion reactions [12-19]. The appearance of a band at approximately 1600 cm⁻¹ has been usually related to the presence of polyaromatic species, its intensity being proportional to the coke content. Monitoring of this absorption band makes it possible to follow spectroscopically the deposition of coke on the catalyst [12-19]. A comprehensive review examining coke formation is usually visualised as the build up of bulky polyaromatic systems with graphite like structure. Karge explained that this definition should be extended to describe carbonaceous deposits which are olefinic or to some extent paraffinic in nature. A more general definition of coke was proposed. "coke consists of carbonaceous deposits which are deficient in hydrogen compared with the coke forming reactant molecules".

Eisenbach and Gallei studied the formation of coke upon conversion of n-hexane and hexene over acidic faujasite catalysts by FTIR [12]. The appearance of a band at approximately 1600 cm⁻¹ was observed upon coke formation. This "coke band" around 1600 cm⁻¹ was assigned to highly dehydrogenated species, probably aromatic compounds with a graphitic structure. A good correlation between the intensity of this band and coke content was found. Adsorption of hexene on CaY, at ambient temperature affords IR absorption bands at 2965 and 2925 cm⁻¹ attributable to symmetric stretching vibrations, and at 1460 and 1380 cm⁻¹ attributable to deformation modes of CH₃ and CH₂. Observations

indicated that saturated hydrocarbon species were present on the zeolite surface. Hexene was also adsorbed on Ca/Y and PtCa/Y at higher temperatures. The ratio of CH₃/CH₂ band intensity in the C-H stretching region increased and in the deformation range two new absorption bands at 1584 and 1345 cm⁻¹ were observed. The absorption bands at 1345 cm⁻¹ and at 1380 cm⁻¹ were assigned to vibrations of tertiary CH groups and to the symmetrical vibration of CH₃-C groups respectively. These IR bands provided evidence for branched surface species. The absorption band at 1585 cm⁻¹ is weak at lower temperatures but becomes dominant, as coke formation increased at higher temperatures. The 1585 cm⁻¹ band was assigned to C=C stretching vibrations of carbon structures present in polyaromatic compounds, and which were inferred to make up the carbonaceous deposit on the catalysts. The results again suggest a relationship between the 1585 cm⁻¹ band and coke formation, its intensity was found to be a measure of the amount of coke deposited on the catalyst surface. From their results Eisenbach and Gallei concluded that during adsorption of hexene on faujasite zeolites, primarily the same linear surface species was formed at ambient or higher adsorption temperatures. At higher temperatures the interaction of adsorbed species with the gas phase initiates rearrangements on the surface of the zeolite producing branched hydrocarbon species with tertiary carbon atoms, with an absorption band at 1345 cm⁻¹. With increasing temperature the band at 1585 cm⁻¹ becomes more intense. This band was assigned to a structural vibration of coke and is a good probe to follow the deposition of carbonaceous materials upon catalytic surfaces. The IR spectrum of coke between 900 and 700 cm⁻¹ show adsorption bands for CH-wagging vibrations of polyaromatic compounds. Coke species formed were therefore described as highly dehydrogenated species, probably aromatic compounds with a graphitic structure. A simultaneous decrease of the absorption band at 3640 cm⁻¹, corresponding to acidic supercage OH groups, and the increase of a coke band at 1585 cm⁻¹ was observed in dynamic and static experiments. This was suggested to support the importance of acidic OH groups for the coking reaction.

Coke formation over HY zeolites, during catalytic cracking reactions of 1-hexene and 4methylcyclohexene, was investigated by Blackmond *et al* [13]. FTIR was used to monitor changes on the catalyst surface during the adsorption of hydrocarbons and subsequent development of highly carbonaceous coke species. Blackmond *et al* observed a large IR band near 1585 cm⁻¹, a moderate band near 1340 cm⁻¹ and a small band near 1460 cm⁻¹ for coke deposited by exposure to hexene at 673 K. The formation of adsorbed hydrocarbons

was observed in the region 2800-3000 cm⁻¹ and below 1500 cm⁻¹. The large band near 1585 cm⁻¹ is commonly ascribed to the carbon-carbon stretching vibration in aromatic rings. This peak was assigned to the highly carbonaceous coke species. The initial coking rate was more rapid for 4-methylcyclohexene than for hexene, suggesting that ring compounds are preferential coke precursors, since coke deposits are thought to be aromatic in nature. The C-H and ring mode absorption regions of the IR spectrum however showed little evidence of aromatic character during reaction of either hydrocarbon reactant; any aromatic bands < 1200 cm⁻¹ were obscured by vibrations of the zeolite structure. Methyl and methylene groups were observed during the reaction and their associated IR bands were noted to intensify as the reaction progressed. The growth of the coke peak at 1585 cm⁻¹ was the only indication of the process of coke formation. It was suggested that the reaction of hydrocarbon to dehydrogenated coke species may proceed so fast that the appearance of intermediates cannot be observed. The coke deposits which remain on the catalyst must then be so highly dehydrogenated that little or no aromatic -CH linkages remain visible in the spectrum. Since aliphatic -CH₂ and -CH₃ groups are observed on the catalyst; another suggestion was put forward, that the coke deposit consists of highly dehydrogenated linear or branched compounds which retain some aliphatic groups. This is supported by the formation of peak at 1340 cm⁻¹, which grows as coke is formed. This peak is assigned to tertiary C-H vibrations of branched hydrocarbons. The hydrocarbon adsorption investigations showed that the composition of the coke exhibited a lack of aromatic character, suggesting that coke formation need not always proceed through aromatic precursors. The coke species appeared to be highly dehydrogenated structures with some aliphatic residues, although coke with a higher aromatic content was observed to be formed on the catalysts possessing a higher concentration of Bronsted acid OH groups. During the cracking reaction of hexene, the growth of the coke band was accompanied by a decrease in the concentration of Bronsted OH groups. It was suggested that this relationship supports the hypothesis that Bronsted acid OH sites act as active sites for coke formation.

Lange *et al* utilised FTIR spectroscopy to examine the carbonaceous species formed during the reaction of ethene over H-mordenite [14]. Upon adsorption at room temperature ethene polymerised to branched and possibly also linear alkanes. Paraffinic IR bands appeared in the region of the CH stretching modes, between 2800 and 3000 cm⁻¹ and in the corresponding deformation region between 1300 and 1500 cm⁻¹. The presence of branched

alkanes was evidenced by a doublet at 1368 and 1382 cm⁻¹, ascribable to a deformation mode of iso-propylic or tert-butylic CH3 groups. When the sample was heated to 450 K under ethene the ratio CH₂/CH₃ groups of the oligomers decreased; indicating substantial cracking and branching of the carbonaceous residues on the surface. When the reaction temperature was increased above 500 K a high temperature coke began to form. This was evidenced by a simultaneous increase of the so called coke band, suggested to be indicative of polyalkenes and for aromatics, around 1600 cm⁻¹ and a decrease of the paraffinic bands between 2800 and 3000 cm⁻¹. Upon further increase of the temperature to 650 K the coke band intensified and a broad band appeared around 1540 cm⁻¹. This band may be ascribed to alkylnaphthalenes, however it may also indicate polyphenylene structures. Finally both bands overlapped and collapsed into a broad band at 1570 cm⁻¹. After a long time on stream the high temperature coke which had formed on the mordenite exhibited a weak band approximately 3080 cm⁻¹, indicative of CH stretch of aromatics. No stretching vibration indicative of paraffinic C-H bands were observed between 2800-3000 cm⁻¹. The in situ IR results suggested the presence of at least two types of coke; a so called low temperature coke, constituted mainly of paraffinic and to a lesser extent olefinic or polyolefinic species, and so called high temperature coke, which consists of polyalkenes, but predominantly of alkylaromatics and polyaromatics.

Sotelo *et al* [16] studied coke deposition during toluene alkylation with methanol over a Mg modified ZSM-5 catalyst. IR difference spectra were obtained by subtraction of the spectra corresponding to the uncoked catalyst. The coke band at 1600 cm⁻¹ was clearly seen, and was proposed to provide evidence for the presence of polyaromatic species. The presence of a doublet at 1365 and 1380 cm⁻¹, typical of branched alkanes, suggests that the coke species deposits also have a certain paraffinic character. The ratio between the intensity of the coke band at 1600 cm⁻¹ and that of the doublet increases with increasing coke content, indicating an increase in the polyaromatic character of the deposited coke.

The nature of coke formed upon a H-ZSM-5 zeolite catalyst, during the transformation of methanol into gasoline, was studied by Benito *et al* [17]. FTIR analysis of coke deposited at 623-723 K revealed bands at 2855, 2930 and 2960 cm⁻¹ corresponding to vibrations of CH₃, CH₂ and CH groups respectively, and at 1460 and 1380 cm⁻¹ corresponding to CH₂ and CH₃ bendings. IR bands were also observed at 3050 cm⁻¹ corresponding to the vibrations of C-H aromatic bonds; and at 1590 cm⁻¹, previously referred to as the coke band, assigned to

the aromatic carbon-carbon stretch. The FTIR results indicate a hydrogenated coke with aromatic nature, constituted of alkylated mono and bi aromatics, oligomers and paraffins.

Uguina *et al* [19] compared the IR spectra of H-ZSM-5 samples subsequent to coke deposition with mesitylene, toluene and iso-butene. The coke band at 1585 cm⁻¹ indicative of polyaromatic species was clearly seen in H-ZSM-5 coked with toluene but appeared as a broad band at 1600cm⁻¹ and with low intensity in the sample coked with iso-butene. The most intense peak in the spectra of the latter is a doublet at 1365 and 1380 cm⁻¹, typical of branched alkanes. Paraffinic absorption bands were observed in the region between 2860 and 3000 cm⁻¹, in the sample coked with iso-butene, but were absent in the samples coked with toluene and mesitylene. The absence of absorption bands in the region between 1600 and 1700 cm⁻¹ is remarkable for all coked samples, showing non-olefinic nature of coke even for that formed from iso-butene. In the case of the sample coked with mesitylene the coke band appeared as a broad band with low intensity, which may be caused by the low coke content of this sample. The results show higher polyaromatic character for the coke formed from toluene than that from iso-butene. From the mesitylene the coke deposits have a more paraffinic character with a high proportion of branched alkanes.

Controlled coking of H-ZSM-5 and dealuminated H-ZSM-5 zeolites, during the conversion of acetone/n-butanol mixtures to hydrocarbons was performed by Lucas et al [18]. The nature of the species present in the coke deposited was investigated by IR spectroscopy. Dealuminated samples showed a more aromatic/olefinic type of coke, whereas coke formed in the unmodified H-ZSM-5 has polyolefinic character. The IR spectrum of the coked parent H-ZSM-5 presents a wide absorption band around 1600-1650 cm⁻¹ attributed to alkenes and bands between 1350 and 1470 cm⁻¹ typical of branched alkanes. Paraffinic bands were also observed between 2800 and 3000 cm⁻¹. The so called coke band usually appearing at 1585 cm⁻¹, and indicative of polyalkenes and or aromatic structures, is observed but with low intensity. As regards coke deposited on dealuminated H-ZSM-5 samples, an important band was observed at 1700-1750 cm⁻¹, and was suggested to be due to aromatic species in the coke deposited on these catalysts. A high intensity of the coke band at approximately 1600 cm⁻¹ was clearly evident. These results indicated a more aromatic character in the coke deposited dealuminated H-ZSM-5 zeolites and a polyolefinic nature in the coke on the parent H-ZSM-5 zeolite. It was reported that the results are in good agreement with acid site densities observed for these catalysts.

6.1.2 Powder XRD Studies of Zeolites

Powder XRD [20-24] has shown that the zeolite ZSM-5 can exist in crystallographically different modifications, phase transitions can take place between monoclinic and orthorhombic forms. Such changes in the ZSM-5 framework structure may be induced by both temperature effects and the presence of organic adsorbates. The reversible orthorhombic to monoclinic transition observed with XRD on ZSM-5 is realised by a complicated displacement of framework atoms. As synthesised ZSM-5 containing tetrapropylammonium bromide as a template has been shown to exhibit orthorhombic symmetry, whereas removal of the template by calcination changes the symmetry to monoclinic [20]. At higher temperatures the monoclinic structure of template free ZSM-5 undergoes a reversible symmetry change to the orthorhombic form. Zeolite ZSM-5 has been shown to demonstrate this reversible phase transition at approximately 330 K, and exhibits monoclinic symmetry below and orthorhombic symmetry above this temperature [22,23]. At room temperature the symmetry change can be reversibly induced by loading and unloading H-ZSM-5 powder samples with ammonia and with various organic molecules [21]. The sorbate loaded and unloaded H-ZSM-5 show orthorhombic and monoclinic symmetry respectively. XRD show that the framework structure of ZSM-5 distorts with the sorption of organic molecules [21,22]. Similar framework changes have also been observed to occur upon coke formation in the channel system ZSM-5.[24].

A thorough study of factors affecting crystal symmetry in ZSM-5 type materials, utilising crystallographic computations and experimental powder XRD was performed by Wu *et al* [20]. Their data indicate that the framework structure of ZSM-5 can undergo a reversible displacive transformation, between apparent orthorhombic and monoclinic symmetry forms. Powder XRD patterns of as synthesised ZSM-5 materials are consistent with orthorhombic crystal symmetry. A change to monoclinic symmetry is observed upon certain treatments, such as calcination and ion exchange. A typical powder XRD pattern of an as synthesised form of ZSM-5, characteristic of orthorhombic symmetry, is described. The most intense peak occurs at $2\theta = 23.2^{\circ}$; due to the presence of organic material in the intracrystalline voids, the intensities of the first two lines at 7.9 and 8.8° 20 are lowered. When ZSM-5 is transformed to the ammonium form, changes are observed in the powder XRD pattern. Alterations to the relative intensity of some peaks are noted. The first two lines increased in intensity. Shifts in reflection

position are also observed. The doublet centred at 14.7° 20 merged to form an apparent single line, the doublet nature of the line at 23.2° 20 became more apparent, and that at 23.9° 20 became less distinct. The appearance of doublets in place of singlets at 24.4, 29.2, and 48.6 ° 20 were also observed. The position of the lines, splitting of the peaks and changes in intensity observed can be accounted for by introduction of lattice parameters, characteristic of monoclinic symmetry. According to Wu *et al* this transformation from orthorhombic to monoclinic symmetry appears to be as a consequence of a reversible displacive transformation resulting from changes of the chemical content in the structural voids. In the as synthesised form of ZSM-5, the intracrystalline voids, are loaded with organic template matter, upon removal of this organic matter these samples display an XRD pattern characteristic of monoclinic symmetry. Therefore the results are said to indicate that the content and location of extraframework species within the zeolite ZSM-5 are critical variables in controlling the symmetry change, from apparent orthorhombic to monoclinic. Wu also demonstrated that the orthorhombic monoclinic symmetry change can be reversibly induced by loading and unloading H-ZSM-5 powder samples with ammonia.

Sorbate induced structural changes in a ZSM-5 material have also been reported by Fyfe *et al* [21]. In their investigation they demonstrate that the presence of sorbed molecules can cause reversible changes in the silicalite framework structure. That the effect of sorbed molecules is due to modification of the lattice structure, is confirmed by changes in the powder XRD pattern, particularly in the region 22 - 25° 20. The lowering of the relative intensity of the two peaks 7.9 and 8.9° 20 reflects the presence of an adsorbate. Changes in the peaks at 23.3 and 23.8° 20, analogous to those reported by Wu et al [20], clearly indicate that structural changes causing lattice distortion are occurring, resulting in changes in cell dimension. The loss of the doublet splitting of the peak at $20 = 24.4^{\circ}$ is observed and indicative of a change from a monoclinic to orthorhombic symmetry.

The orthorhombic monoclinic phase transition in the ZSM-5 zeolite silicalite has also been investigated by Hay *et al* [22,23]. XRD experiments have shown that the framework symmetry change between monoclinic and orthorhombic, exhibited in ZSM-5 zeolite, depends not only on factors such as the presence of sorbate molecules [20,21] but also on sample temperature. Powder XRD measurements were carried out on silicalite samples at selected temperatures within the range 262-798 K. Hay *et al* [22,23] reported that the peak positions in the XRD pattern measured within the range 7-35° 20 at 298K matched those

calculated from a monoclinic model, whilst at 325 K, the positions matched those calculated from an orthorhombic model. Peaks observed at 24.5-25° 20 were separated in the monoclinic but not in the orthorhombic pattern, whilst the separation between the peaks at 23-23.5° 20 was more obvious in the in the orthorhombic than in the monoclinic pattern. The last observation, however, is at odds with previous observations made upon the monoclinic / orthorhombic phase transition in ZSM-5 type materials. Wu *et al* [20] and Fyfe *et al* [21] both report that the doublet nature of the line at 23.3 - 23.2° 20 became more apparent upon the transition from orthorhombic to monoclinic symmetry. In conclusion it was shown by Hay *et al* [22,23] by the use of powder XRD, that the change in framework symmetry between monoclinic and orthorhombic in ZSM-5 zeolite also depends on temperature of the sample and is reversible.

Powder XRD is also capable of detecting phase changes induced when coke occupies zeolite ZSM-5 channels. As demonstrated by Bibby et al [24], the presence of internal coke in ZSM-5 catalysts for methanol conversions was deduced from XRD experiments. These experiments were carried out investigate the site of coke formation. Bibby et al attributed changes in the relative positions and intensities of peaks in the XRD patterns of coked samples to a distortion of the ZSM-5 structure by internal coke deposits. As documented above [20,22], ZSM-5 can undergo a displacive transformation from monoclinic to orthorhombic when it occludes bulky ions or sorbs organic molecules. Bibby et al showed that as the coke content of the ZSM-5 increased, relevant peak positions in the powder XRD pattern shifted from those found in the H form to those typical of precursor containing occluded TPA ions. Changes in the XRD pattern were studied particularly in the region 23-25° 2 θ . The doublet nature of the line at 23.2° 2 θ became less apparent, and that at 23.9° 20 became more distinct. A transformation of the doublet to a singlet peak in the region of 24.4° 20 was also noted. These changes in the XRD pattern, upon coke formation, are characteristic of the transformation of ZSM-5 framework structure from that of monoclinic to orthorhombic symmetry. By analogy with previous work [20,21], Bibby et al stated that a proportion of the coke which formed during methanol conversion was present inside the zeolite channel system. On removal of the coke the original XRD pattern was regenerated, indicating that ZSM-5 framework symmetry reverted from that of orthorhombic back to the monoclinic form. Therefore ZSM-5 undergoes a displacive transformation from monoclinic to orthorhombic upon internal coke deposition, altering the relative peak positions and

intensities in the XRD patterns. Coke caused the same lattice structural changes as did the occlusion of large organic molecules or bulky ions, indicating the presence of internal coke. In a study of coke formation upon dealuminated H-ZSM-5 zeolites; Lucas *et al* [18] report that their XRD results indicate that coke formation produces the same effect as occluded TPA ions [20]. As synthesised ZSM-5 with TPA ions occluded, displayed an XRD pattern with no doublet nature to the peak at $2\theta = 23^{\circ}$ and a singlet peak at $2\theta = 24.4^{\circ}$. The XRD pattern of H-ZSM-5 without coke, exhibited a shoulder on peak at $2\theta = 23^{\circ}$ and a split peak was observed at $2\theta = 24.4^{\circ}$. The XRD pattern obtained for H-ZSM-5 with coke was similar to that observed for the as synthesised material with TPA ions occluded, the shoulder on the peak at $2\theta = 23^{\circ}$ disappeared and the singlet peak at $2\theta = 24.4^{\circ}$ returned. Therefore Lucas *et al* concluded that at least part of the total coke formed is deposited inside the channel system

Work carried out by Uguina et al [19] compared the powder XRD pattern of uncoked H-ZSM-5 samples with those subsequent to coke deposition with mesitylene, toluene and isobutene. The XRD patterns were collected in the region of the most intense peaks ($2\theta = 22$ - 25°). The pattern of the fresh ZSM-5 presented an intense doublet at $2\theta = 23.1$ and 23.3° . This doublet was also observed in the pattern observed with mesitylene. It was absent however in the XRD pattern of samples coked with toluene and iso-butene; both peaks had collapsed into one at $2\theta \ 23.2^{\circ}$. Results showed that coke from toluene and iso-butene cause lattice distortions in the zeolite, indicating that at least part of the coke was deposited within the pore structure. Coke from mesitylene, however, did not seem to change the cell dimensions of ZSM-5 which suggested its location on the outer surface.

In the studies outlined above [18,19,24], XRD proved valuable in the investigation of coke formation within zeolites. Powder XRD is used in this work to investigate structural changes to Cu-ZSM-5 catalysts upon the deposition of a carbonaceous deposit and after its subsequent removal by reaction with NO. The reversible monoclinic to orthorhombic transition observed by powder XRD should allow us to determine whether internal coke is formed upon the Cu-ZSM-5 catalyst. XRD should also be valuable to study whether all carbonaceous deposits are eliminated from the catalyst subsequent to the reaction with NO. Deductions from XRD regarding the location of coke deposits within ZSM-5 should be treated with caution. XRD allows us to infer the presence of internal coke but does not allow us to assume or eliminate the possibility of external coke deposition.

6.2 Results and Discussion

Ion exchanged Cu-ZSM-5 zeolite catalysts examined by FTIR and powder XRD are listed below in Table 6.1

Cu-ZSM-5	Parent	Framework	wt% Copper	% Exchange	Preparation
Catalyst	Zeolite	Si:Al Ratio	loading	Level	medium
1	C405	31	0.96	60.6	Aqueous
2	C411	34	0.93	62.2	Aqueous

Table 6.1 Cu-ZSM-5 catalysts investigated by FTIR and XRD

Carbonaceous deposits, formed on Cu-ZSM-5 catalysts by interaction at low temperature with C_3H_6 , NO and O_2 are characterised spectroscopically. In this study in situ FTIR was used to obtain information about the nature of the species present in coke deposited on a Cu-ZSM-5 zeolite catalyst during the selective catalytic reduction of NOx. IR spectroscopy has been used extensively within the literature to obtain information about the nature of the species present in the coke deposited on different zeolites during hydrocarbon conversion reactions [12-19].

IR spectroscopic measurements were carried out in transmission mode using a specially constructed *in situ* vacuum cell which can be heated to temperatures > 800 K and an ATI RS1 Fourier transform infra red spectrometer.

The catalyst used in this study is a 60.6% exchanged Cu-ZSM-5, catalyst 1 in Table 6.1 above. The catalyst was loaded into the in situ cell and was activated for 1 hour in 10 mbar of oxygen at 773 K. The sample was then cooled to 473 K, and an IR spectrum measured. The IR spectrum of this activated Cu-ZSM-5 is illustrated in Figure 6.1. The IR spectrum exhibit the expected bands in the OH stretching vibration region [26,27]; that at 3670 cm⁻¹ is assigned to extraframework species, those at 3600-3610 cm⁻¹ to bridging, acidic hydroxyl stretching vibrations, and that at 3740 cm⁻¹ is attributed to stretching vibrations of terminal Si-OH groups. The region of the spectrum between 1600-2100 cm⁻¹ is dominated by absorption bands ascribed to overtone bands of the zeolite structure [27]. This spectrum is useful for reference, when comparing the catalyst subsequent to coke deposition.

Coke was deposited by exposing the Cu-ZSM-5 catalyst to a simulated SCR reaction mixture; consisting of 2 mbar NO, 1 mbar C_3H_6 and 7 mbar O_2 at 773 K. The temperature of the in situ cell was then lowered slowly to 473 K, at which point a further deposition of simulated reaction mixture was made. The IR spectrum of the carbonaceous deposit on the

Cu-ZSM-5 catalyst is shown in Figure 6.2. The bands at 2879, 2937 and 2971 cm⁻¹ are typical of hydrocarbons adsorbed on zeolites such as H-ZSM-5, and are due to C-H stretching vibrations [12-19]. These bands are considered to be indicative of an adsorbed species with paraffinic character. It is important to note that the bands characteristic of zeolite Bronsted acidity, normally observed at 3610 cm⁻¹, have been suppressed, indicating that these sites have played their expected role in hydrocarbon activation. The intense band observed at approximately 1600 cm⁻¹, commonly referred to as the "coke band", is assigned to C=C stretching vibrations in adsorbed aromatic molecules. This coke band is characteristic of polyaromatic species, which are considered to make up the carbonaceous / coke deposits on zeolites [12-19]. Observing this absorption band makes it possible to confirm spectroscopically the deposition of coke on the Cu exchanged ZSM-5 catalyst studied here. The band at 1600 cm⁻¹, is however superimposed on an overtone band associated with zeolite lattice vibrations. The presence of this coke band at 1600 cm⁻¹ is confirmed by comparing the IR spectrum obtained for clean activated Cu- ZSM-5, Figure 6.1, with the IR spectrum of the carbonaceous deposit on the Cu-ZSM-5 illustrated in Figure 6.2. The intensity of the coke band at 1600 cm^{-1} is significantly more intense in the IR spectrum corresponding to the coked Cu-ZSM-5 than that in the spectra for the clean catalysts. An IR difference spectrum is obtained by subtracting the spectra collected for the clean Cu-ZSM-5 catalyst, obtained prior to coke deposition, presented in Figure 6.1; from the spectra obtained for the carbonaceous deposit on the Cu-ZSM-5 catalyst, depicted in Figure 6.2. The difference spectrum is presented in Figure 6.3. The coke band at 1600 cm⁻¹ was clearly seen in this spectrum, and is suggested to provide further evidence for the presence of polyaromatic coke species.

The coke band at 1600 cm⁻¹ provides evidence for the presence of polyaromatic species within the coke deposit. IR bands in the region of the CH stretching modes, between 2800 and 3000 cm⁻¹, suggests that the deposited coke species also has some paraffinic character. Other significant features are observed from the spectrum of the carbonaceous deposit on Cu exchanged ZSM-5. A band observed at 2250 cm⁻¹, accepted to be due to cyanide species; has previously been observed by Hayes et al [1] upon a Cu-ZSM-5 catalyst under similar conditions. Hayes *et al* [1] reported that organic cyanide species, formed upon Cu-ZSM-5 catalysts under typical lean SCR reaction conditions; and proposed that the nitrile is

an important intermediate in the selective reduction of nitrogen oxides to dinitrogen in the presence of hydrocarbons and excess oxygen.

IR Bands are observed at 3300 and 3375 cm⁻¹, these are N-H stretches which probably reflect the presence both of =NH and -NH₂ groups. NH stretches have been observed previously under similar conditions by Poignant *et al* [25]. This observation provides important evidence that the organic nitro groups which are formed first in the sequences of reactions leading to the release of nitrogen [26], can undergo sequential reduction to form cyanide

$$-\mathrm{NO}_2 \rightarrow \mathrm{N-OH} \rightarrow -\mathrm{NH}_2 \rightarrow =\mathrm{NH} \rightarrow \equiv \mathrm{N}$$

The zeolite is unable to activate oxygen at the relatively low temperatures where the hydrocarbon deposit is formed. Coupled with the presence of readily activated propene the result is an atmosphere_which is more strongly reducing than is the case where steady state reactivity is high and where the reduction sequence may not progress as far as the cyanide.


Wavenumbers / cm-1

Figure 6.1 IR spectrum of activated 60.6% Cu-ZSM-5

.





Wavenumbers / cm-1



Absorbance



Wavenumbers / cm-1





Figure 6.4 Powder XRD Pattern of 62.2% Cu-ZSM-5; subsequent to calcination at 773 K for 1 hour in static air.



Figure 6.5 Powder XRD Pattern of 62.2% Cu-ZSM-5, subsequent to coke deposition. Carbonaceous deposits were laid down on the Cu-ZSM-5 catalysts by exposure to a typical SCR reaction mixture at low temperatures. The reactant gas mixture NO, C_3H_6 , O_2 was passed over the Cu-ZSM-5 catalysts at 473 K,



Figure 6.6 Powder XRD Pattern of 62.2% Cu-ZSM-5; subsequent to reaction of the carbonaceous deposit with NO.

The reactivity of the hydrocarbon deposit for NO reduction, was studied by exposing the catalysts to a mixture of NO, O_2 and heating from 473 - 920 K at 10 K min⁻¹.

Powder XRD is used in this work to investigate structural changes that occur within Cu-ZSM-5 catalysts upon the deposition of a carbonaceous deposit and after its subsequent removal by reaction with NO. XRD should enable us to determine whether the coke formed upon the Cu-ZSM-5 catalyst resides in a intrazeolite location. XRD should also allow us to determine whether all of the carbonaceous deposit is eliminated from the catalyst subsequent to the transient reaction with NO and oxygen.

The catalyst used in this study is 62.2% exchanged Cu-ZSM-5, catalyst 2 in Table 6.1. Powder XRD patterns were recorded for this Cu-ZSM-5 catalyst, subsequent to three different treatments.

1: Cu-ZSM-5; calcination at 773 K for 1 hour in static air.

2 : Cu-ZSM-5, subsequent to coke deposition, Carbonaceous deposits were laid down on the Cu-ZSM-5 catalysts by exposure to a typical SCR reaction mixture at low temperatures. The reactant gas mixture NO, C_3H_6 , O_2 was passed over the Cu-ZSM-5 catalysts at 473 K.

3 : Cu-ZSM-5; subsequent to reaction of the carbonaceous deposit with NO, The reactivity of the hydrocarbon deposit for NO reduction, was studied by exposing the catalysts to a mixture of NO, O_2 and heating from 473 - 920 K at 10 K min⁻¹.

The treatments listed above were all conducted within the catalytic microreactor, described fully in chapter 2 of this thesis.

The XRD pattern of freshly calcined Cu-ZSM-5, illustrated in Figure 6.4, exhibited a shoulder on the peak at $2\theta = 23^{\circ}$, a singlet peak at 23.9 and a split peak at $2\theta = 24.4^{\circ}$. In line with previous XRD studies of ZSM-5 zeolites, from the powder XRD pattern presented it is clear that the calcined Cu-ZSM-5 zeolite exhibits monoclinic crystal symmetry. This sample has not been utilised for the selective catalytic reduction reaction, therefore it does not possess any occluded material within its channels. Monoclinic framework symmetry is almost expected for this sample. A low copper ion exchange level was utilised to avoid any possible interference which may occur as a result of the higher cation exchange levels.

Upon coke deposition, the Cu-ZSM-5 sample displayed the XRD pattern depicted in Figure 6.5. The lowering of the relative intensity of the two peaks 7.9 and 8.9° 2 θ reflects the presence of an adsorbate. The sample displayed an XRD pattern with no doublet nature to the peak at $2\theta = 23^{\circ}$; a doublet at $2\theta = 23.9^{\circ}$ and the peak at $2\theta = 24.4^{\circ}$ was single. The changes observed in the XRD pattern, upon coke formation, are characteristic of the transformation of ZSM-5 framework structure from that of monoclinic to orthorhombic

symmetry. The orthorhombic and monoclinic symmetry transition has been observed to occur upon coke formation in the internal channel system of ZSM-5 [18,19,24]. It can be concluded therefore that a proportion of the coke which formed during low temperature catalytic reduction of NO, must be present inside the zeolite channel system. We cannot detect the presence of external coke using powder XRD in this manner, only internal coke. For a detailed representation of internal and external coke an adsorption study measuring pore volume would be required. It therefore may be concluded from these results that coke has indeed formed within the internal channels of Cu ZSM-5 catalysts in this study, indicated from the observed symmetry change of monoclinic to orthorhombic. As already mentioned, the formation of external coke however can neither be confirmed or denied using the powder XRD technique in the manner.

The XRD pattern of the coked Cu-ZSM-5 subsequent to reaction with NO is shown in Figure 6.6. The increase in intensity of the two peaks 7.9 and 8.9° 20, to a level comparable to the original level prior to coke deposition, reflects the removal of the adsorbate. The pattern demonstrated a shoulder on the peak at $20 = 23^{\circ}$ a singlet peak at $20 = 23.5^{\circ}$ and a split peak was observed at $20 = 24.4^{\circ}$. On reaction of the coke deposit with NO the XRD pattern observed was identical to the original XRD pattern. This indicated that ZSM-5 reverted from orthorhombic back to the monoclinic structure. From these results, I conclude the internal coke was removed from the zeolite subsequent to reaction of NO. As mentioned previously however this does not allow us to exclude the possibility of some external coke remaining. It is likely however that all coke deposits have been removed. From visual inspection, the catalyst had lost its black colour characteristic of a coked sample. It emerged from the catalytic reactor a blue colour, the same as it had been prior to any coke deposition.

It may be concluded that prior to exposure to the SCR reaction mixture a calcined Cu-ZSM-5 catalysts exhibits a framework structure with monoclinic symmetry. Upon coke deposition, the framework symmetry is transformed from monoclinic to orthorhombic. Removal of the coke species from the zeolite upon reaction with NO and O_2 , results in the transformation of the zeolite symmetry from orthorhombic back to monoclinic. Therefore it is observed that a reversible symmetry transition takes place within the ZSM-5 framework structure during coke deposition and coke burn off upon reaction with NO and O_2 .

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Chapter 7 Conclusions

The subject matter of this thesis examines two distinct but related problems, the influence of ion exchange level and the nature of copper species present in Cu-ZSM-5 catalysts on activity for the SCR reaction; and the reactivity and nature of carbonaceous deposits formed on Cu-ZSM-5 catalysts during the SCR reaction

The relationship between copper content and activity for the selective catalytic reduction (SCR) of NOx using propene as a reductant in excess oxygen, for a series of Cu-ZSM-5 zeolite catalysts has been investigated. Experiments were carried out in order to determine whether the portion of copper exchanged into ZSM-5 above the nominal exchange capacity was responsible for the special activity observed for excessively ion exchanged Cu-ZSM-5 catalysts. Stoichiometry dictates that degrees of ion exchange above 100% cannot be achieved by isolated Cu (II) ions, but must involve the formation of metal-oxygen clusters such as [Cu-O-Cu]²⁺ containing two close Cu atoms. Therefore as dimeric clusters are likely to be formed preferentially at higher copper loadings, if they are of any special catalytic significance, turnover numbers should increase with copper content.

Turnover numbers, defined as the number of NOx molecules converted to nitrogen per copper site per second, were determined for a series of otherwise identical Cu-ZSM-5 catalysts with different copper contents. Catalysts were prepared via a conventional multiple ion exchange technique, from an aqueous solution of copper (II) acetate. The turnover number was found to be roughly constant at copper contents < 90-100% exchange. Above this degree of exchange the turnover increased by a factor of two, then remained constant up to the highest nominal extent of exchange studied. This approximate doubling of the turnover number suggests that in this range of copper loading new types of copper entity are created, with greater unit activity than is found in the zeolite at lower copper loading.

These results suggested that both isolated copper ions and small metal/oxygen clusters, including dimers catalyse the SCR reaction, with the dimeric species being roughly twice as active per copper ion. It was shown therefore that the most active sites consisted of these clustered copper species, they demonstrate greater unit activity for the SCR reaction than copper present at lower levels of ion exchange.

The entities introduced into the catalyst by overexchange are thus dimers or small metal / oxygen clusters such as [Cu-O-Cu]²⁺, and these must therefore be the species with the

highest turnover number. It is interesting to note that on the basis of turnover number calculations, the activity of a dimer cluster is about 4 times that of an isolated copper ion.

A series of experiments were conducted in order to determine whether the maintenance of copper(II) acetate in its dimeric form in an ethanol ion exchange solution, improves the activity of the resulting Cu-ZSM-5 catalysts. A direct comparison was made between Cu-ZSM-5 catalysts on the basis of the ion exchange medium, aqueous or ethanol. The results indicate that the retention of copper (II) acetate in the dimeric form in an ethanol ion exchange solution introduces copper into the catalysts with greater unit activity per copper ion than catalysts prepared from an aqueous ion exchange solution of copper (II) acetate. At higher levels of copper loading, turnover numbers calculated for excessively ion exchanged Cu-ZSM-5 catalysts prepared via ethanol or aqueous ion exchange are found to be comparable. These results support conclusions already drawn from this study; that the most active sites in Cu-ZSM-5 SCR catalysts consist of dimeric or clustered copper species consisting of two close copper ions.

The X-ray excited electron and X-ray absorption spectroscopy results provide complementary data for the investigation of copper species present in Cu-ZSM-5 catalysts, prepared from an aqueous ion exchange solution. XPS/XAES and EXAFS showed that copper is well dispersed within the zeolite channels of both the overexchanged and the low level ion exchanged Cu-ZSM-5 catalyst. Copper was found to be in the form of both isolated copper species and small Cu-O clusters in overexchanged Cu-ZSM-5 catalysts. Evidence for the presence of Cu-O clusters was not found in the Cu-ZSM-5 catalysts with a low level of copper ion exchange, therefore it is likely that copper is present only in the form of isolated copper ions in these-catalysts.

The entities introduced into the catalyst by overexchange are thus dimers or small metal / oxygen clusters such as [Cu-O-Cu]²⁺, these species were shown to exhibit the highest turnover number for the SCR reaction. The presence of these dimeric clusters are suggested to explain the higher activity for the SCR of NOx exhibited by overexchanged Cu-ZSM-5 catalysts.

The reactivity of carbonaceous material deliberately deposited on Cu-ZSM-5 zeolite catalysts under lean SCR reaction conditions was examined. These carbonaceous deposits, also referred to as coke, were laid down on the Cu-ZSM-5 catalysts by exposure to a typical SCR reaction mixture at low temperatures. Reactivity of the carbonaceous material

was investigated by exposing the precoked catalysts at 473 K to the same concentration of NO and oxygen as was present in the reaction mixture, (but no propene), and then heating to approximately 873-973 K at 10 K min⁻¹.

The coke deposited on the catalysts showed significant activity for NOx reduction. It was observed that peak activity for catalysts with the highest degrees of copper exchange occurred at 100 K lower reaction temperature than for catalysts with lowest levels of copper ion exchange. Generally catalysts with higher levels of copper ion exchange convert less NOx, consequently catalysts with lower levels of copper ion exchange and higher levels of residual Bronsted acidity convert more NOx. The amount of NOx converted ranged from 21-31 mg g⁻¹ catalyst. The total amount of NOx converted was of the same order of magnitude as the amount of deposited coke upon the catalysts surface. The higher levels of NOx conversion, observed for catalysts with lower levels of copper ion exchange may be directly attributed to the presence of a greater concentration of reductant, present as coke. The larger coke deposition capacity of catalysts with lower levels of copper ion exchange is brought about by the higher number of residual Bronsted acid sites, which are suspected to be primarily responsible for hydrocarbon activation.

The reactivity of carbonaceous deposits for the SCR of NOx was significantly different for the catalysts studied, with maximum reactivity being observed at a much lower temperature for precoked catalysts with higher degrees of copper ion exchange.

A simple kinetic model has been formulated in an effort to understand the differences in reactivity between catalysts with different degrees of copper exchange. This model allowed comparisons between experimental and calculated NOx conversions to be made. There is very good agreement between calculated and experimental values for such a simple model. The apparent activation energy of the reaction was observed to decrease as the copper content of the zeolite increased. The model indicated that the greater activity of precoked catalysts with higher levels of copper exchange was mainly due to a lower activation energy, compared with precoked catalysts with lower levels of copper ion exchange.

These results showed a variation in the stability of the hydrocarbon deposit towards NO, which was inversely dependent on copper content. This suggested that the residual acidity of the zeolite could be a factor in determining how catalyst activity varies with copper loading. These results imply that the presence of too many Bronsted zeolite acid sites, consequently higher levels of carbonaceous deposits, inhibits the NOx reduction reaction.

The present study compared catalysts with low levels of ion exchange with catalysts having little residual Bronsted acidity. These materials were pretreated under conditions which allowed the acid sites to have maximal influence in hydrocarbon activation, namely at low temperature, the result on the most acid catalysts was a hydrocarbon deposit which was less active in NOx reduction at low temperatures than formed at steady state. Comparison of transient experiments with steady state reaction profiles of the lean SCR of NOx shows that the steady state process occurs more quickly at lower temperatures. Equally the deposit produced on catalysts with lower copper content, and therefore higher residual Bronsted acidity, is even less active in NO reduction. The results of this study suggested that there was an inverse correlation between Bronsted acidity and catalysts performance.

FTIR was used to characterise the nature of carbonaceous deposits formed on a Cu-ZSM-5 catalyst, upon exposure to a typical SCR reaction mixture at low temperatures. IR bands, due to C-H stretching vibrations were detected. These bands were considered to indicate that the coke deposit exhibited some paraffinic character. An intense band, was observed at approximately 1600 cm⁻¹, this band, commonly referred to as the "coke band", is reported to be characteristic of a C=C stretching vibrations in aromatic and polyaromatic molecules. This coke band provides evidence for the presence of polyaromatic species within the coke deposit. Observing this absorption band makes it possible to confirm spectroscopically the deposition of coke on the Cu-ZSM-5 catalyst. An IR band was also observed at 2250 cm⁻¹, which has previously been assigned to a cyanide species, a suspected intermediate in the selective reduction of NOx to N₂ in the presence of hydrocarbons and excess O₂. IR Bands were also detected at 3300 and 3375 cm⁻¹, these are N-H stretches which probably reflect the presence both of =NH and -NH₂ groups. This observation provides evidence that the organic nitro groups which are formed first in the sequences of reactions leading to the release of nitrogen, may undergo sequential reduction to form cyanide

Powder XRD was used in this work to investigate structural changes that occur within Cu-ZSM-5 catalysts upon the deposition of a coke deposit and after its subsequent removal by reaction with NO and O_2 . Powder XRD is capable of detecting phase changes induced when coke occupies the channels of zeolite ZSM-5. Cu-ZSM-5 catalysts are observed to undergo a displacive transformation from monoclinic to orthorhombic framework symmetry upon internal coke deposition. This transformation is reversible upon the subsequent removal of coke, by reaction with NO and O_2 .



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