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Zeolite ZSM5 Catalysts for Abatement of Nitrogen Oxide

Bager Ganemi

Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Reaction Engineering

Stockholm 1999

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Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Reaction Engineering SE – 100 44 Stockholm

> TRITA-KET R109 ISSN 1104-3466 ISRN KTH/KET/R--109--SE

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Zeolite ZSM5 Catalysts for Abatement of Nitrogen Oxide

Bager Ganemi Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Reaction Engineering

Abstract

Airborne pollutants from the combustion of fossil fuels are a global problem. Emission of nitrogen oxides (NO_x) is increasing with the worldwide increase in the use of energy. Atmospheric and photochemical reactions link nitrogen oxides to hydrocarbons and tropospheric ozone. The emission of NO_x has to be tackled urgently in order to limit the harmful effects of anthropogenic activity on the environment.

The subject of this thesis is catalytic nitrogen oxide abatement through direct decomposition and reduction by methane over ion-exchanged zeolite ZSM5. The work covers catalytic conversion and surface intermediates, including correlations with the level of exchanged Cu^{2+} cations and Ni²⁺ or Pd²⁺ co-cations. Special attention is given to the aluminium content of the support and changes in structural parameters. It was found that NO_x conversion over cation-exchanged ZSM5 is strongly influenced by the ion-exchange procedure and by the above material parameters.

Characterization of Cu-ZSM5 reveals that approximately two molecules of water per Cu^{2+} ion desorb at temperatures between 150 and 350 °C, in addition to the conventional dehydration at lower temperatures. The desorbed water comes from the decomposition of $Cu(OH)_2$. Decomposition of hydroxylated copper ions results in the formation of Cu^{2+} -O- Cu^{2+} dimers, which are suggested to be the active sites for catalytic decomposition of NO.

Acid sites are important for the dispersion of copper ions on the catalyst surface. Acid sites are also important for the interaction between copper species and the zeolite. Increased acidity leads to a stronger interaction between the exchanged cation and the framework, i.e. the exchanged cations become more resistant to mobility. The stronger bond between the exchanged cations and lattice oxygen also prevents dealumination of the catalyst and decreases the thermal expansion at higher temperatures.

The temperature of dehydroxylation of acid sites on H-ZSM5 overlaps with the light-off temperature for NO reduction over Cu-ZSM5. Bridged nitrato groups ligated to Cu^{2+} -O- Cu^{2+} dimers act as site blockers below the light-off temperature. At the light-off temperature zeolite lattice vibrations destabilize surface nitrates and open the sites for catalytic reactions via short-lived N₂O₃ intermediates. The same lattice movements decompose OH-groups on the H-form of the zeolite and it was suggested that zeolite ZSM5 should be noted mainly for its flexibility rather than its narrow channels with strong electrostatic fields or metal exchange sites with open coordination.

Keywords:

NO, NO₂, Decomposition, Reduction, Methane, ZSM5, Ion-exchange, Cu, Pd, Ni

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Zeolite ZSM5 Catalysts for Abatement of Nitrogen Oxide

Bager Ganemi

Dissertation

Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Reaction Engineering

Stockholm 1999

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Bager Ganemi Royal Institute of Technology Department of Chemical Engineering and Technology Chemical Reaction Engineering

Abstract

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The subject of this thesis is catalytic nitrogen oxide abatement through direct decomposition and reduction by methane over ion-exchanged zeolite ZSM5. The work covers catalytic conversion and surface intermediates, including correlations with the level of exchanged Cu^{2+} cations and Ni^{2+} or Pd^{2+} co-cations. Special attention is given to the aluminium content of the support and changes in structural parameters. It was found that NO_x conversion over cation-exchanged ZSM5 is strongly influenced by the ion-exchange procedure and by the above material parameters.

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Keywords:

NO, NO2, Decomposition, Reduction, Methane, ZSM5, Ion-exchange, Cu, Pd, Ni



List of papers

This doctoral thesis is based on the research work included in the following five papers, referred to by their Roman numerals (I-V).

- I Conversion and *in situ* FTIR studies of direct NO decomposition over Cu-ZSM5
 B. Ganemi, E. Björnbom, and J. Paul
 Applied Catalysis B: Environmental 17(1998)293
- II Study of copper ion-exchanged ZSM5 zeolites for direct decomposition of nitrogen oxide

B. Ganemi, E. Björnbom, J. Paul, and P. Björnbom Proceeding of the 8th international symposium on heterogeneous catalysis, Bulgaria, 1(1996)341

III Zeolite Cu-ZSM5: Materials Characteristics and NO DecompositionB. Ganemi, E. Björnbom, B. Demirel, and J. Paul

Revised for publication in 'Microporous and Mesoporous Materials'

IV Nitrogen oxide Reduction by Methane over Cu, Ni, Pd, CuNi, and CuPd-ZSM5: Ion Exchange and IR-Spectroscopy

B. Ganemi, K. Rahkamaa, R.L. Keiski, L.O. Öhman, E. Björnbom, and J. Paul *To be submitted for publication*

V Adsorption of NO and O₂ on ZSM5 Zeolites ion-exchanged with Cu, Pd, and Ni
 K. Rahkamaa, B. Ganemi, J. Paul, T. Salmi, and R.L. Keiski
 To be submitted for publication

Other publications not presented in this thesis, are:

Decomposition of nitrogen oxide in presence of Cu-ZSM5 zeolite catalysts E. Björnbom, B. Ganemi, H. Lecoq, P. Björnbom and S. Järås Proceedings of the First World Conference in Environmental Catalysis, Italy, 1995

2) Reduction of nitrogen oxides by methane

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S. Vesecky, P. Norlander, L. O. Öhman, P. Persson, E. Björnbom, B. Ganemi, J. Lunsford, D. Wayne Goodman, R. Keiski, and J. Paul Proceedings of the 10th World Clean Air Congress, Finland, 1995

3) Direct NO decomposition over Cu-ZSM5

J. Paul, E. Björnborn, B. Ganemi, and S. Järås Oral presentation at the North American Catalysis Society Meeting, USA, 1995

4) Decomposition of NO in presence of Cu-ZSM5 catalysts

E. Björnbom, B. Ganemi, S. Järås, and P. Björnbom Proceedings of Third Nordic Conference on SO_x and NO_x from Heat and Power Generation, Denmark, 1996

5) Adsorption of NO, O₂, and CH₄ on ZSM5 zeolites ion-exchanged with Cu, Pd, and Ni

K. Rahkamaa, B. Ganemi, R. Keiski, J. Paul, L. O. Öhman, T. Salmi, and E. Björnbom Proceedings of 8th Nordic Symposium on Catalysis, Norway, 1998

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1 Introduction

1.1 Background

Emissions, environmental pollution, and studies on preventing and/or facing these problems, are one of the twentieth century's most noticed subjects. The emissions from mobile and stationary combustion sources cause enormous environmental damage such as depletion of the ozone layer and an increase of greenhouse gases. During the last four decades, however, this uninterrupted increase of the level of man-made pollution has resulted in a growth of environmental awareness, which has been the driving force in establishing new environmental regulations.

Among the major man-made sources of atmospheric pollution are different types of industrial activities, stationary and mobile combustion systems. Scientists and catalyst manufacturers, however, have paid special attention to emission problems related to automotive systems. The available space on mobile combustion systems is limited and, hence, it is more difficult to apply a multistage cleaning process on such systems. The catalytic system for treating the exhaust gases must be compact and effective enough for treatment of all gases. The emission level of nitrogen oxides (NO_x), incompletely combusted hydrocarbons including volatile organic compounds (VOC), carbon monoxide (CO), and particulates is a function of the type of combustion system, type of fuel, and the air-to-fuel ratio. These aspects make it even more complicated to develop a catalyst which is applicable to all these systems.

 NO_x gases are formed through combustion processes, lightning, microbial decomposition of proteins in the soil, and volcanic activity. These gases, together with their derived products, are hazardous to humans, animals and vegetation as well as to various materials [Wypkema, 1991].

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The two major oxides of nitrogen, i.e. nitrogen oxide (NO) and nitrogen dioxide (NO₂), which henceforth will be denoted as NO_x are classified as major pollutants in the atmosphere. The direct hazard towards man is mainly caused by NO₂, which is strongly toxic, irritant, and harms cell structure. Already at low concentrations, NO₂ causes irritation of the eyes, headache, breathing problems, and asthma attacks [Wypkema, 1991].

NO is an intermediate in the global cycle of nitrogen and it participates in chemical reactions with OH radicals and ozone to form HNO_3 which is a major component of acid rain. In most of the industrialised countries, about 50% of the NO_x emissions are caused by road traffic [Wypkema, 1991].

 NO_x also contributes to the formation of urban smog and thinning of the ozone layer in the upper atmosphere [Atkins, 1989]. The depletion of the ozone layer proceeds through the following reaction scheme:

NO + C	$D_3 \rightarrow$	NO ₂ +	O ₂	(1)
NO ₂ +	$0 \rightarrow$	NO +	O ₂	(2)

The regeneration of NO according to the above-mentioned reactions leads to decomposition of a large amount of the ozone [Atkins, 1989].

Changes in global climate and the rapid increase in global mean temperature demands radical and concerted world-wide action. The global temperature during last year has been the highest in at least 1200 years and the registered global mean temperature in October 1998 was 1.08 °F above the global mean temperature (57.10 °F) between 1880 and 1997 [Chem. & Eng., 1998]. At a meeting organised by the United Nations in November 1998, 160 countries agreed to finalise rules for emission trading and other market-based mechanisms to cut greenhouse gas emissions by late 2000 [Chem. & Eng., 1998].

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1.2 Formation of NO_x in combustion systems

Formation of NO_x proceeds according to the following three paths:

1."Thermal" formation of NO proceeds through oxidation of atmospheric nitrogen and is significant at temperatures above 1300 °C [Ismagilov and Kerzhentsev, 1990]. Zeldovich [1946] suggested the following chain reactions for thermal formation of NO:

O ₂	$\rightarrow 20$	(3)
N ₂ + O	\rightarrow NO + N	(4)
$N + O_2$	\rightarrow NO + O	(5)

The level of thermal NO_x emissions is linearly dependent on the residence time and rises exponentially with the flame temperature, i.e. $NO_x \propto e^{0.009T}$ [Gupta and Lilley, 1992; Jones, 1978].

2."Fuel" NO formation, in which NO is formed directly by oxidation of nitrogencontaining compounds in the fuel. Fuel nitrogen is converted to simple nitrogen compounds, like amines and cyanides. These compounds are in turn converted to nitrogen-containing organic complexes which react rapidly with OH-radicals and other oxygen-containing compounds. Formation of fuel NO is mainly dependent on the content of nitrogen in the fuel, the residence time, and the concentration of oxygen in the system. The effect of combustion temperature on formation of fuel NO is generally weak [Fenimore, 1972].

3. Formation of "prompt" NO occurs through oxidation of HCN, an intermediate formed during the combustion process. Fenimore [1970] was the first to identify "prompt" NO. In rich premixed hydrocarbon-air flames, radicals formed from the fuel can react with molecular nitrogen and form hydrogen cyanide:

7

$CH + N_2 \rightarrow HCN + N$	(6)
HCN + oxidants $\rightarrow \dots \rightarrow NO + \dots$	(7)

The quantities of prompt NO formed are significant in very fuel-rich flames [Hayhurst and McLean, 1974].

1.3 Control of NO, emissions

In order to control the level of NO_x emissions, the problems may be attacked in different ways. The first and the most important way is to avoid the formation of NO_x . This may be achieved by improvement of the combustion systems and modification of the fuel quality. Major objectives for control of NO_x emission are (i) decrease of oxygen concentration at peak temperature; (ii) reduction of peak temperature and the residence time in the combustion zone; (iii) reduction of the level of fuel nitrogen [Bosch and Janssen, 1988].

Another way is to minimise the generated hazardous components by one or several cleaning steps. Catalytic technology, non-catalytic technology, or a combination of both can be applied for this purpose.

1.3.1 Non-catalytic technologies for removal of NO.

Current technologies for non-catalytic removal of NO_x employ wet scrubbing, adsorption, and selective non-catalytic reduction (SNCR).

Exxon developed the homogeneous gas-phase reduction process (thermal de-NO_x). In this process NO_x is selectively reduced to N₂ and H₂O by NH₃ which is introduced into the upper part of the boiler where the temperature is between 850 and 1050 °C [Lyon, 1976; Bosch and Janssen, 1988]. The overall reactions are:

$$6 \text{ NO} + 4 \text{ NH}_3 \rightarrow 5 \text{ N}_2 + 6 \text{ H}_2\text{O}$$
 (8)

 $6 \text{ NO}_2 + 8 \text{ NH}_3 \rightarrow 7 \text{ N}_2 + 12 \text{ H}_2\text{O}$ (9)

and the side reaction is:

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$$4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O}$$
 (10)

Reduction levels of 50 % can be achieved and the technique requires a low capital investment. The narrow temperature window over which this process is active, a high NH_3 : NO_x ratio and thereby problems with leakage of ammonia, salt formation, and adsorption of ammonia on the fly-ash in high dust systems such as coal-fired boilers, are the drawbacks for this technique [Lyon and Tenner, 1978; Bosch and Janssen, 1988].

1.3.2 Catalytic technologies for removal of NO_x

Nitrogen oxide is thermodynamically unstable and it decomposes according to the following reaction [Armor, 1994]:

$$2 \text{ NO} \rightarrow \text{N}_2 + \text{O}_2 \qquad (11)$$

The reaction kinetics are, however, slow and the time to reach equilibrium in the absence of a catalyst is several days even at temperatures as high as 1000 °C [Winter, 1971].

One of the interesting catalytic approaches for removal of nitrogen oxide is to decompose it directly, i.e. to convert NO into N_2 and O_2 without addition of any reducing agent. This approach is often called one of the simplest methods for removal of NO from flue gases [Shimada, 1988]. A variety of catalysts have been studied for direct decomposition of NO. Noble metal catalysts have high catalytic activity for decomposition of NO [Kruse, 1987; Whitman, 1988]. Platinum, one of the most active catalysts for decomposition of NO [Ogata, 1990; Gohndrone, 1989; Siera 1990; Van Delft, 1988], is the most studied noble metal for this reaction. The problem with noble metal catalysts for direct decomposition of NO, however, is the strong adsorption of oxygen generated during the reaction process on the surface of the catalyst. A study of the catalytic activity for decomposition of NO on 40 metallic oxides also revealed that strong adsorption of O_2 on the active sites depresses the kinetics of the this reaction [Winter, 1971]. Compared to the metallic oxides, adsorption of O_2 on some zeolites is not so strong [Winter, 1971; Meubus, 1977; Teraoka, 1990]. This is an advantage in using zeolite catalysts for direct decomposition of NO.

The catalytic approach used in industrial applications, selective catalytic reduction, SCR, has been widely studied. Reducing agents such as low molecular-weight hydrocarbons, carbon monoxide, ammonia, and hydrogen reduce the NO_x effectively over various catalysts at low temperatures [Bosch and Janssen, 1988; Halasz et al., 1993; Hamada et al., 1991-92; Held et al., 1987, 1990; Iwamoto et al., 1991-92; Panayotov, 1995].

There are obvious advantages in applying reduction methods to eliminate nitrogen oxide from the exhaust systems which already contain reducing agents, i.e. there is no need for an addition of reducing agent. This technique has a widespread application in automotive systems. The currently used commercial three-way catalysts (TWC) which are equipped with an oxygen sensor for control of air/fuel ratio are effective for removal of NO_x emissions from gasoline-fuelled vehicle exhausts. Today's most applied three-way catalysts for reduction of NO are constructed with fine platinum-rhodium particles supported on high surface area ceria-alumina (CeO_2/Al_2O_3) mixed oxides. The ceria-alumina (CeO_2/Al_2O_3) mixed oxides are in turn coated onto a monolithic surface. The catalytic reduction of nitrogen oxide with CO and unburned hydrocarbon over TWC proceeds through the following reactions [Thomas and Thomas, 1996]: The reduction of NO is facilitated by co-adsorption of CO and atomic oxygen on platinum, and promoted uptake of NO by rhodium. CeO_2 not only stabilises the Al_2O_3 , but also offers the advantage of releasing and taking up oxygen under reducing and oxidising conditions [Thomas and Thomas, 1996].

This technique is, however, not effective for NO_x reduction in lean-burn applications where excess oxygen has to be used in order to reach the highest possible fuel efficiency, i.e. for conditions where CO and non-combusted hydrocarbon are absent from the exhaust gas stream. The removal of NO_x in oxygen-rich systems is still in its infancy both with respect to fundamental understanding and practical application [Armor, 1994].

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Selective catalytic reduction of NO using ammonia as reducing agent is the most applied technology for control of NO_x emissions from stationary sources. Development of this technique started already as early as 1960 in connection with the production of nitric acid. The first catalyst used in this application was V_2O_5 -coated Al_2O_3 . The high activity of copper oxide in the reduction of NO with ammonia in the presence of O_2 was also recognised earlier [Centi and Perathoner, 1995]. The low-temperature (110 °C) activity of this catalyst in the reduction of NO with ammonia in the presence of O_2 is comparable to that of Pt-based catalysts [Centi and Perathoner, 1995]. However, due to high resistance to poisoning and high stability, one of today's most applied catalyst is V_2O_5 -coated TiO₂. Although reduction technologies using ammonia are effective, they are accompanied by problems such as ammonia slip, storage capacities and handling of ammonia.

In the light of the above discussion regarding the activity of different catalytic systems, it is obvious that there is a need to develop new generations of catalysts which may be applied in lean-burn applications. It is of special interest to use methane, which is the main component in natural gas (>90 %), as the reducing agent for reduction of NO_x . Natural gas is widely used as the main source of energy generation in many combustion processes and is easily available in most parts of the world [Armor, 1996].

1.4 Zeolite catalysts for abatement of NO

1.4.1 ZSM5 Zeolites

<u>Zeolites</u> are microporous and crystalline aluminosilicates, consisting of three-dimensional networks of oxygen ions in which the tetrahedral sites are occupied by Si⁴⁺ and Al³⁺. Due to their well-defined pore-size, structure, acidity, and shape selectivity, zeolites are widely used in petrochemical processes such as cracking and hydrocracking [Thomas and Thomas, 1996].

ZSM5 is a synthetic zeolite and its framework structure is often called the MFI structure (from Mobile Five). The structure is often described by what is called secondary building units, SBUs. The SBU found in molecular sieves with the MFI structure is the 5-1 unit. These units can be combined into chain-building units to produce a two-dimensional sheet unit. The final generated structure from these two-dimensional sheet units is a zeolitic framework. Figure 1 demonstrates the successive transition from 5-1 SBU to the projection of the MFI framework. The small circles in the SBU represent what is called T-atoms (the common name for the tetrahedral positions occupied by either aluminium or silicon atoms). The lines between represent the oxygen bridges linking the T-atoms together [Persson, 1995].



Figure 1. The successive transition from the 5-1 SBU to the sheet projection of the MFI framework [Persson, 1995].

Unlike many other zeolites, ZSM5 is not defined by a certain SiO_2 : Al_2O_3 ratio. ZSM5 is a family of materials with SiO_2 : Al_2O_3 ratios ranging from 5 to almost infinity [Persson, 1995]. The crystals of ZSM5 have the regular shape typical for high-silicate pentasils with a size ranging between 3 and 5 μ m [Kosanovic et al., 1995]. The framework of ZSM5 can be constructed from a building unit consisting of 12 tetrahedrons [Olson et al., 1981; Post, 1984].

The three-dimensional structure of the ZSM5 framework can be illustrated by the "hollow tube representation" in figure 2, showing the characteristic intersection of the 10-ring zigzag channel system and the 10-ring straight channel system. The cross-section of the two channel types is also shown.

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Figure 2. The "hollow tube" representation of ZSM5 and the cross section of the two channel systems [Persson, 1995].

Due to their resistance to poisoning beside the other properties, ZSM-5 catalysts are widely used in petrochemical industries. Conversion of methanol to gasoline (the MTG-process) is an example of the application of this zeolite in industrial processes [Thomas and Thomas, 1996].

1.4.2 ZSM5 catalysts for DeNO

ZSM5 zeolite catalysts have been shown to be very promising both for direct decomposition and for reduction of NO. Oxygen is a reaction product in direct decomposition of NO, and, as already mentioned, oxygen adsorbs strongly onto the surface of metallic oxide catalysts and causes poisoning. It is therefore important that oxygen desorb easily from the active sites of the catalyst surface. The adsorption of oxygen on ZSM5 catalysts is not as strong as the adsorption of oxygen on other types of catalysts. For example, the sorption affinities of some gases on hydrogen mordenite and hydrogen ZSM5 zeolites have been found to be as follows [Furuyama, 1984]:

$Ar < O_2 < N_2 < NO < CO$

The Al^{3+} ion at a tetrahedral site causes a negative charge which is compensated by a cation. This neutralising cation in the zeolite can be replaced by a second cation through ion-exchange in a diluted solution of the desired specific salt, such as NaNO₃ or Cu(CH₃COO)₂.

The exchange behaviour of zeolites depends on [Breck, 1974]:

- 1) the nature of the cation species,
- 2) the temperature,

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- 3) the pH of the solution,
- 4) the concentration of the cation species in the solution,
- 5) the anion species associated with the cation in the solution,
- 6) the solvent, and
- 7) the structural characteristics of the particular zeolite.

The activity of the catalysts is influenced by the structure of the zeolite and the nature as well as the amount of the exchanged cations.

The catalytic properties of copper ion-exchanged ZSM5 zeolites (Cu-ZSM5), for direct decomposition and selective reduction of nitrogen oxide was initially discovered by Iwamoto et al. [1989-94] and Held et al [1987, 1990]. The catalysts were shown to have high catalytic activity both for the direct decomposition and selective reduction of nitrogen oxide by hydrocarbons [Bennet et al., 1992; Hamada et al., 1990-91; Held et al., 1987, 1990; Ishihara et al., 1992; Iwamoto et al., 1989-94; Li and Armor, 1992-93; Truex et al., 1992; Yogo et al., 1992-93]. Well-defined crystal structures of the zeolites offer suitable models for understanding the reaction mechanism for decomposition and reduction of NO_x. Detailed information on the exact mechanism provides valuable basic knowledge which can help find possible ways to improve the catalytic properties of this kind of materials.

The catalytic activity for reduction and decomposition of NO over ZSM-5 which is ionexchanged by copper, gallium, cerium, cobalt, iron or some other cations has been studied by several researchers [Admiris et al., 1996; Iwamoto et al., 1989-94; Björnbom et al., 1996; Paul et al., 1995]. The activities for reduction and decomposition of NO as well as the stability of some of the above-mentioned cation-exchanged ZSM-5 catalysts in the presence of water and sulphur dioxide have been reported in the literature [Admiris et al., 1996]. For example Cu-ZSM-5 was found to be a poor catalyst for reduction of NO by methane (CH₄), since CH₄ reacts more readily with O₂. By contrast Co-ZSM-5 and Ga-ZSM-5 catalysts were found to be active for reduction of NO with methane [Li and Armor, 1993]. At high space velocities (above 60 000 h^{-1}) and in the presence of sulphur dioxide and steam the zeolite catalysts are not very promising. At these conditions the ZSM5-based catalysts may deactivate through sulphur poisoning, or by formation of copper clusters which may block the pore entrances and/or cause a local destruction of the zeolite structure, or by dealumination (ca. 700 °C) [Grinsted et al., 1993; Martin et al., 1991].

A unique feature of the Cu-ZSM5 catalysts is the fact that excess oxygen inhibits, but does not poison, the decomposition reaction of nitrogen oxide [Iwamoto et al., 1989]. Thus the decomposition reaction of nitrogen oxide can also be carried out in the presence of excess oxygen [Li and Hall, 1990]. This reaction, however, does not occur to any significant extent under realistic lean-burn exhaust conditions [Truex et al., 1992].

Strong electric fields in the smaller-pore zeolites (including zeolite ZSM5) arising from the various charged species result in large energy gradients within the zeolite pores. These fields dictate the final co-ordination of the exchanged ionic species which in turn affects the activity and the selectivity of the prepared catalyst. The effect of electric fields in zeolite pores was also discussed by Mirodatos and Barthomeuf [1985]. The Lewis/BrØnsted acidity model is usually employed to describe the active sites of molecular sieves [Szostak, 1989]. Figure 3 depicts a zeolite surface, showing possible types of structures expected to be present at various stages of treatment of a silica-rich zeolite [Szostak, 1989].

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Figure 3. Diagram of the "surface" of a zeolite framework. (a) In the as-synthesised form, M^+ is either an organic cation or an alkali metal cation. (b) Ammonium ion exchange produce the NH_4^+ exchanged form. (c) Thermal treatment is used to remove ammonia, producing the H^+ , acid form. (d) The acid form in (c) is in equilibrium with the form shown in (d), [Szostak, 1989]

Changes in structural parameters in ZSM5 zeolites

It is known that ZSM5 zeolites undergo a reversible phase transition and exhibit monoclinic (Mono) symmetry below and orthorhombic (Ortho) symmetry above the transition temperature [Wu et al., 1979]. The exact transition temperature depends on the SiO_2 : Al_2O_3 ratio [Hay et al., 1984-85; Klinowski et al., 1987]. Silicate and high ratio ZSM5 (SiO_2 : $Al_2O_3 > 460$) undergo phase transformation at temperatures of about 44 - 47 °C, and low ratio zeolites (SiO_2 : $Al_2O_3 < 110$) undergo phase transformation at a temperature of about 0 °C [Hay and Jaeger, 1984]. This phase transition is reversible, but exposure of the zeolite to rapid temperature changes can result in mechanical stress and structural damage [van Koningsveld et al., 1987, 1989; Kosanovic et al., 1984], and the remaining aluminium is removed from the structure, as extra framework matter [Oldfield et al., 1994]. The framework aluminium content governs the symmetry changes of the ZSM5 structure, the location and the extent of loading of metal ions in the zeolite channels.

There are two significant differences in the geometry of the framework between monoclinic and orthorhombic structures. The first difference is the Si-O distances d(Si-O). The minimum value of d(Si-O) is significantly larger in Mono than in Ortho; the maximum value is essentially the same in both frameworks. The second notable difference concerns the limiting values of the Si-O-Si angles: the maximum, as well as the minimum value in Mono is significantly lower. The pore shape in Ortho is nearly circular with pore diameter of about 5.3 Å (with a variation between 2.7 and 8.0 Å), while in Mono the window profile is more elliptical with maximal and minimal dimensions of about 5.4 and 5.0 Å [van Koningsveld et al., 1990].

Changes in crystalline parameters of ZSM5 with temperature result in a distinct physical change in the structure of the crystal, i.e. both sorption and catalytic properties may be affected [Fitzpatrick, 1992].

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In spite of the reported studies on ion-exchanged ZSM5 catalysts, the information regarding the relation between catalytic activity, stability, and changes in the structural parameters as a function of temperature is quite poor. In fact, Parvulescu et al. [1998] describe the reason for effectivity of ZSM-5-based catalysts in NO_x removal as "an unsolved mystery". Therefore the study of the effect of changes in structural parameters with temperature for a certain pronounced reaction may contribute essentially to further development of the zeolite-based catalysts.

The objective of the present work is to study the connections between the above-mentioned parameters and the activity and stability of ZSM5-based catalysts in NO_x removal. Papers I and II deal with the relationship between the activity of Cu-ZSM5 and temperature, the amount of exchanged copper ions and aluminium content, as well as surface intermediates. Paper III covers the changes in the structural parameters and release of water in ZSM-5 as function of copper content and temperature. Papers IV and V present the effect of co-cations i.e. Ni(II), and Pd(II) on the formation of surface intermediates in direct decomposition and selective reduction of NO with methane.

2 Experimental

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2.1 Catalyst preparation

<u>Ammonium-form ZSM5</u> (NH₄-ZSM5, supplied by Eka Nobel, with SiO₂ : Al₂O₃ molar ratios of 53 and 33 was converted to H-ZSM5, after calcination at about 500 °C in air for 3 hours [van Koningsveld et al., 1990; Post, 1984]. 30 g H-ZSM5 was ion-exchanged in 2 litres of 0.04 M NaNO₃, at room temperature. This first ion exchange step was followed by a second, in which 2 litres of diluted solutions of Cu(II) acetate (11 mM), or Pd(II) chloride (2 mM), or Ni(II) nitrate (11 mM) was used. The procedure was repeated until the desired level of Na⁺, Cu²⁺, Ni²⁺, or Pd²⁺ ions was reached. The catalysts with co-cations were first ionexchanged by Pd(II) chloride (2 mM) or Ni(II) nitrate (11 mM), before they were ionexchanged using Cu(II) acetate (11 mM). pH control was employed throughout all ionexchanges. The pH was adjusted to the desired range for adsorption of each metal ion by introducing ammonia before introducing the zeolite. The ion-exchanged zeolite was then washed twice in 2 litres of de-ionised water for 2 hours. The washing step was followed by decanting of the eluate, leaving a sediment of zeolite slurry at the bottom of the vessel. The slurry was then dried in two steps, first at 55 °C and then at a maximum temperature of 110 °C. The catalysts were then pelletized (300 kg/cm^2), crushed and sieved. For kinetics, temperature-programmed desorption (TPD), and BET surface area measurements, particle sizes of 250 to 425 mm (60-100 mesh) were employed. For *in-situ* FTIR and XRD studies both powder and catalyst pellets were used.

The exchange level is given in percent, normalised to 100 % for a copper to aluminium ratio of 1:2, i.e. one Cu^{2+} or Pd^{2+} or Ni^{2+} ion for every two ion-exchange sites [Iwamoto et al., 1989]. The assignment Cu-ZSM5-53-168 means that the ZSM5 zeolite catalyst has a SiO₂ : Al₂O₃ ratio of 53 and a level of ion-exchange of 168 %. The prepared and studied catalysts are listed in table I.

Catalyst	$SiO_2: Al_2O_3$	Ion-exchange level %
	ratio	
ZSM5	53	0
Cu-ZSM5-53-74	53	74
Cu-ZSM5-53-144	53	144
Cu-ZSM5-53-145	53	145
Cu-ZSM5-53-160	53	160
Cu-ZSM5-53-170	53	170
Cu-ZSM5-53-168	53	168
Ni-ZSM5-53-62	53	62
Pd-ZSM5-53-196	53	196
Cu/Ni-ZSM5-53-76/41	53	76-Cu, 41-Ni
Cu/Pd-ZSM5-53-87/181	53	87-Cu, 181-Pd
ZSM5	33	0
Cu-ZSM5-33-108	33	108
Cu-ZSM5-33-210	33	210

Table I. Studied ion-exchanged ZSM5 catalysts

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Atomic Adsorption Spectroscopy (AAS), and Inductive Coupled Plasma (ICP) technique, were employed to ascertain the amount of exchanged metallic cations. About 5 mg of each catalyst was first dissolved in hydrofluoric acid. The catalyst dissolved in acid was further diluted with de-ionised water to a total volume of 0.5 litres before the solution was analysed. For ICP and AAS analyses, a Kebo standard solution with a concentration of 1000 mg/l of metallic cations was employed. For analysis of each sample, four calibration solutions with concentrations of 100, 50, 20, and 5 mg/l were prepared and used.

H-ZSM5 and Cu-ZSM5 were characterised also by x-ray diffraction spectroscopy (XRD) in order to identify possible changes of structural parameters in zeolite catalysts as a function of copper content and temperature.

Thermogravimetric analysis (TGA) was carried out in order to study the relation between water release and the content of copper ions exchanged into ZSM5 as a function of temperature. The thermal analyser was integrated with a mass-spectrometer. All measurements were performed in a flow of helium and the temperature was ramped from 25 to 500 °C with a heating rate of 11 °C/min, followed by re-cooling to room temperature. All reported spectra are truncated at 500 °C, normalised against the sample weight, and shown as a function of temperature.

X-ray photo-emission spectroscopy, XPS/ESCA, was employed as a complementary analysis for studying the status of the copper ions. Samples were analysed after evacuation at room temperature and after annealing at 500 °C for 45 minutes and 600 °C for 30 minutes followed by re-cooling to below 200 °C.

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Temperature programmed desorption (TPD) of ammonia on samples of H-ZSM5 and Cu-ZSM5, was carried out in order to study the possible effect of zeolite acidity on the direct decomposition of nitrogen oxide. A 0.5 g sample of the catalyst was pre-treated for two hours at 500 °C in the quartz reactor under a flow of helium. The temperature was then decreased to 150 °C and the catalyst was saturated with ammonia. The TPD trace of desorbing ammonia was recorded at 10 °C/min.

2.3 Measurements of activity for direct decomposition of nitrogen oxide

For measurements of the catalytic activity for Cu-ZSM5 in direct decomposition of nitrogen oxide, a stainless steel tube reactor with an inner diameter of 7 mm was employed. Before the experiments the desired amount of catalyst (0.15, 0.30, or 0.90 g) was heated in the reactor at 500, 550 or 600 °C, depending on the desired *in situ* pre-treatment, for a period of 2 hours under a flow of He (1.8 l/h). The heat-treatment was aimed at removing impurities from the surface and the channels of the zeolite. After the pre-heating period, the temperature in the catalytic bed was decreased to the selected level and a gas flow with 2000 ppm NO in helium was introduced into the reactor (Paper I). All activity tests were made at atmospheric pressure. The heating or cooling rate never exceeded 10 °C/min during any part of the pre-treatment or subsequent reactor studies and acidity tests. Temperature changes above 40 °C/min can cause irreversible lattice damage to the zeolite structure [Deckman]. The concentration of NO in the input gas, 2000 ppm in He, was not varied. The flow rates were 1.5, 2.1, 3.0, or 4.2 l/h. The temperature was monitored by a chrome-nickel thermocouple in contact with the catalytic bed.

The gas product was analysed with an on-line gas chromatograph (VARIAN Model 3700). Manual injection with a sample loop was applied. The gas submitted to the analysis passed two consecutively connected columns: a primary column, 2 m x 1/8" SS, packed with Porapak Q, 80/100, and a secondary column: 30 ft x 1/8" SS, packed with GasChrom MP-1, 100/120. The column temperature was 25 °C and the flow rate of the carrier gas (helium) was 18 ml/min. The chromatograph was equipped with a thermal conductivity detector (TCD). The temperature of the filaments in the TCD was 250 °C. The analytical data were

integrated and plotted with a HEWLETT-PACKARD integrator. Figure 4 shows a simplified scheme of the analytical instrumentation for activity measurements.

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Figure 4. Equipment for kinetic measurements of direct NO decomposition

It was assumed that the participation of N₂O, i.e. disproportionation, could be neglected. GC analysis did not show the presence of N₂O in the product gas. The formation of N₂O is thermodynamically more favourable at temperatures below 400 °C. N₂O decomposition precedes NO decomposition at temperatures above 400 °C [Iwamoto et al.; 1989]; the kinetic measurements of this work were carried out at temperatures above 400 °C.

The concentrations of O_2 and NO in the gas at the reactor outlet were determined directly by gas chromatographic (GC) analysis. These concentrations were used to calculate the amounts of nitrogen and nitrogen dioxide, which are produced, using reactions 14-15 (Paper I):

Decomposition of NO:	$2NO \rightarrow N_2 + O_2$	(14)
Oxidation of NO:	$2NO + O_2 \rightarrow 2NO_2$	(15)

If ΔY_{NO} is the amount of NO consumed in (14) and (15), ΔY_{O2} the amount of O₂ produced in (14) minus the amount consumed in (15), and ΔY_{NO2} and ΔY_{N2} the amounts of NO₂ and N₂ produced it follows that:

$$\Delta Y_{NO2} = 1/2 \Delta Y_{NO} - \Delta Y_{O2}$$
(16)
$$\Delta Y_{N2} = 1/4 \Delta Y_{O2} + 1/2 \Delta Y_{NO}$$
(17)

If all oxygen generated in reaction (14) is consumed by oxidation of the unreacted NO, i.e. ΔY_{O2} equals zero, then (14) and (15) are combined to:

$$4NO \rightarrow N_2 + 2NO_2 \tag{18}$$

The conversion of nitrogen oxide and the yields of N_2 , NO_2 and O_2 were calculated using the following expressions:

Conversion of NO:	$X_{NO} = \Delta Y_{NO} / Y_{NO}^0$	(19)
Yield of N_2 (Conversion of NO into N_2):	$X_{N2} = 2*\Delta Y_{N2}/Y_{NO}^{0}$	(20)
Yield of NO ₂ (Conversion of NO into NO ₂):	$X_{NO2} = \Delta Y_{NO2} / Y_{NO}^0$	(21)
Yield of O_2 (Conversion into O_2):	$X_{O2} = 2*\Delta Y_{O2}/Y_{NO}^{0}$	(22)

Where Y_{NO}^{0} is the initial amount of NO at the input of the reactor.

The selectivity for formation of nitrogen, oxygen and nitrogen dioxide is calculated using the following expressions:

Selectivity for the formation of N ₂ :	$S_{N2} = 2*\Delta Y_{N2}/\Delta Y_{NO}$	(23)
Selectivity for the formation of O ₂ :	$S_{O2} = 2*\Delta Y_{O2}/\Delta Y_{NO}$	(24)

Selectivity for the formation of NO₂: $S_{NO2} = \Delta Y_{NO2} / \Delta Y_{NO}$ (25)

2.4 In-situ FTIR-measurements

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The *in situ* FTIR studies were carried out on two different occasions. On the first occasion samples of Cu-ZSM5-53-0, Cu-ZSM5-53-74, and Cu-ZSM5-53-160 were studied by a Mattson Cygnus infrared spectrometer. For *in situ* FTIR studies approximately 50 mg of each sample was pressed into a gold-coated stainless steel net (Paper I).

On the second occasion *in situ* infrared adsorption studies of NO, O₂, and CH₄ on Cu-ZSM5-53-168, Ni-ZSM5-53-62, Pd-ZSM5-53-196, Cu/Pd-ZSM5-53-87/181, and Cu/Ni-ZSM5-53-76/41 were carried out employing a Spectra-Tech Inc spectrometer (Paper IV and V).

Two main *in situ* pre-treatment methods denoted as (pre)oxidation or (pre)reduction were employed. The samples were prepared by mixing and milling a 1:1 proportion of each catalyst with potassium bromide (KBr). The prepared sample was then placed in a sample cup (0.06 cc) of a diffuse reflectance infrared cell (Spectra-Tech Model 0030-103) equipped for *in situ* pre-treatment and reaction studies. The sample was further oxidised with 10% O_2 in helium (He) or reduced with 10% H_2 in He after heating and evacuation pre-treatment at 500 °C. The oxidation or reduction was continued for one hour after which the sample was quenched to room temperature. In the case of oxidation pre-treatment, the quenching was carried out in oxygen atmosphere in order to prevent the self reduction of the sample at higher temperatures. After the reduction pre-treatment of the catalyst however, the sample was quenched from 500 °C to room temperature under vacuum.

Following introduction of sample, evacuation, and pre-treatment 'static' experiments were conducted as follows: (i) background spectrum in vacuum at 25, 150, 300, or 450 °C;

(ii) exposure to gases at the same temperature; (iii) cooling to 25 $^{\circ}$ C; (iv) evacuation for 5 min at 25 $^{\circ}$ C; (v) annealing in vacuum at 500 $^{\circ}$ C for 5 minutes and re-cooling to 25 $^{\circ}$ C. The steps (i) to (v) were subsequently repeated for the above four temperatures. This means that steps (i) and (ii) always were obtained at the same temperature and can be readily compared. Steps (iii) to (v) were obtained at 25 $^{\circ}$ C and need to be compared with a single beam spectrum obtained at the same temperature.

'Dynamic' experiments were designed to follow adsorption (25 °C) and reaction studies (300 °C, 450 °C) and to elucidate the effects of each gas component. 'Quenching' experiments means that the sample after completion of a 'dynamic' experiment was cooled to room temperature from 300 °C in the reactant gas mixture, then evacuated at 25 °C, and flashed in vacuum to the preceding reaction temperature 300 °C.

The ceramic holder was used as a continuous flow reactor. The input reaction gas had a total flow of 93 cm³/min and a NO and/or O_2 and/or CH₄ concentration of 10% in helium.

3 Results and discussion

3.1 Catalytic activity

Copper loading

Conversion of nitrogen oxide over Cu-ZSM5 increases with the level of exchanged copper ions in the zeolite. Figure 5 shows a linear approximation of the correlation between copper content and conversion of NO for the zeolite with a SiO₂: Al₂O₃ ratio of 53 at a temperature of 450 °C. Catalysts prepared by ZSM5 with a SiO₂ : Al₂O₃ ratio of 33 show a similar correlation between the level of exchanged copper ions and the level of NO conversion. A high level of ion-exchanged copper enhances the formation of catalytically active sites, i.e. Cu^+-O-Cu^+ . The maximum level of ion-exchange is, however, limited by formation of larger agglomerates of copper. These agglomerates may have a dual function in decreasing the catalytic activity. The first function is a blockage of the pore intersection in the catalyst cavities. Loss of catalytic active sites is the second effect of copper agglomeration. It is important to point out that larger copper clusters which are not directly interacting with the ion-exchange sites are not active for NO_x abatement [Chajar et al., 1994].

Space velocity

At space velocities between 560 and 5400 h^{-1} and at a temperature of 450 °C, the catalyst samples Cu-ZSM5-53-160 and Cu-ZSM5-53-145 gave an approximately linear correlation for the conversion level of NO [Björnbom et al., 1995; Paper I].

Conversion of NO (%) = 75 - 0.008 * Space velocity
$$(h^{-1})$$

At a space velocity of about 5000 h^{-1} the conversion of NO was as low as 25%. Considering the space velocities of at least 30 000 h^{-1} in a real exhaust system, this value is quite poor.

Effect of temperature

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The conversion of NO reaches a maximum at 450 $^{\circ}$ C above which it decreases slightly (figure 6). The decrease in activity at temperatures above 450 $^{\circ}$ C depends on the changes in adsorption characteristics of the active sites with temperature. Note that the catalytic activity of Cu-ZSM5 at 450 $^{\circ}$ C or below was not affected by treatment of the catalysts at temperatures up to 600 $^{\circ}$ C, i.e. the catalysts were not deactivated by exposure to temperatures up to 600 $^{\circ}$ C.

Selectivity

The Cu-ZSM5 catalysts chosen for this study have high selectivity for formation of N_2 and O_2 in decomposition of NO. In all cases during the kinetic measurements the selectivity for formation of N_2 and O_2 was above 80 % and it increased with increasing temperature. High temperature depresses the disproportionation of NO into N_2O .



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Figure 5. Effect of the level of exchanged copper ions on the conversion of NO (Space Velocity 5400 h^{-1} ; Temperature 450 °C)



Figure 6. Effect of temperature on the conversion of nitrogen oxide and the yield of N_2 , O_2 , and NO_2 in the presence of Cu-ZSM5-53-160 catalyst at a space velocity of 5400 h⁻¹

SiO, : Al,O, ratio

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Figure 7 shows the conversion of NO as a function of temperature over two catalysts with equal amounts of copper per gram catalyst but with different SiO₂ : Al₂O₃ ratios. It is clear that the catalyst with a SiO₂: Al₂O₃ ratio of 53 (Cu-ZSM5-53-170) shows a higher catalytic activity than the catalyst (Cu-ZSM5-33-108) with a SiO₂ : Al₂O₃ ratio of 33 at equal concentration of copper. In fact, catalyst Cu-ZSM5-53-74 showed a higher activity than catalyst Cu-ZSM5-33-108 at 430 °C, despite less than half the copper content. This behaviour can partly be explained by a higher concentration of stable and well-isolated bridged copper species, and partly by the existence of one Al atom, i.e. one ion-exchange site, per pore intersection for zeolites with a SiO₂: Al₂O₃ molar ratio above 48 [Post, 1984]. The catalyst prepared using ZSM5 zeolite with a SiO_2 : Al_2O_3 ratio of 33 contains a higher amount of exchangeable acidic sites, but the strength in acidity of these sites is lower than for the sites which exist in a zeolite with SiO_2 : Al_2O_3 ratio of 53. This means that the interaction between copper species and the zeolite lattice is stronger in ZSM5 with SiO₂: Al₂O₃ ratio of 53, i.e. the bridge copper species are more stable in catalyst Cu-ZSM5-53-74 than those in catalyst Cu-ZSM5-33-108. The mobility of less stable copper species form inactive agglomerates of copper. As mentioned previously, blockage of pore intersections in the catalyst is an additional disadvantage resulting from copper agglomeration.



Figure 7. Effect of SiO₂: Al₂O₃ ratio on the conversion of NO (Space Velocity 5400 h⁻¹)

Effect of drying

To compare the effect of drying after washing, the two catalysts Cu-ZSM5-53-145 and Cu-ZSM5-53-144 were prepared following identical ion-exchange procedures. Whereas sample Cu-ZSM5-53-145, was filtered and dried directly at a temperature of 110 °C, the eluate from the last washing step of sample Cu-ZSM5-53-144, was decanted after two days. Some of this eluate was still left in touch with the sediment of ion-exchanged zeolite when it was placed in an oven at 55 °C. After 24 h the oven temperature was raised to 110 °C and sample Cu-ZSM5-53-144 was dried at this temperature for 12 hours. The activity tests of these two samples showed that sample Cu-ZSM5-53-144 was active over a broader temperature range than sample Cu-ZSM5-53-145 (Fig. 8). Prolonged water contact may not only lead to enhanced wetting and thus a better dispersion in smaller pores and narrow channels but also improve the mobility of copper ions in the zeolite cavities through hydration and hydroxylation.



Figure 8. Pre-treatment. Effect of drying conditions on the NO conversion. Catalyst Cu ZSM5-53-145 was dried directly at 110 °C, while catalyst Cu-ZSM5-53-144 was dried at 55 and 110 °C (see the text), (Space Velocity 5400 h^{-1})

3.2 Characterisation of the catalysts

3.2.1 Stability of copper ions

Water co-ordination

Figure 9a-b displays the positions of two peaks from XRD-analysis (around 9.3 and 23 degrees) as a function of temperature. Two significant irregular regimes below 50 °C and between 150 and 350 °C can be observed.

The peak around 9.3 degrees shifts to lower values with increasing temperature. This irregular behaviour in combination with a significant loss in intensity clearly indicates that the peak position reflects more than a lattice expansion.

The peak around 23 degrees shifts in regular manner except for Cu-ZSM5-53-0 at temperatures between 150 and 350 °C. No evidence was found for an amorphous phase, resulting from structural damage for any Cu-ZSM5-53 catalyst.



Figure 9a-b. Positions of two peaks from Cu-ZSM5-53 exchanged with 0, 74, and 160 % Cu²⁺ ions as a function of temperature

Adsorption of water vapour in zeolites increases linearly with the concentration of framework aluminium atoms and each exchangeable site can be associated with five molecules of water [Iwamoto et al., 1990]. Water can bind to both Al^{3+} ions and Cu^{2+} ions and since the absolute amount of aluminium is constant for the three catalysts in Figure 10, the TGA data concentrate only on the exchanged copper ions.

TGA analyses of the catalysts Cu-ZSM5-53-0, Cu-ZSM5-53-74, Cu-ZSM5-53-160 as a function of temperature demonstrate an additional loss of water with increasing level of ion-exchange (Figure 10). Water is released at low temperature, with a release maximum at 75 °C, and again at 350 to 500 °C. At temperatures between 350 and 500 °C, however, the amount of released water decreases with an increase of the level of ion-exchange (Figure 11). It means that dissociation of Al-OH bonds and thus release of structural water occurs at higher temperatures.



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Figure 10. Relative sample weigh of 'as prepared' samples annealed in helium as a function of temperature



Figure 11. Mass-spectrometer signal of mass 18 (partial pressure of water) vs. annealing temperature for Cu-ZSM5-53 exchanged with 0, 74, and 160 % Cu²⁺ ions. Normalised for initial sample weight. Helium atmosphere.

Similar results for desorption of water from Cu-ZSM5-166 between 350 and 550 °C were reported by Li and Hall [1991], however the desorbed species were attributed to desorption of dioxygen.

The results from x-ray analysis reveal that the lattice parameters of ZSM5 catalysts change as a function of temperature. The peak at 9 degrees changes rapidly below 50 °C for all samples. The observed results from XRD and TGA- mass-spectrometry together reveal that these changes correspond to the desorption of 'liquid' water from the zeolite pores.

The results from TGA analysis further reveal that between 100 and 300 °C, two water molecules per copper ion are released from the catalysts. Mechanistic models presented

previously [Breck, 1974] suggest that water is released from formed divalent hydroxylated metallic cations, i.e. decomposition of $CuOH^+$ and formation of $Cu^{2+}O-Cu^{2+}$ species.

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Departure of two water molecules per metal ion may also be explained by decomposition of $Cu(OH)_2$ and co-ordination of Cu^{2+} to the exchangeable sites in zeolite. The decomposition of bulk copper hydroxide is dependent on moisture but it starts at 160 °C [Meier and Olson, 1992]. An alternative explanation could be release of water from incomplete hydration shells of zeolite bound Cu^{2+} ions [Centi and Perathoner, 1995; Jirka and Bosácek, 1991; Praliaud et al., 1998].

The copper co-ordinated water desorption is terminated at a temperature of about 350 °C. The water released above this temperature tunes with the increase of copper concentration. It is suggested that this water is correlated to the reversible decomposition of framework water from exchangeable acid sites in zeolites. It means that copper stabilises the crystallinity of the structure at higher temperature. This information is also supported by the results from infrared spectra (figure 12a-c).



Figure 12a-c. Absorbance spectra through Cu-ZSM5-53 before and after annealing to 477 °C in vacuum. (a) 0 % Cu^{2+} , (b) 74 % Cu^{2+} , and (c) 160 % Cu^{2+}



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The 'weight loss' of Cu-ZSM5 at temperatures between 100 and 300 °C (Figure 10), coincides with the temperature of irregular thermal expansion of H-ZSM5 (Figure 9b). The demonstrated anomalous behaviour in H-ZSM5 is nullified by copper ions in Cu-ZSM5. The changes in lattice parameters at these temperatures give favourable conditions for a higher interaction between stabilising copper ions and the zeolite lattice [Kucherov et al., 1995; Praliaud et al., 1998].

Dealumination and Agglomeration of Dehydrated Copper Ions

Previous discussion reveals that the exchanged cations in zeolites are stabilised by lattice aluminium. It is also known that the activity of exchanged copper in zeolites is correlated to the content of lattice aluminium and not only to the dispersion of copper [Chajar et al., 1994]. This behaviour is due to the changes in the physical and/or chemical form of the ion-exchanged copper with temperature, concurrent with their interaction with lattice aluminium in the zeolite.

Zeolites are crystalline materials which respond strongly to the intracrystalline aluminium content, extra framework matter [Wu et al., 1979], and the prevailing environmental conditions, such as adsorbing species on the surface [Fyfe et al., 1984] and temperature. Changes in electrostatic forces within the zeolite cavities as a result of changes in lattice parameters such as d(Si-O) and d(Al-O) followed by lattice expansion or compression as a result, are some of the responses which are of major importance for their catalytic activity. It means that changes in the catalytic property of a zeolite-based catalyst for a certain reaction is a function of all the above-mentioned parameters together.

An increase in aluminium content in the zeolite results in a decrease of bond strength between the exchanged cation and the lattice oxygen, i.e. the cations can be mobilised more easily. Though the strength of Al-O bond in the Si-O-Al bridge is much smaller than that of the Si-O and O-H bonds [Senchenya and Borovkov, 1991], a mobilisation of the cations can

undermine the dealumination process of the zeolite. This in turn will lead to release of structural water which is demonstrated in figure 11. The water release between 350 to 500 °C decreases with an increase in the level of exchanged copper ions.

Figure 13 shows XRD-spectra for 'used' Cu-ZSM5-33 catalyst which are ion-exchanged with 0, 108, and 210 % Cu^{2+} ions. These catalysts were heated in a flow of NO to 550 °C and then cooled in NO and finally analysed in air at room temperature. The only catalyst which showed a sintered phase of copper after the heat treatment was Cu-ZSM5-33-210. The colour of this catalyst had changed from light blue to dark grey after the test.



Fig. 13. X-ray diffractogram of 'used' catalysts Cu-ZSM-33 exchanged with 0, 108, and 210% Cu^{2+} . All diffractograms were obtained in air at 25 °C

Formation of copper agglomerates in deactivated ion-exchanged Cu-ZSM5 is analogous to the formation of copper agglomerates using the impregnation method for catalyst

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preparation. In both processes formation of well-dispersed small agglomerates in the zeolite is favoured. In spite of the high dispersion level of copper in impregnated Cu-ZSM5, the catalytic activity for decomposition of NO is much lower compared to the activity of ionexchanged Cu-ZSM5 [Chajar et al., 1994]. This is an important issue, which demonstrates the significance of interaction between the framework lattice aluminium and the copper ions.

A decrease in lattice aluminium content in a zeolite results in a decrease of the oxygen charge and an increase in the charge of the neutralising protons [Barthomeuf, 1991], i.e. the strength of the acid sites increases. An increase in acidity strength of the exchangeable ion sites leads to enhanced interaction between the lattice oxygen and the exchanged metallic cations. These well-distributed intra-molecular atomic forces act as structural stabilisers in the zeolite. As the temperature increases, the mean value of the O-O distance along the diagonals of the 10-ring windows in the zeolites increases [Deem et al., 1992]. This means that the Si-O distances decrease with increasing temperature, and the role of the metallic charge in the stabilisation of the Al-O bond becomes more important.

Figure 11 demonstrates the lattice OH removal in ZSM5-53 as a function of copper content at temperatures between 350 and 500 °C. The influence of copper content on the departure of zeolite structural water is obvious. Copper ions act as electron donor species to the oxygen atoms which are bonded to the structural aluminium and decrease the effect of temperature on the expansion of the Al-O bond length.

The above-discussion supports the results generated from XRD analysis which show formation of larger clusters of Cu^0 and CuO on Cu-ZSM5-33-210 (Figure 13). On the contrary, no agglomeration of copper could be distinguished on Cu-ZSM5-53 either by XRD or ESCA. Neither could changes in the crystallinity of the zeolite structure be observed. This result can be explained by an optimum aluminium content and thus a better dispersion of copper ions compared to catalysts prepared from ZSM5 zeolite with a SiO_2 : Al_2O_3 ratio of 33.

3.2.2 Acidity

Ion exchange with Cu^{2+} tunes the acidity. Figure 14 shows a decrease in the acidity of the catalysts above 350 °C with increasing ion-exchange level of copper. The temperature interval 375-500 °C corresponds to the peak activity for direct decomposition. Acidity does not promote NO direct decomposition which is logical considering the absence of a reducing agent.

The maximum strength in acidity in ZSM5 zeolite is found at a SiO_2 : Al_2O_3 molar ratio of 48 which corresponds to 4 Al^{3+} ions per unit cell or one per pore intersection [Post, 1984]. Cu²⁺ ions are considered to adsorb preferentially at these intersections [Anderson and Kevan, 1987].



Figure 14. Temperature programmed desorption of ammonia from Cu-ZSM5-53 exchanged with 0, 74, 145 and 160 % Cu²⁺

Indirect information about changes in structural parameters is given by acidity measurements. Temperature programmed desorption of ammonia reveals that at temperatures above 350 °C the number of stronger sites for adsorption of ammonia decreases with an increase of the level of exchanged copper ions. At temperatures below 300 °C, however, an inverse relation is observed for copper ion-exchanged ZSM5.

3.3 Intermediate surface species

3.3.1 Direct decomposition

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In order to set up a plausible reaction scheme for decomposition of nitrogen oxide, detailed information regarding the oxidation state of copper, cupric (Cu^{2+}) or cuprous (Cu^{+}) , during the course of the reaction, and the nature of the surface intermediates is required.

Surface co-ordinated nitrogen oxides can be found in one or several forms, bound to the zeolite lattice or to copper or copper ions. Nitrato (NO_3), nitro (NO_2), nitrito (ONO), nitrosyl (NO) and nitrido (N) are common forms [Nakamoto, 1986].

Figure 15a-c shows sequences of FTIR spectra after exposing the samples to reaction gas (pure NO) at reaction temperature, followed by evacuation. Three surface species can be distinguished from these spectra, (i) the broad band at 2130 cm⁻¹, (ii) a double band at 1575 cm⁻¹ and 1598 cm⁻¹, and (iii) a single peak at 1631 cm⁻¹. The peak at 1631 cm⁻¹ which is observed on the surface of ion-exchanged catalysts, is clearly related to another surface species than the double band at 1575 cm⁻¹ and 1598 cm⁻¹. The intensity of the peak at 1631 cm⁻¹ increases more rapidly with increasing of the level of ion-exchange of copper compared to the intensity of the double band.

Figure 15a-c. IR-spectra after decomposition of NO at 477 °C over Cu-ZSM5-53 exchanged with 0, 74, and 160% Cu^{2+} . 'last' represents the last spectrum through the catalyst at reactant gas composition and reaction temperature. 'gas' is the gas phase. 'que' the sample and gas phase adsorption after the sample was cooled in the reactant gas mixture. 'evac' adsorption in the sample after evacuation to 10^{-5} Torr at room temperature. 'ann' the sample again below 10^{-5} Torr but after annealing in vacuum to previous reaction temperature and re-cooling to room temperature







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Two types of surface species can be attributed to the above-mentioned bands, i.e. two different co-ordination of nitrates. The double band at 1575 cm^{-1} and 1598 cm^{-1} is attributed to co-ordination of unidentate nitrato groups and the single peak at 1631 cm^{-1} is attributed to bidentate nitrato groups.

The presence of two different coordinations for nitrates implies two different adsorption sites. The intensity of the bidentate nitrato group increases more rapidly with copper coverage than the intensity of the unidentate nitrato ligands. As discussed earlier it is also known that increase in copper concentration favours formation of clusters of copper ions, as suggested by $Cu^{2+}-O-Cu^{2+}$. Similar models of divalent cations on zeolites X and Y were suggested by other investigators [Breck, 1974]. It is then conceivable to assume unidentate co-ordination with one Cu^{2+} ion and bidentate co-ordination with two Cu^{2+} ions.

The decomposition temperature for the above nitrates is around 400 °C [Eränen et al., 1994; Li and Armor, 1991; Zhang et al., 1993]. This coincides with the light-off temperature for NO decomposition on Cu-ZSM5 catalysts [Iwamoto, 1990; Valyon and Hall, 1993]. Nitrato ligands block copper sites below the light-off temperature. The high stability of the nitrato complexes and exclusion of the unidentate co-ordination of the reaction intermediates

suggests that the reaction intermediates should have a similar co-ordination with copper ions as bidentate nitrato ligands.



Figure 16. Suggested geometry of the active site for NO decomposition, a $Cu^{2+}-O-Cu^{2+}$ dimer with ligand. N₂O₃ is short lived intermediate under reaction condition and NO₃ is a site blocker under ca. 300 °C. The Cu²⁺ monomer with a unidentate nitrato group is drawn for comparison

The most available [Aylor et al., 1995] and likely true reaction intermediate is two fold coordinated N_2O_3 . Similar to the co-ordination of bidentate nitrato ligands, $O_2N=NO$ fits into the bridge copper species.

The intensity of the peak at 2130 cm⁻¹ decreases with increasing copper content of the catalyst. It is suggested that the sites which, together with adsorbed species, give this band have no relevance for catalytic direct decomposition of nitrogen oxide since the catalytic activity of Cu-ZSM5 increases with the content of copper. The band has the same characteristics in pure NO and in a mixture of $NO_2 + O_2$.

14

Studies on copper ion-exchanged ZSM5 zeolite reveal that the concentration of Cu⁺ is proportional to both the temperature at in inert atmosphere [Liu and Robota, 1993; Paper III] and to the rate of NO decomposition at temperatures below 500 °C. It also reveals that at temperatures between 500 and 600 °C the conversion of nitrogen oxide decreases while the concentration of Cu⁺ continues to increase [Liu and Robota, 1993]. It means that the redox cycle of copper is only of importance in combination with structural lattice parameters of the zeolitic material. It can be concluded that changes in structural lattice parameters of the zeolite together with exchanged cationic species govern the strength of the adsorbed gaseous molecules and thus the formation of intermediate surface species.

The FTIR data for the catalysts: Cu-ZSM5-53-168, Ni-ZSM5-53-62, and Pd-ZSM5-53-196 are quite similar to the above-discussed data for Cu-ZSM5-160. Slight differences in intensity of the features were, however, observed. Considering to the different levels of interaction between the exchanged cations and the zeolite lattice and thereby differences in sorption and desorption characteristics of different catalysts, this is logical.

Co-cations

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Co-cations affect the catalytic activity of Cu-ZSM5 both in direct decomposition and selective reduction of NO and different co-exchanged cations, such as Ca, Fe, Ni, Co, and Sr in Cu-ZSM5 have been observed to increase the catalytic activity [Admiris et al., 1996]. It has also been reported that the temperature range within which the catalysts show the highest catalytic activity is broadened when co-cations are exchanged into the zeolites. The presence of co-cations decreases the light-off temperature [Keiski et al.; Teraoka et al., 1992]. Some co-cations can also suppress the oxidation of the reducing agent in selective reduction of NO [Admiris et al., 1996].

In addition, the FTIR data for Cu/Ni-ZSM5-53-76/41 and Cu/Pd-ZSM5-53-87/181 reveal similar information from the observed features as the other studied catalysts, which are discussed above.

3.3.2 Reduction of NO with methane

Methane is the only hydrocarbon that may pass largely unchanged through today's catalytic converters. The amount of up to 0.5% in the emitted gases is often larger than the concentration of other hydrocarbons. It means that methane is an ideal hydrocarbon for catalytic reduction of NO_x.

Copper ion-exchanged ZSM5 is known to be effective for reduction of NO_x with different low molecular-weight hydrocarbons, except methane. A dual ion-exchange of other co-cations such as Pd(II), however, improves the activity of copper ion-exchanged ZSM5 catalyst for reduction of NO_x with methane [Zhang et al., 1994] i.e. activation of methane is dependent on the type of exchanged metallic cation. Development of these types of catalysts requires a better understanding and identification of the surface processes, i.e. identification of the intermediate surface species and the possible reaction paths.

Cu-ZSM5

Figure 17a-c shows reaction data for pre-oxidised Cu-ZSM5-53-168 catalyst exposed to NO $+ O_2 + CH_4$ at 25, 300, and 450 °C, respectively. Methane gives a characteristic band at 3017 cm⁻¹ surrounded by rotational side bands. An additional strong methane band is identifiable at 1300-1304 cm⁻¹. Gas phase nitric oxide is revealed by a band at 1875 cm⁻¹. This NO fingerprint is obvious in figure 17b-c but obstructed by intense features at 1857 cm⁻¹ and 1870 cm⁻¹ in figure 17a. These two features disappear upon evacuation but lack the rotational fine structure characteristic of a gas phase species. They are assigned to a weakly adsorbed nitrosyl (NO) (Paper V). Gaseous nitrogen dioxide (NO₂) shows characteristic rotational bands around 1607 cm⁻¹. The bands at 1743 cm⁻¹ (1 minute) and 1745 cm⁻¹ (10 minutes) come from N₂O₄ gas (Paper I). N₂O₄ also gives a band at 743/744 cm⁻¹ and an additional feature at 1260 cm⁻¹ [Paper I; Armor, 1994].

Figure 17. Infrared-spectra of Cu-ZSM5 exposed to NO + O_2 + CH₄ at (a) 25 °C, (b) 300 °C and (c) 450 °C. Each figure displays the catalyst after 1 min and 10 min in the reactant gas and after evacuation at 25, 300 and 450 °C, respectively. The catalyst was pretreated in the IR chamber by oxidation in O_2 at 500 °C. The emissivities after calcination but before gas exposure at 25, 300 and 450 °C were used as background intensities.

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Figure 18a-c compares the spectra obtained under reaction conditions. These spectra are taken after rapid cooling in the reactant gas, evacuation, and annealing. The reaction spectra, 'last450' and 'last300' approach steady state conditions. The figure shows parallel data for Cu-ZSM5-53-168 in (a) NO + O_2 + CH₄, (b) NO + O_2 and (c) NO + CH₄. NO₂ gives dominant bands when NO is introduced together with oxygen. Upon quenching to room temperature the gas phase NO at 1875 cm⁻¹ is converted to weakly adsorbed nitrosyl groups at 1869 cm⁻¹.

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Figure 18. (a) Infrared-spectra of Cu-ZSM5 after reactions with a mixture of NO, O_2 and CH₄. 'last450' is the last spectrum with the catalyst exposed to the reactant gas at reaction temperature 450 °C. 'last300' is the last spectrum at reactant gas composition and reaction temperature 300 °C. 'quench' was obtained at 25 °C after cooling in the reactant gas mixture, 'evac' after evacuating the gas to 10^{-5} Torr at 25 °C and 'ann' after annealing to 300 °C in vacuum and re-cooling to 25 °C. The bottom spectrum displays the magnified 'ann' spectrum. (b) Same as above but for Cu-ZSM5 exposed to a mixture of NO and O_2 . (c) Same as above but for Cu-ZSM5 exposed to NO + CH₄.





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Ni-ZSM5

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Figure 19a-b characterises the interaction of NO + O_2 + CH₄ and NO + O_2 with Ni-ZSM5-53-62 at reaction condition and after rapid cooling in the reactant gas mixture. CH₄ and NO in the gas phase, rapid oxidation of NO to NO₂, and formation of N₂O₄ dimers upon cooling are observed.



Figure 19. (a) Infrared-spectra of Ni-ZSM5 after reactions with a mixture of NO, O_2 and CH₄. 'last450' is the last spectrum with the catalyst exposed to the reactant gas at reaction temperature 450 °C. 'last300' is the last spectrum at reactant gas composition and reaction temperature 300 °C. 'quench' was obtained at 25 °C after cooling in the reactant gas mixture, 'evac' after evacuating the gas to 10-5 Torr at 25 °C and 'ann' after annealing to 300 °C in vacuum and re-cooling to 25 °C. The bottom spectrum displays the magnified 'ann' spectrum,(b) Same as above but for Ni-ZSM5 exposed to a mixture of NO and O_2

Pd-ZSM5

Figure 20a-c shows data for Pd-ZSM5-53-196 catalyst quenched in the reactant gas. The gas phase components have been previously assigned although only the low frequency band at 743 cm⁻¹ is well separated.



Figure 20a-c. (a) Infrared-spectra of Pd-ZSM5 after reactions with a mixture of NO, O_2 and CH₄. 'last450' is the last spectrum with the catalyst exposed to the reactant gas at reaction temperature 450 °C. 'last300' is the last spectrum at reactant gas composition and reaction temperature 300 °C. 'quench' was obtained at 25 °C after cooling in the reactant gas mixture, 'evac' after evacuating the gas to 10-5 Torr at 25 °C and 'ann' after annealing to 300 °C in vacuum and re-cooling to 25 °C. The bottom spectrum displays the magnified 'ann' spectrum, (b) Same as above but for Pd-ZSM5 exposed to NO + O_2 . (c) Same as above but for Pd-ZSM5 in NO + CH₄

Cu/Ni-ZSM5

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Figure 21 represents data for pre-oxidised Cu/Ni-ZSM5-53-76/41 in NO + O_2 + CH₄ at 25, 300, and 450 °C. Copper is the dominant component and the data are in many details similar to the data of figure 18a.



Figure 21. Infrared-spectra of CuNi-ZSM5 after reactions with a mixture of NO, O_2 and CH₄. 'last450' is the last spectrum with the catalyst exposed to the reactant gas at reaction temperature 450 °C. 'last300' is the last spectrum at reactant gas composition and reaction temperature 300 °C. 'quench' was obtained at 25 °C after cooling in the reactant gas mixture, 'evac' after evacuating the gas to 10-5 Torr at 25 °C and 'ann' after annealing to 300 °C in vacuum and re-cooling to 25 °C. The bottom spectrum displays the magnified 'ann' spectrum.

Cu/Pd-ZSM5

Figure 22a-c presents infrared spectra for the quenched Cu/Pd-ZSM5-53-87/181 catalyst in $NO + O_2 + CH_4$, $NO + O_2$ and $NO + CH_4$. Some nitrous oxide (N₂O) is always produced for reactions between NO and CH₄ over unsupported Pd (NO : CH₄ ratios 1:1 to 1:8) [Vesecky et al., 1996]. N₂O was also observed in direct decomposition of NO over Cu-ZSM5 (Paper I). N₂O comes from disproportionation of NO in the latter case and either from disproportionation or partial reduction of NO in the former case. Only quenched NO + CH₄ mixtures over Cu-ZSM5-53-168, Cu/Ni-ZSM5-53-76/41 and Cu/Pd-ZSM5-53-87/181 show any traces of nitrous oxide in the present study. N₂O gives a vibrational band at 2225 cm⁻¹ surrounded by rotational fine structure (Paper I).



Figure 22a-c. (a) Infrared-spectra of CuPd-ZSM5 after reactions with a mixture of NO, O_2 and CH₄. 'last450' is the last spectrum with the catalyst exposed to the reactant gas at reaction temperature 450 °C. 'last300' is the last spectrum at reactant gas composition and reaction temperature 300 °C. 'quench' was obtained at 25 °C after cooling in the reactant gas mixture, 'evac' after evacuating the gas to 10-5 Torr at 25 °C and 'ann' after annealing to 300 °C in vacuum and re-cooling to 25 °C. The bottom spectrum displays the magnified 'ann' spectrum. (b) Same as above but for CuPd-ZSM5 in NO + O_2 . (c) Same as above but for CuPd-ZSM5 exposed to NO + CH₄.

The B peak at 2409 cm⁻¹ commonly shows some asymmetry, often identifiable as a shoulder or a separate peak on the high frequency side. It is most visible for Cu-ZSM5-53-168 and Cu/Ni-ZSM5-53-76/41 at 450 °C but may remain also for the quenched and evacuated samples at room temperature. The position is at 2460 ± 5 cm⁻¹ and does not shift with temperature in NO + O₂ + CH₄ and NO + O₂. In features for NO + CH₄, it is observed that a peak at 2449 ± 3 cm⁻¹ at 450 °C shifts to 2468 ± 4 cm⁻¹ at room temperature. The peak does not change when the quenched samples are evacuated.

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A separate peak at $2544 \pm 6 \text{ cm}^{-1}$ appears exclusively in NO + CH₄, i.e. gas mixtures without oxygen and only at room temperature for quenched or evacuated samples. It disappears upon annealing in an inert atmosphere.

The broad peak 'A' appears readily in NO + O_2 + CH₄ and NO + O_2 but its character changes upon exposure to NO + CH₄. In the absence of O_2 it occurs as a shoulder on the 'E' peak at around 836 cm⁻¹. Other regularly occurring species are three bands at 1767±1 cm⁻¹, 1667±1 cm⁻¹ and 1497±1 cm⁻¹, observed after adsorption of NO + O_2 + CH₄ at 25 °C and evacuation at the same temperature.

Another common feature is a band at $1667 \pm 2 \text{ cm}^{-1}$, always in combination with a narrow peak at $717 \pm 2 \text{ cm}^{-1}$. These bands become clear after evacuation, following reactions with NO + O₂ or NO + O₂ + CH₄ and they are present also after quenching. These features are not observed after exposure to NO + CH₄.

Miscellaneous adsorbed species are conceivable, some from adsorbed derivatives of nitrogen oxides, others from activated methane and yet others from reactions between the two. Nitrogen oxide-derived intermediates have been discussed at length [Curtin et al., 1997; Hadjiivanov et al., 1996; Aylor et al., 1997; Hoost et al., 1995; Hayes et al., 1996]. Methane adsorbs as a methyl group following C-H bond activation. Methyl groups have limited stability on unsupported metal surfaces, where methylidyne (CH) is observed at non-

cryogenic temperatures [Wu and Goodman, 1994]. These groups have characteristic vibrational bands around 3000 cm⁻¹ and 800 cm⁻¹. Partial oxidation of hydrocarbons has long been discussed as an important step for NO_x reduction with C_{2*} molecules. Partial oxidation of methyl groups would result in methoxy species (CH₃O), known intermediates of methanol adsorption on oxidized metal catalysts. Copper-bound CH₃O groups have vibrational bands at 395 cm⁻¹, 1020 cm⁻¹, 1430 cm⁻¹, 2770 cm⁻¹ and 2880 cm⁻¹ [Hrbek et al., 1984]. Iso-cyanide complexes, (NCO), constitute alternative intermediates or possible side products. The NCO band comes at 2170-2270 cm⁻¹ [Okuhara et al., 1997; Solymosi and Bansagi, 1995; Hecker and Bell, 1984].

Mechanism

The mechanism of NO_x reduction with methane has been discussed extensively [Lukyanov et al., 1996; Fripiat and Deroune, 1985; Pirone et al., 1996]. Isotope effects show that methane activation is the rate-limiting step in CH_4/NO reactions [Cant and Cowan, 1997].

Conversion data over supported catalysts indicate that reactions occur between CH_4 and NO_2 and that free radicals are crucial [Lukyanov et al., 1996]. Reaction between adsorbed nitrates and adsorbed CH_3 is also suggested [Paul, 1999]. Similar ideas have been brought forward for the SCR reaction between ammonia and nitrogen oxides [Hadjiivanov et al., 1996]. 400 °C is a low temperature for any significant desorption of CH_3 radicals [Lunsford et al., 1984] and the key feature for the reaction between NO and CH_4 is that NO_3 is ligated to the same site as CH_3 .

The reaction tentatively proceeds via unidentate NO₃, bound to copper in a dual metal dimer. Methyl or a another CH_x intermediate is coordinated to the co-cation, Ni²⁺ or Pd²⁺, since methane lacks the ability to reduce Cu²⁺ to Cu⁺, which is crucial for the formation of a bound CH₃ species [Liu and Robota, 1994]. Simultaneous formation of NO₃ and a CH_x species facilitates rapid partial reduction of the former and the possible formation of

methoxy groups. This reaction scheme incorporates the documented role of partially oxidised hydrocarbons in HC-SCR reactions [Paul, 1999]. Work on unsupported Pd reveals that excess methane is needed unless sites selective for CH_4 are available, otherwise NO will simply replace or block adsorption of CH_4 [Vesecky et al., 1996]. Co-cations in metal dimers create sites with this selectivity. Unsupported Pd shows very high selectivity for complete reduction of NO by CH_4 to N_2 in the presence of O_2 [Vesecky et al., 1996], the problem is that the reaction is slow.

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Hydrocarbons (except methane) react directly with acid sites on doped supports and built carbonaceous residues. Methane can produce similar surface carbon on unsupported Pd and likely also on supported catalysts [Ono, 1992; Wu et al., 1994] and nitrogen oxides can react very fast with surface-deposited carbonaceous material. It was observed that the reduced Pd-ZSM5 catalyst is active for NO/CH₄ reactions but the catalyst deactivates rapidly in the presence of oxygen [Loughran and Resasco, 1994].

Conclusions

Prolonged immersion of the catalyst in water during preparation enhances the hydroxylation of copper which in turn improves the formation of active bridged cationic species.

A high level of exchanged copper in the zeolite in combination with a low concentration of acid sites, together with a high SiO_2 : Al_2O_3 ratio, enhances the conversion of NO.

Characterization of Cu-ZSM5 reveals that approximately two molecules of water per Cu²⁺ ion desorb at temperatures between 150 and 350 °C, in addition to the conventional dehydration at lower temperatures. The desorbed water comes from the decomposition of Cu(OH)₂. Decomposition of hydroxylated copper ions results in the formation of Cu²⁺-O-Cu²⁺ dimers, which are suggested to be the active sites for catalytic decomposition of NO.

The temperature of dehydroxylation of acid sites on H-ZSM5 overlaps with the light-off temperature of NO reduction over Cu-ZSM5. Bridged nitrato groups ligated to $Cu^{2+}O-Cu^{2+}$ dimers act as site blockers below the light-off temperature. At the light-off temperature zeolite lattice vibrations destabilize surface nitrates and open the sites for catalytic reactions via short-lived N₂O₃ intermediates. The same lattice movements decompose OH-groups on the H-form of the zeolite.

A model for reduction of NO with methane is suggested based on reactions at dual metal dimers, Cu^{2+} -O-Pd²⁺, between ligated NO₃ and CH_x. Cu is known to be efficient for NO oxidation and Pd good for methane activation, i.e. Cu produces NO₂ or even nitrates and the second metal CH₃ groups. Dual metal dimers facilitate rapid reactions between the two ligands.

The mobility of the exchanged copper ions and the formation of large agglomerates which may cause diffusion limitations in the pore intersections was found to be related to the SiO_2 : Al_2O_3 molar ratio of the zeolite.

4 Acknowledgements

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