Mika Huuhtanen

ZEOLITE CATALYSTS IN THE REDUCTION OF NOₓ IN LEAN AUTOMOTIVE EXHAUST GAS CONDITIONS

BEHAVIOUR OF CATALYSTS IN ACTIVITY, DRIFT AND TPD STUDIES

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ZEOLITE CATALYSTS IN
THE REDUCTION OF NO\textsubscript{X}
IN LEAN AUTOMOTIVE EXHAUST
GAS CONDITIONS
Behaviour of catalysts in activity, DRIFT and
TPD studies

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Oulu, Finland

Abstract

The aim of the thesis is to expand the knowledge of the catalytic properties of platinum-loaded zeolite catalysts in the reduction of NOx by hydrocarbons. The work is divided into three parts. First the recent literature of zeolite catalysts has been introduced, secondly the adsorption capacity, activity, and acidity of the catalysts have been studied by TPD and IR techniques, and thirdly the derived reaction mechanisms based on the obtained data are presented.

Parent and 1 wt-% Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolite catalysts have been studied in the C3H6-assisted reduction of NO. The Pd/Al2O3-based catalyst was used as a reference material for the reaction mechanistic studies. Several experimental techniques (in situ DRIFT, activity measurements, CO chemisorption, N2 physisorption, TPD, and TEM) have been used for the characterisation of the catalysts properties. The IR technique was used as the main technique for the determination of activities, surface species, and the acidic properties of the zeolite-based catalysts. The activity studies carried out by the gaseous FTIR technique provide information on the desired reaction products as well as the undesired by-products. The detection and identification of the surface species as well as the reaction intermediates formed were done by the DRIFT method.

The activity experiments indicate the effectiveness of the Pt-loaded zeolite catalysts. The reduction of NO was found to decrease in the order: Pt/Beta > Pt/Y > Pt/Ferrierite > Pt/ZSM-5 in the conditions with excess O2. Platinum can be concluded to have an effect on O2 and NO dissociation. Oxidation reactions of NO to NO2 and propene to CO2 were observed to be more intense over the platinum-loaded zeolites than over the parent zeolites.

In this work the reaction mechanisms for the C3H6-SCR of NO were derived over the Pt-loaded zeolite as well as the Pd/alumina catalysts based on the data obtained by DRIFT and activity experiments. The kinetics for the NO reduction by CO over Pd/Al2O3 was also derived. With the methods employed, the mechanistic steps over the Pt-loaded zeolites and Pd/Al2O3-based catalysts could be derived quite precisely and easily for C3H6-SCR of NO. Reaction routes were determined to go via different formations of intermediates over the two catalysts, i.e. via organonitrogen and isocyanate routes, respectively. The IR techniques were discovered to be effective tools in applied engineering studies.

Keywords: acidity, aluminium oxide catalysts, catalyst activity, characterisation, infrared techniques, palladium, platinum, reaction mechanisms, temperature programmed desorption, zeolite catalysts
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Oulu, 30 October 2006

Mika Huuhtanen
List of symbols and abbreviations

Latin letters

\( c_i \)  Concentration of the component i, mol/dm\(^3\)
\( E_{a,i} \)  Energy of activation for component i, kJ/mol
\( F_i \)  Molar inlet rate of component i, mol/s
\( \Delta G_i^0 \)  Gibbs energy, kJ/mol
\( H_i \)  Enthalpy, kJ/mol
\( h \)  Hour(s)
\( k \)  Reaction rate constant, (different units, see Table 10)
\( K_i \)  Equilibrium constant, m\(^3\)/mol
\( l \)  Length, m
\( m_{\text{cat}} \)  Catalyst mass, g
\( r_i \)  Reaction rate, mol/g s
\( R^2 \)  Regression determination coefficient, %
\( S_{\text{BET}} \)  Specific surface area by BET method, m\(^2\)/g
\( T \)  Temperature, ºC, K
\( T_{50} \)  Temperature when conversion reaches 50%, ºC
\( v \)  Gas velocity, cm\(^3\)/h
\( x_i \)  Fractional conversion of component i, (dimensionless)
\( X_i \)  Conversion of component i, %
\( \text{Å} \)  Ångström, 1×10\(^{-10}\) m
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>A/F</td>
<td>Air-to-fuel-ratio. In stoichiometry A/F = 14.7</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller -theory</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda -theory</td>
</tr>
<tr>
<td>cpsi</td>
<td>Cell per square inch, 1/in²</td>
</tr>
<tr>
<td>DI</td>
<td>Direct injection</td>
</tr>
<tr>
<td>DRIFT(S)</td>
<td>Diffuse Reflectance Infrared Fourier Transform (Spectroscopy)</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy-Filtered Transmission Electron Microscopy</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>Euro 1-5</td>
<td>European Union Emission Standards, stages 1-5</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas Hourly Space Velocity</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>HC-SCR</td>
<td>Hydrocarbon-assisted Selective Catalytic Reduction</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LEV II</td>
<td>Californian Low Emission Vehicle standard II</td>
</tr>
<tr>
<td>NMHC</td>
<td>Non-methane hydrocarbons</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Nitrogen oxides, NO, NO₂, N₂O</td>
</tr>
<tr>
<td>OBD</td>
<td>On-Board Diagnostics</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary Differential Equation</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metals (Pt, Pd, Rh, Ru, Os, Ir)</td>
</tr>
<tr>
<td>PyB</td>
<td>Brønsted acid site</td>
</tr>
<tr>
<td>PyL</td>
<td>Lewis acid site</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective Catalytic Reduction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>TWC</td>
<td>Three-Way Catalyst</td>
</tr>
</tbody>
</table>
List of original papers

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The manuscripts for the publications (Papers I-III and V) were written by the author of this thesis. In Paper IV the experiments and data analyses were the author’s contribution and the manuscript was written in close collaboration with the first author.
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1 Introduction

1.1 General

The abatement of nitrogen oxide (NO\textsubscript{X}) species, such as NO, NO\textsubscript{2}, and N\textsubscript{2}O from the exhaust gases of automotive as well as stationary sources is a very important aspect of emission control in terms of having a cleaner environment. The emissions from motor vehicles were documented as a potential environmental problem more than 60 years ago, when the first reports of photochemical smog formation by the complex reaction of NO\textsubscript{X} with hydrocarbons (HC) were introduced. (Haagen-Smit 1952, Haagen-Smit & Fox 1956, Acres and Harrison 2004) NO\textsubscript{X} species are known to cause health problems, including bronchitis, asthma, and lung cancer, as well as environmental problems such as acid rain and material corrosion (Acres and Harrison 2004, Topsøe 1997, ACEA 2004, Fritz & Pitchon 1997). The main sources of NO\textsubscript{X} emissions are the combustion processes e.g. burning of fossil fuels in power plants and gasoline in motor vehicles.

Nitrogen oxides are formed from anthropogenic sources via three reactions: oxidation of nitrogen-containing compounds in fuel (fuel NO\textsubscript{X}), fixation of atmospheric nitrogen (thermal NO\textsubscript{X}), and oxidation of intermediate HCN (prompt NO\textsubscript{X}). The formation of NO\textsubscript{X} depends on the temperature, residence time and oxygen concentration in the combustion process. Nitrogen oxides in exhaust and flue gases from fossil fuel operating motors, combustion units and reactors contain mainly NO. (Wojciechowska & Lomnicki 1999, König et al. 2004, Topsøe 1997)

Nitric oxide (NO) is reported to be thermodynamically unstable. The decomposition energy of NO is $\Delta G_f^\circ = -86$ kJ/mol. Unfortunately, the decomposition reaction of NO is inhibited by the high activation energy of 365 kJ/mol. Due to this energy barrier a catalyst is required to decrease the activation energy. (Fritz & Pitchon 1997, Glick et al. 1957)

Automotive emissions have been regulated since the early 1970s. The legislation started in the United States by the US Clean Air Act of 1970, which allows for the controlling of emissions of nitrogen oxides, unburned hydrocarbons and carbon monoxide (CO). The first catalytic converters able to achieve the emission limits were installed on cars for the model year 1975. (Acres & Harrison 2004) Over the decades the
legislation has become more demanding in the European Union (EU) and by national governments as well e.g. in USA, Japan and India. (Heck & Farrauto 1997, Acres & Harrison 2004, Burch 2004, EU 1970, EU 1998) The Euro emission standards stated by the EU for automotive exhaust gas emissions were set in action for the first time in 1992 (Euro 1). The most recent emission standard, Euro 4, came into force in January 2005. Euro emission standards regulate the releases of pollutants of NOx (NO and NO2), hydrocarbons (HC), and CO as well as particulates. Nitrous oxide (N2O) is not, however, regulated by Euro emission standards.

The European Commission (EC) adopted the proposal for a new emission standard (Euro 5) in December 2005. The circulation of the proposal for comments is going on in the European Parliament and Council. The new regulation is expected to enter into force at the earliest in mid-2008, and at the latest in 2010. The Euro 5 standard will cut both NOx and HC emissions by 25% from gasoline driven cars. The standard also contains particulate regulation of 0.005 g/km, which will be applicable only to vehicles using lean direct inject (DI) engines. For gasoline driven engines the Euro emission standards have been tightened as shown in Table 1 (Dieselnet_EU 2005, ACEA 2004, Burch 2004, EU 2005).

Table 1. EU emission standards for gasoline passenger cars (g/km) (Dieselnet_EU 2005, ACEA 2004, Burch 2004, EU 2005).

<table>
<thead>
<tr>
<th>Tier</th>
<th>Date</th>
<th>CO</th>
<th>HC</th>
<th>HC + NOx</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro 1</td>
<td>1992.07</td>
<td>2.72</td>
<td>-</td>
<td>0.97</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2</td>
<td>1996.01</td>
<td>2.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>2.30</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro 5 (EC 12/2005)</td>
<td>mid-2008 - 2010</td>
<td>1.0</td>
<td>0.075</td>
<td>-</td>
<td>0.06</td>
</tr>
</tbody>
</table>

During the 1990s, several countries all over the world enacted national laws and emission standards, mostly based on Euro standards. Figure 1 presents the current and subsequent stage of the automotive exhaust gas emission standards for NOX, unburned hydrocarbons, and CO in the EU, USA Federal, and Japan. The regulations of particulate emissions are also set for diesel vehicles. The emission values of the USA Federal standard have been changed from g mil⁻¹ to g km⁻¹, and hydrocarbon values do not include methane, i.e. non-methane hydrocarbons (NMHC), so the values in the table are comparable. The USA/Tier 2 bin 5 -values are the “average” values, which are also equivalent to the values in the California LEV II standard. (Dieselnet_USA 2004, EPA 2002, Hybrid Cars 2005) As can be seen in Figure 1, the most demanding standard for the NOx emissions is the USA/Tier 2, which has been phased in the beginning of 2004 and will come fully into force by 2007. In 2005, 50 per cent of new passenger cars must fulfil the Tier 2 regulations. (EPA 1999)
Fig. 1. Current and subsequent stage of the emission standards in the EU, USA Federal, and Japan (Dieleenet_USA 2004, Walsh 1999, EPA 2000, EPA 2002).

The combustion and operation conditions in engines have been further developed to be leaner, i.e. oxygen rich, to decrease fuel consumption. As a result, the traditional three-way catalysts (TWC) are no longer effective in reducing NOX. To meet the automotive emission standards, engines and system control also have to be developed. The combination system with oxygen sensors, on-board diagnostics (OBD), and a catalytic converter is required to diminish the emissions at the requisite levels. Provisions for the use of these applications are proposed in the EU Commission Draft for the new emission directive. All manufacturers should always provide the OBD-related information to the manufactures and/or repairers of all components, diagnostic tools or test equipment. (EU 2005, Dieselnet_EU 2005) The stringent environmental legislation and regulations have also forced petroleum refiners to produce cleaner fuels with lower levels of e.g. sulphur and aromatics (Dai 1995).

1.2 Selective catalytic reduction (SCR)

For several years, the reduction of NOX in lean conditions and at low temperatures has been the object of researchers’ great interest because the majority of the harmful emissions are formed instantly after the starting of the engine (ignition). The combustion and operation conditions in engines have been further developed to be leaner i.e. oxygen rich. As a result, the traditional three-way catalysts (TWC) are no longer as effective in the selective catalytic reduction (SCR) of NOX. This is the main reason for developing new catalysts and more efficient NOX abatement techniques. (Sirilumpen et al. 1999, Ingelsten et al. 2004)

Nitrogen oxides can be reduced by using hydrocarbons, ammonia or urea as reductants in SCR. The injection of unburned fuel or other reductants makes the conditions in the

Pt-containing zeolite materials such as Pt/ZSM-5 (e.g. Burch & Scire 1994, Cho and Yie 1996, Deeba et al. 1999, Guo et al. 1995, Iwamoto et al. 1994, Keiski et al. 1996, Obuchi et al. 1998, Shin et al. 1995, Takami et al. 1997, Xin et al. 1997a), Pt/Beta (e.g. García-Cortéz et al. 2003a & 2003b, Satsuma et al. 2003), Pt/Y (e.g. Amiridis et al. 1997, Satsuma et al. 2003, Pérez-Ramirez et al. 2001), Pt/FER (e.g. Martens et al. 2001), as well as Co-Pt/HY (Maisuls et al. 2003) and Pt-transition metal mordenites (Sakamoto et al. 1997) have been investigated for NOx reduction by hydrocarbons. Platinum-loaded zeolite catalysts have been found to be effective in the reduction of NOx and at the same time in the oxidation of hydrocarbons and CO. Pt-zeolite catalysts might be a solution for the HC-SCR and the oxidation reactions in lean conditions and at low temperatures. To understand the mechanisms and furthermore the kinetics of the SCR reactions of NOx there is a need to investigate the surface species and intermediates formed under the reaction conditions as well as the gas-phase by-products at the catalytic converter outlet.

1.3 Scope and aims of the research

This thesis work is a part of a larger research project, ‘FT-IR studies and kinetic modelling of catalytic NO-CO-O2 and NO-hydrocarbon-O2 reactions’ carried out in the Laboratory of Mass and Heat Transfer Process Engineering at the University of Oulu. The goal of this thesis is to improve the present-day understanding of the reactions occurring on the surfaces of noble metal catalysts supported on zeolite carriers and to find correlations between the results obtained by different experimental methods, i.e. in situ DRIFT, activity, acidity, physisorption, chemisorption, TPD and TEM/EDS studies. An extensive analysis of present-day literature was used to support the experimental observations when deriving the reaction mechanism for HC-SCR of NOx. The scope of this thesis was to gain new knowledge on the selective catalytic reduction of NOx by propene. The knowledge of the reaction mechanisms and kinetics form the basis for the development of SCR catalysts and reactors and thus the reaction mechanisms and reaction intermediates and products have been studied in this work.

The main goal of this work was to derive the plausible reaction mechanisms for NO reduction by hydrocarbons with propene in particular being the reductant. The platinum-loaded zeolites have been studied and the formation of intermediates on the catalysts surfaces has been detected. Pd/Al2O3-based catalysts have been used as a reference material. Based on the infrared (IR) technique, the catalytic activity and performance of the catalysts have been investigated and the mechanism of NO reduction in lean conditions and at low temperatures has been derived. The reaction mechanisms can be
determined via the combined analysis of gaseous products and the identification of the adsorbed surface species formed during the reactions, and likewise the kinetic equations can be further derived for the C\textsubscript{3}H\textsubscript{6}-SCR of NO\textsubscript{X}. The kinetic analysis can be utilised in the reactor design. Studies were carried out by gas-IR and by \textit{in situ} Diffuse Reflectance Infrared Fourier Transform Spectroscopy, DRIFTS.

The other main focus was to study the use of the infrared technique, in surface species identification and activity experiments as well as in acidity measurements, and to study the applicability of IR and DRIFT techniques as an engineering tool for mechanistic studies. Temperature Programmed Desorption (TPD) is used to investigate the adsorption and desorption performances of the catalysts as a function of temperature.

The study has been carried out in collaboration with Ecocat Oy (formerly Kemira Metalkat Oy), which provided the zeolites and other catalysts’ materials studied. The experiments were carried out partly in Ecocat Oy’s (DRIFT studies) laboratory and partly in the Department of Process and Environmental Engineering at the University of Oulu.

This work is comprised of a short overview of the relevant literature, the experimental part, results, and discussion. Chapter 2 offers a brief review of the recent literature of the reduction of NO\textsubscript{X} by hydrocarbons in lean conditions over zeolite and alumina-based precious metal loaded catalysts. The catalysts studied are introduced in Chapter 3, and the experimental set-ups and procedures are presented in Chapter 4. In Chapter 5 the experimental results of the characterisation, activity and surface studies of the catalysts are presented. The mechanistic models introduced in the recent literature and the derived mechanistic models based on the observations are reported in Chapter 6. The results and observations are discussed in Chapter 7. The conclusions of the study are presented in Chapter 8.
2 Lean gasoline and diesel conditions

Diesel and lean burn engines have oxygen rich conditions in the burning chambers (cylinders). In the excess oxygen the air/fuel (A/F) ratio of the mixture is clearly above the stoichiometric value of 14.7, and can be over 24. Excess oxygen in the exhaust gas makes traditional three-way catalysts inefficient in reducing harmful NO-containing exhaust gas emissions. (Kašpar et al. 2003, Burch 2004) The majority of the reductants are combusted by the excess oxygen. Thus, the selective oxidation of propene with NO is limited by the competing oxidation with O₂ (Ioan et al. 2005).

Figure 2 presents the component removal efficiency of NO, CO, and hydrocarbons as a function of the air/fuel (A/F) ratio by traditional TWCs (Heck & Farrauto 2001).

Fig. 2. Conversions of hydrocarbons, CO, and NO by three-way catalysts (Reprinted from Appl. Catal. A 221, Heck & Farrauto, 2001 with the permission of Elsevier).
Typical exhaust gas compositions resulting from incomplete combustion in gasoline and diesel engines are presented in Table 2. HC, CO, and NOX are found to be the major pollutants. Unburned, partially oxidised HCs and CO are due the incomplete oxidation of the reaction gases, and NOX are formed from the nitrogen in air at high engine temperatures. The $\lambda$-values of gasoline, lean gasoline and diesel engines are 1, 1.16, and 1.26, respectively. (Heck & Farrauto 2001, Gabrielsson 2004, Skoglundh & Fridell 2004, Kašpar et al. 2003).


<table>
<thead>
<tr>
<th></th>
<th>NOX (ppm)</th>
<th>HC (ppm)</th>
<th>CO (ppm)</th>
<th>H2 (ppm)</th>
<th>O2 (%)</th>
<th>CO2 (%)</th>
<th>H2O (%)</th>
<th>SO2 (%)</th>
<th>N2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>900</td>
<td>350</td>
<td>5000</td>
<td>1700</td>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>15-60</td>
<td>bal.</td>
</tr>
<tr>
<td>Lean</td>
<td>1200</td>
<td>1300</td>
<td>a</td>
<td>1300</td>
<td>n.i.</td>
<td>4-12</td>
<td>11</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>Diesel</td>
<td>1135</td>
<td>30</td>
<td>490</td>
<td>n.i.</td>
<td>10.5</td>
<td>7.1</td>
<td>4-5</td>
<td>30</td>
<td>bal</td>
</tr>
<tr>
<td>Diesel $^b$</td>
<td>650</td>
<td>330</td>
<td>195</td>
<td>n.i.</td>
<td>14.8</td>
<td>4.3</td>
<td>5</td>
<td>78</td>
<td>bal</td>
</tr>
</tbody>
</table>

$^a$ calculated as C1, $^b$ 50% loading, n.i. not indicated.

The removal of undesired and harmful pollutants from automotive exhaust gases has been regulated for decades. The catalytic converters used are mainly TWCs. TWC converters have been developed to operate at the stoichiometric air/fuel-ratio. Lean conditions make the removal of nitrogen oxides, NO and N2O, more difficult due to the competing reactions and the lack of reductants (CO and HCs) in the exhaust gas mixture.

### 2.1 Hydrocarbon-assisted reduction of NOX

The hydrocarbon-assisted selective catalytic reduction (HC-SCR) of NOX has been studied widely over numerous catalytic materials such as metal oxides and zeolites. Precious metals (Pt, Pd, Rh, Ir) and base metals (Cu, Fe, Co, Ag, Ni, Ga, Ce, Mn) loaded on various zeolitic supports have been studied in oxygen rich conditions. The NO reduction is proposed to go via decomposition or via formation of nitrogen containing organic species, and further the reactions between these intermediates and NO take place. (Traa et al. 1999, Brosius & Martens 2004, Obuchi et al. 1998, Xin et al. 1997a, Gerlach et al. 1999a, Shen & Kawi 2003, Amiridis et al. 1997, Burch & Scire 1994b, Iwamoto et al. 1994, Petunchi & Hall 1994, Wang et al. 2003).

PGM-loaded oxide-based (e.g. $\gamma$-Al2O3, SiO2, TiO2, ZrO2) catalysts have been studied in the HC-SCR of NOX in recent decades and they have been found to be active catalysts for the reduction of NOX (Bamwenda et al. 1995, Burch & Watling 1997, Nikolopoulos et al. 1999).

Zeolite-supported base and precious metal catalysts have been studied in the removal of nitrogen oxides by hydrocarbons since 1982, when Iwamoto indicated the Cu-ZSM-5 catalyst having activity in NOX reduction. The drawback for the first Cu-based zeolite
catalysts was the activity decrease in the presence of water or sulphur. (Wojciechowska & Lomnicki 1999)

Several zeolite catalysts (e.g. ZSM-5, zeolite Beta, Ferrierite, Mordenite, and faujasites) have been studied to find a possible reaction mechanism for the NO\textsubscript{X} reduction by hydrocarbons, e.g. methane (Ciambelli et al. 2001, Dedeček et al. 2002, Mihaylov et al. 2004), ethane, ethene (Li & Armor 1994, Burch & Scire 1994b, Iwamoto et al. 1994, Cho et al. 1995, Cho & Yie 1996), propene, propane (Poignant et al. 2001, Acke & Skoglundh 1999, Wichterlová 2004, Corma et al. 1997, Papers I-III) and higher hydrocarbons (Petunchi & Hall 1994, Martens et al. 2001), as well as in simulated diesel engine exhaust gases (Iwamoto et al. 1994, Wögerbauer et al. 2001, Pontikakis et al. 2001, Ciambelli et al. 2001, Guo et al. 1995). Recently the use of natural gas as a fuel for automotive engines has raised the level of interest in reducing NO\textsubscript{X} from the exhaust gases of natural gas engines. (Ciambelli et al. 2001)

Hydrocarbon-assisted SCR of NO has also been studied with dual pore zeolite catalysts (Brosius & Martens 2004, Holma et al. 2004) as well as with other metal cation besides Pt e.g. Co, Mg, La, Ce, In, Ti, or Au (Maisuls et al. 2003, Terada et al. 1997, Nakatsuji et al. 1995, Traa et al. 1999). Studies have also been carried out with catalysts which contain metal oxides such as aluminium, cerium and zirconium oxides besides zeolite materials (Tanabe et al. 2002, Krishna et al. 2002, Kamijo et al. 2001).

Platinum-loaded catalysts have been found to be effective in the abatement of NO\textsubscript{X} and at the same time in the oxidation of hydrocarbons (Xin et al. 1997a, Shen & Kawi 2003, Deeba et al. 1999). Platinum-loaded zeolites have been studied in lean exhaust gas conditions, and they have been found to have good activity in the reduction of NO\textsubscript{X}. Moreover, the lower light-off temperature and minor effect of the presence of water in the case of NO\textsubscript{X} reduction are reported with Pt-loaded zeolites when compared to Cu-ZSM-5 (Guo et al. 1995). Pt-loaded catalysts are also reported to be more resistant to sulphur poisoning by SO\textsubscript{2} than other catalysts. Pt/ZSM-5 is reported to have good durability under real exhaust gas conditions. (Gilot et al. 1997, Xin et al. 1997a, Iwamoto et al. 1994, Burch & Watling 1998)

The assumption has been made that Pt-zeolite catalysts might be one possible solution for the HC-SCR of NO\textsubscript{X} and the oxidation of HC and CO in lean conditions at low temperatures. To understand the mechanisms and furthermore to derive the kinetics of the SCR reactions there is a need to investigate the surface species formed under the reaction conditions as well as the by-products in the gas phase at the reactor outlet.

The Pt loadings of zeolite catalysts are reported to be generally between 0.05 and 2.4 wt-%, although higher Pt-loaded catalysts, such 7.2 wt-% Pt/ZSM-5, have also been studied (Burch & Scire 1994, Machida & Watanabe 2004, Xin et al. 1997a & 1997b, Cho & Yie 1996, Obuchi et al. 1998). Typical loading of the PGM metals has been reported to be around 1 wt-%, while with the base metals (e.g. Cu, Fe, Co) the metal loading is reported to be higher. In addition, some studies of propene-assisted SCR of NO\textsubscript{X} have been carried out with rather high base metal loadings, e.g. 14 wt-% for Co/Ferrierite (Ciambelli et al. 2001) or 5.4 wt-% for Cu-ZSM-5 by Amiridis et al. (1997).

The reaction inlet gas generally contained components in the following concentrations: NO 250-2000 ppm, C\textsubscript{3}H\textsubscript{6} 100-2000 ppm, O\textsubscript{2} 2.5-10%, and H\textsubscript{2}O 0-10% (e.g. Acke & Skoglundh 1999, Chen et al. 2004, Giroir-Fendler et al. 2001). In some
studies, SO2 has also been introduced into the inlet gas of the reactor (e.g. Deeba et al. 1999).

The catalytic properties of the zeolite materials are strongly affected by the structural and acidic properties of the zeolite. The aluminium concentration in the framework or extraframework also has an influence on the catalytic properties. Acid zeolites are reported to be effective HC-SCR catalysts when the inlet gases are dry. Zeolites acid sites are also reported to be the active sites for the hydrocarbon cracking process. (Brosius & Martens 2004, Corma 1995, Martin et al. 1991) The material acidity is defined relative to the base used in acid-base interaction. Two types of acidity are found: Brønsted and Lewis acidity. Many different reactions are catalysed by the acid sites of the material. With IR spectroscopy the acidity of the materials can be determined and it has been found to be a very powerful technique allowing the determination of the hydroxyl groups directly. To measure the acidity of solid catalysts many different probe molecules such as pyridine, quinoline, diazines, NH3 and CO have been used. The most commonly used probes are pyridine and NH3 because of their stability and rather easy determination of Brønsted and Lewis sites by IR spectroscopy. (Corma 1995, Bludau et al. 1998, Zheng et al. 2004)

The acidic sites can be observed in the 3600-3200 cm⁻¹ region (Si-OH groups), around 3730 cm⁻¹ (terminal silanol groups) and at 1650-1440 cm⁻¹ (probe molecule adsorption). Brønsted OH on Al can be detected at around 3610 cm⁻¹. (Janin et al. 1991, Parker et al. 1993)

Pyridine is rather bulky, and it has a kinetic diameter of about 0.6 nm. In the case of zeolites and zeolite-like materials, such as large-pore zeolites (faujasites and mordenites) as well as medium pore materials (ZSM-5, ZSM-11), pyridine is a suitable molecule for probing acidic properties. According to Bludau et al. (1998) almost nothing is yet known about the transport behaviour of pyridine in zeolites’ porous structure. Pyridine can be adsorbed on the surface in coordinated (Lewis sites) and protonated (Brønsted sites) forms. The adsorbed pyridine on the Brønsted (PyB) and Lewis (PyL) sites can be detected at the wavenumbers of 1632 and 1540 cm⁻¹ (PyB), 1490 cm⁻¹ (both PyL and PyB) and 1620 and 1450 cm⁻¹ (PyL). (Maache et al. 1993, Bludau et al. 1998)

2.2 Abatement of NOX by other reductants

Other reducing components besides HC, such as CO, urea, and ammonia can be used as reductants for the SCR reactions. Hydrogen is also being studied for the non-selective reduction of NOX. Small molecules present in the real exhaust gas composition, such as hydrogen and CO, have been studied as reductants over catalytic materials to understand the reaction mechanism. (Yokota et al. 1997, Burch & Scire 1994a) In real systems the hydrocarbon (fuel) or urea injections have been taken into consideration and some applications have been introduced. (e.g. Gabrielsson 2004)

Yokota et al. (1997) have studied the removal of NO with hydrogen in the presence of excess oxygen over Pt/mordenite catalysts. The NO conversion was reported to reach the efficiency of over 80% at low temperatures. They have also suggested that the rate determining step could be the same in NOX removal with hydrogen and propene in the
presence of excess O$_2$ over Pt-loaded catalysts. (Yokota et al. 1997) Burch & Scire (1994a) have examined PGM- and Cu-loaded as well as H-ZSM-5 zeolite catalysts in NO reduction by H$_2$ in the absence of O$_2$. They found out that the PGM-loaded catalysts are very active (complete NO conversions) at low temperatures and the activity order is as follows Pt > Rh > Co loaded ZSM-5. The conversions of NO were, however, lower over Cu- ($X_{NO}=90\%$) and H-ZSM-5 ($X_{NO}=25\%$) catalysts. (Burch & Scire 1994a)

Carbon monoxide is one of the main components present in exhaust gas, and one of the most important reactions is the NO reduction by CO (Pârvulescu et al. 1998). CO adsorption has been studied and the CO-SCR experiments have been carried out over the Pd-loaded TWC and metal substrated zeolite catalysts (Paper V, Keiski et al. 1995, Kolli et al. 2005).

Both urea and ammonia can be used as reductants in large scale applications like lorries and busses (Dieselnet_USA 2004, Gabrielsson 2004). The urea or ammonia addition needs an extra container and, when utilising urea, refuelling has to be provided by gasoline stations, for instance. The urea-assisted SCR over zeolites has not been reported widely. Sjövall et al. (2006), Xu et al. (2002) and Sullivan et al. (1995) have reported the performance and activity of Cu-loaded zeolite catalysts for ammonia and urea-SCR reactions. In a zeolite catalyst, the large surface area provides a good ammonia storage capacity. In our studies, the H-, Cu-, and Fe-zeolite-based catalysts were studied in the ammonia-SCR of NO$_X$ with excess oxygen. The results indicate that the best NO$_X$ conversions were achieved over the Fe-loaded Beta and ZSM-5 as well as Cu-loaded Ferrierite and Mordenite catalysts. (Rahkamaa-Tolonen et al. 2005)
3 Catalyst materials

Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were studied in NO abatement in lean conditions by propene. The zeolite catalysts were powders and the Pt loading was 1 wt-% in the zeolite catalysts, except for Ferrierite (0.8 wt-% Pt). Platinum was inserted into the zeolite material by the wet impregnation procedure (Keiski et al. 1996).

A palladium-loaded Al₂O₃-based catalyst was also studied in the reduction of NO by CO and propene. Pd-loading was 1 and 3 wt-% on the Al₂O₃-based support. The porous catalytic material was mounted on a thin (50 µm) flat metal foil.

3.1 Zeolite catalysts

3.1.1 General

In 1756, Swedish mineralogist and nobleman, baron Axel Cronstedt (1722-1765), heated an unknown mineral and observed water boiling out. He named the new mineral zeolite from the Greek words: “zeo” and “lithos” meaning boiling stone. (UMIST 2004, Guisnet & Gilson 2002)

Zeolites are inorganic porous aluminosilicate materials with the general formula of MₓO·Al₂O₃·ySiO₂ and having a highly regular structure of pores and cavities. Zeolites have a three-dimensional, microporous and crystalline structure and they are a composition of aluminium, silicon and oxygen. Some other alkaline and transition elements can also be found in the zeolitic structures. Today, numerous natural zeolite materials have been found and more synthetic zeolites are prepared continuously in several research laboratories and institutes. (Zeolyst International 1999)

The structures of ZSM-5 (010), Beta (100), Y (111), and Ferrierite (001) zeolites are presented in Figure 3. Zeolites have a wide range of channels and ring openings. With the studied zeolites the main channel openings are as follows: ZSM-5 (5.6 x 5.3 Å), Beta (6.6 x 6.7 Å), zeolite Y (7.4 x 7.4 Å), and Ferrierite (4.2 x 5.4 Å). (Baerlocher & McCusker 2000, Armaroli et al. 2001)
ZSM-5 has been studied widely as a catalytic material in several different processes (e.g. xylene isomerisation) and its structural characters are well defined, having a two-dimensional structure with 10-ring intersecting channels (Armaroli et al. 2001). Zeolite Beta has a 12-membered ring and it has been used in the refining and petroleum industry (Ho et al. 1998). Zeolite Y has been used for several decades as a catalyst for hydrocarbon reactions (isomerisation, cracking), especially zeolite Y exchanged with rare earth metals (Ribeiro 1984). Ferrierite is found to be an interesting catalyst for the isomerisation of linear butenes. Ferrierite contains 10-, 8-, 6- and 5-membered rings in the structure. (Bordiga et al. 2000, Armaroli et al. 2001)

3.1.2 Pt/zeolite catalyst preparation

The materials studied were powders of parent and Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolite powders. The SiO$_2$/Al$_2$O$_3$ ratios of zeolites were 29, 150, 80, and 20, respectively. Pt-loaded zeolite catalysts were prepared by an aqueous impregnation procedure. The parent H-from zeolites (zeolite Y as NH$_4$-form) were mixed with a Pt tetraammine solution and stirred for 10 minutes at 25°C. The zeolite/water mixture was centrifuged and the Pt-zeolite was dried at 100°C overnight. After drying, the Pt-zeolites were calcined in air at 550°C for 1 hour. The Pt loading was verified by atomic absorption spectroscopy (AAS) analysis. The platinum loadings of the catalysts were 1 wt-% for ZSM-5, Beta, and Y zeolite catalyst, and 0.8 wt-% for Ferrierite. The desired 1 wt-% Pt loading of Ferrierite was not attained due to the preparation method used. The calculated ion-exchange ratios of the Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were 9, 47, 25, and 5%, respectively.
3.2 Alumina-based materials

3.2.1 General

Precious metal-loaded Al₂O₃ has been studied widely in automotive exhaust gas catalysis. Aluminium oxide (alumina)-based catalysts have been found to be effective in the reduction of NOₓ in three-way catalytic converters. Alumina is in the form of γ-Al₂O₃ in catalytic support in most cases, because γ-Al₂O₃ has been found to be one of the most active porous single oxides and to omit a high surface area. (Shimizu et al. 1999) The Al₂O₃ catalysts can also contain other oxides besides alumina, such as Ce, Zr, La, and Ba oxides, which are used in the catalyst structure as stabilisers and oxygen storage materials. (Kolli et al. 2005, Paper IV, Paper V)

3.2.2 Pd/Al₂O₃ catalyst preparation

Al₂O₃-based Pd-loaded catalysts provided by Ecocat Oy were also investigated. Besides Al₂O₃, the support material also contained La₂O₃ and CeₓZr₁₋ₓO₂. The porous catalyst material was mounted on a thin (~50 µm) flat metal foil, providing a metallic monolith structure. Palladium was added to the washcoat as an active metal. The palladium loading was 1 and 3 wt-% on the Al₂O₃-based support.
4 Experimental

4.1 Catalyst characterisation

The specific surface areas (based on Brunauer-Teller-Emmett-theory, BET), pore sizes, and pore volumes (based on Barrett, Joyner and Halenda-theory, BJH) were measured by N$_2$ adsorption at -196°C. The samples were pre-treated with a heating rate of 10°C min$^{-1}$ in vacuum, followed by evacuation at 90°C for 30 minutes. Samples were then heated (10°C min$^{-1}$) to 350°C in vacuum and evacuated at 350°C for 3 hours and cooled to room temperature. Next the chamber was filled with gaseous nitrogen. Before starting the experimental procedure, evacuation was performed for 30 minutes at room temperature to remove gaseous N$_2$. The specific surface area was calculated from the linear part of the adsorption isotherm. The pore characteristics were determined by the t-plot. Dispersions of platinum over zeolite supports were detected by a CO chemisorption procedure. Experiments were carried out by ASAP 2020 from Micromeritics.

The composition and particle morphology of the Pt-loaded zeolite catalysts have been studied by an Energy-Filtered Transmission Electron Microscopy (EFTEM) Leo 912 Omega equipped with the Energy Dispersive Spectrometer (EDS) detector (Isis). The sample was diluted in ethanol and stirred. A drop of the mixture was placed on the Cu-gauze. The sample was then inserted in a high vacuum chamber. The TEM images were taken with a magnification of 100 000 and the EDS diagram was measured from the presented area. TEM and EDS were done with the resources of the Institute of Electron Optics at the University of Oulu.

4.2 Fourier Transform Infrared Spectroscopy

In this study the FTIR (Fourier Transform Infrared) technique was utilised for obtaining more information about the surface species as well as the reaction products, and to further extend the knowledge of catalysts activities, adsorption capacities and the formation of surface intermediates. The FTIR technique has been used in two different ways, gaseous
FTIR measurements as well as measurements of surface adsorbates and intermediates by the DRIFT method.

The FTIR spectroscopy is a rather old characterisation method, but its use as a tool for characterisation has increased with the development of computer techniques and software. One of the inventors was A. A. Michelson, who developed the interferometer. The FTIR spectrometer consists generally of four pieces: an interferometer, an IR-source, a detector, and optical mirrors.

DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy is one of the FTIR application methods. In the method the IR beam is impinged on the surface of a material and the beam partially reflects and transmits.

Infrared spectroscopy is based on the measurement of the vibration of molecules. When IR radiation is passed through a sample of a gaseous molecule, the molecules absorb certain wavelengths, and these can be measured. The radiation gives energy to the molecules and the molecules start to vibrate or rotate. The different vibrations, rotations and their combinations absorb specific wavelengths of the IR radiation. The modes of the vibration are symmetric and asymmetric stretching and bending as well as rotation. (TEMET 2000)

The FTIR spectroscopy has been found to be quite a powerful technique to detect the gaseous components as well as adsorbed surface species. Another advantage of the FTIR technique is its good accuracy. (Benítez et al. 1994)

### 4.2.1 Activity measurements

In the activity experiments the powder-like zeolite catalyst samples (0.1 g) mixed with quartz sand were packed in a tubular quartz reactor (i.d. 9 mm). Quartz sand was used to keep the gas hourly space velocity (GHSV) constant (around 26 500 h⁻¹) because of the different weight by volume of the samples. The schematic figure of the catalysts packing is presented in Figure 4.

![Fig. 4. Schematic figure of packaging the catalyst samples into the tubular reactor.](image)

The catalysts were heated to 500°C under N₂ flow to clean the catalysts’ surface. After that the catalysts were pre-oxidised by 5% O₂/He at 500°C for 20 minutes and cooled to room temperature under 5% O₂/He flow. The reaction gas mixture (NO 1000 ppm, C₃H₆...
1000 ppm, O₂ variable, N₂ as carrier gas) was inserted into the reactor with a flow rate of 1000 cm³ min⁻¹. The experiments were carried out as light-off experiments from room temperature to 550°C with a heating rate of 10°C min⁻¹. The temperature was measured inside the catalyst bed. The reaction gas mixtures in the kinetic experiments are presented in Table 3.

Table 3. Experimental conditions in activity measurement over the 1 wt-% Pt/zeolite catalysts.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>NO [ppm]</th>
<th>C₃H₆ [ppm]</th>
<th>O₂ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>800</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1200</td>
<td>1200</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>1200</td>
<td>800</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>1200</td>
<td>5</td>
</tr>
</tbody>
</table>

In the case of Al₂O₃-based catalysts, the monolith catalyst (500 cpsi) was pre-treated by heating the catalyst to 500°C in a nitrogen flow and after that the catalyst was oxidised at 500°C for 20 minutes. After cooling the reactor to room temperature under oxidising conditions the reaction chamber was purged with N₂. The reaction gases were inserted into the reactor at 25°C and the reactor was heated to 500°C at a rate of 10°C min⁻¹. The inlet gases used in the experiments were 10% NO/N₂, 5% C₃H₆/N₂, N₂ (99.5%) and dried air (~21% O₂/N₂). The total flow rate of the reaction mixture (NO 5000 ppm, C₃H₆ and O₂ variable, N₂ as carrier gas) was 1000 cm³ min⁻¹. During the NO+CO experiments (Paper V) the inlet gas concentrations were 4000 ppm CO, and 3600 ppm NO in reducing and 4400 ppm NO in oxidizing atmospheres. In some experiments part of NO was replaced with O₂ to set the inlet gas stream to 2000 ppm NO, and 800 ppm O₂ in reducing and 1200 ppm O₂ in oxidizing atmospheres. The heating rate of the catalysts was 20°C min⁻¹.

The outlet gas composition was analysed by Gasmet™ FTIR. The laboratory apparatus consisted of a quartz tube reactor inside an electrically heated furnace, mass flow controllers (Brooks 5850TR), and magnetic valves for flow selection and insertion. The mass flow controllers and magnetic valves were regulated by a PC via a LabView program. The FTIR spectra were recorded for the following components: NO, NO₂, N₂O, NH₃, CH₄, C₃H₆, CO, CO₂, and H₂O. In the case of oxygen measurements the analysis of O₂ was done by a paramagnetic oxygen analyser (ABB Advance Optima). The schematic of the experimental setup for the activity studies is presented in Figure 5.
4.2.2 Surface intermediates studies (DRIFT)

The surface adsorption and intermediates formation over the parent and Pt-loaded zeolite as well as the Pd/Al₂O₃-based catalysts were studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy technique (DRIFTS). The schematic figure of the experimental setup is presented in Figure 6.

In situ DRIFTS studies were carried out by a Perkin Elmer 1760X with a heated reaction chamber (Environmental Chamber, Specac 19930). Catalyst samples were heated under vacuum to 400°C before oxidation by 5% O₂/Ar at 400°C and then cooled down to room temperature under an oxidizing atmosphere. The vibrations of adsorbed surface components were detected in the range of 4000–800 cm⁻¹ at a resolution of 4 cm⁻¹. Measurements of propene adsorption in the presence or absence of oxygen and/or nitric oxide were carried out under a continuous flow.

In the experiments over the zeolite catalysts each spectrum contained 50 scans (in the case of Y zeolite 100 scans). The spectra were measured at 8 different constant temperatures between 25 and 400°C. The heating rate between measurements was 10°C min⁻¹. The reaction gas mixture contained 1000 ppm NO + 1000 ppm C₃H₆, 1000 ppm C₃H₆ + 5% O₂ or 1000 ppm C₃H₆, all balanced by argon. The total flow of the gas mixture was 150 cm³ min⁻¹ in each experiment.
In the case of the Pd/Al₂O₃-based catalysts the inlet gas mixture contained NO from 5.7 to 8.2% depending on the desired stoichiometric value during the DRIFT measurements. The NO gas flow rate was kept constant (10 cm³/min⁻¹). The spectra were measured at 25, 220, and 260°C at a resolution of 4 cm⁻¹ by accumulating 20 scans.

In the experiments of NO reduction by CO the inlet gas mixture contained 4000 ppm CO and 3600 ppm of NO (reducing conditions) or 4400 ppm of NO (oxidizing conditions). Experiments using O₂ were also done by replacing part of NO with O₂ as described in Chapter 4.2.1.

### 4.2.3 Acidity measurements

The acidity of the zeolitic materials is found to be one of the most important characters for catalytic performance. The acidic properties of the catalytic materials were studied by pyridine adsorption. Measurements were done with the DRIFT equipment [Perkin Elmer 1760X with a heated reaction chamber (Environmental Chamber, Specac 19930)]. The catalyst samples were heated to 400°C in vacuum with a heating rate of 10°C min⁻¹ and evacuated at 400°C for 60 minutes. After that the sample was cooled to 150°C and the background spectrum was measured. Pyridine was adsorbed on the catalyst surface at 150°C with bubbling argon gas through pyridine at room temperature for 4 minutes. The first spectrum was measured immediately after the bubbling. The sample was evacuated for 30 minutes at 150°C and the second spectrum was measured. The temperature was then raised to 250°C and the sample was evacuated for 60 minutes and cooled to 150°C for the spectrum measurement. The fourth spectrum was measured after the evacuation of the sample at 350°C for 60 minutes and cooling to 150°C. The resolution was 2 cm⁻¹ and
all the spectra contained 200 scans. The adsorption of pyridine was not done with the parent and 0.8 wt-% Pt-loaded Ferrierite zeolite catalysts.

4.3 Adsorption studies

The temperature-programmed desorption (TPD) technique can provide useful information on solid surfaces, interactions of the surface and adsorbed gas molecules, as well as the thermal stability of surface desorption states. The strength of the bonds between the adsorbed molecule and the surface can be determined by the temperature at which the maximum desorption was determined. (Falconer & Schwarz 1983, Lassi 2003)

A photograph of the experimental set-up for the TPD measurements is presented in Figure 7. The test equipment consisted of a furnace with a chamber of two quartz tubes inside. The sample (45 mg) was set into the inner tube (i.d. 0.8 cm) between the quartz wool seals. The analysis was done by an on-line mass spectrometer (Carlo Erba QTMD). The adsorption gases used were 5% NO/Ar (gas mixture), O₂ (99.998%), and C₃H₆ (99.95%). Helium (99.9996%) was used as a balancing gas.

Fig. 7. Photograph of the TPD experimental set-up.

In the pre-treatment stage, the sample was heated at a linear heating rate (20°C min⁻¹) under vacuum from room temperature to 450°C, followed by evacuation for 20 minutes at 450°C. The sample was oxidised (10% O₂/He) at 450°C for 10 minutes and then cooled to room temperature under a flow of 10% O₂/He, and then purged by a He flow (60 cm³/min⁻¹) for 15 minutes. After the He purge the mixture of adsorption gases was inserted for 10 minutes into the reaction chamber at room temperature. The adsorption gas contained 5% NO/Ar, 5% C₃H₆/He, or (5% C₃H₆ + 5% O₂)/He gas mixtures. The TPD measurements were carried out under vacuum from room temperature to 750°C with a heating rate of 20°C min⁻¹. The masses 16 (O), 18 (H₂O), 28 (CO, N₂), 30 (NO), 32 (O₂), 42 (C₃H₆), 44 (CO₂, N₂O), 46 (NO₂) were recorded.
5 Experimental Results

5.1 Catalyst characterisation

The measured specific surface areas ($S_{\text{BET}}$, $N_2$ adsorption), internal surface areas, pore sizes and volumes of parent and Pt-loaded zeolites as well as the Pt dispersions of Pt-loaded zeolite catalysts are summarised in Table 4. The measured values are in agreement with the literature values (e.g. Kinger & Vinek 2001). With the Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolite samples the $S_{\text{BET}}$ values were measured to be 364, 488, 524, and 295 m$^2$g$^{-1}$, respectively. The accuracy of the total surface area values was ±3%. The internal surface areas have been determined by the t-test method. The Pt loading increased the $S_{\text{BET}}$ value of ZSM-5 and Ferrierite, but reduced that of Beta and Y. (Papers I and II) The average pore volumes of the parent zeolites were 0.13 cm$^3$g$^{-1}$ (ZSM-5), 0.20 cm$^3$g$^{-1}$ (Beta), 0.21 cm$^3$g$^{-1}$ (Y), and 0.17 cm$^3$g$^{-1}$ (Fer). The pore volumes were observed to increase with the platinum loading. The platinum dispersion of the Pt-loaded zeolite catalysts was measured to be around 12%. However, the Pt dispersion of the 0.8 wt-% Pt/Ferrierite was detected to be over 33%.

For the Al$_2$O$_3$, La$_2$O$_3$ and Ce$_x$Zr$_{1-x}$O$_2$-containing Pd-based catalyst the surface area was measured to be around 40 m$^2$g$^{-1}$. The palladium loadings were 1 or 3 wt-% (Paper IV). The average pore sizes of the alumina-based support and the palladium dispersion were not determined.
Table 4. Measured specific surface areas, average pore sizes, pore volumes, and platinum dispersions of the ZSM-5, Beta, Y, and Ferrierite zeolite-based catalysts studied.

<table>
<thead>
<tr>
<th>Pt loading</th>
<th>Total surface area (BET) [m²g⁻¹]</th>
<th>Internal surface area [m²g⁻¹]</th>
<th>Pore size [nm]</th>
<th>Pore volume [cm³g⁻¹]</th>
<th>Pt dispersion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>-</td>
<td>347</td>
<td>224</td>
<td>2.62</td>
<td>0.13</td>
</tr>
<tr>
<td>Beta</td>
<td>-</td>
<td>527</td>
<td>296</td>
<td>6.54</td>
<td>0.20</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>608</td>
<td>482</td>
<td>3.08</td>
<td>0.21</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>-</td>
<td>282</td>
<td>235</td>
<td>3.58</td>
<td>0.17</td>
</tr>
<tr>
<td>Pt/ZSM-5</td>
<td>1.0</td>
<td>364</td>
<td>221</td>
<td>2.83</td>
<td>0.25</td>
</tr>
<tr>
<td>Pt/Beta</td>
<td>1.0</td>
<td>488</td>
<td>274</td>
<td>3.72</td>
<td>0.47</td>
</tr>
<tr>
<td>Pt/Y</td>
<td>1.0</td>
<td>524</td>
<td>291</td>
<td>3.72</td>
<td>0.47</td>
</tr>
<tr>
<td>Pt/Ferrierite</td>
<td>0.8</td>
<td>295</td>
<td>247</td>
<td>2.74</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Figure 8 shows the N₂ physisorption isotherms of the Pt-loaded zeolite catalysts. In the case of the parent zeolites, unique shapes of isotherms were measured. As can be seen, all the studied zeolite materials have the shape of the isotherm of type I. The type I isotherm is reported to be typical for materials that have a microporous structure. (Gregg & Sing 1982, Webb & Orr 1997, Intriago et al. 2006)

The isotherms in Fig. 8 are used, after certain approximations (e.g. pore shape, tortuosity), for the calculations of the numerical values presented in Table 4. The pores may, however, have different structures and they can also be interconnected with one another. (Webb & Orr 1997)
In Figure 9 the EFTEM images of Pt-loaded ZSM-5, Pt-Beta, Pt-Y, and Pt-Ferrierite zeolite catalysts are presented. All images (a-d) are on the same scale (magnification of 100 000). The Pt clusters are found to be of the size of 5-10 nm. In the case of Pt/ZSM-5 some of the Pt clusters are also found to be much bigger than 10 nm. The EFTEM images indicate that the smallest platinum particles are in Pt-loaded Beta zeolite samples. The TEM images ensure that very large extra framework Pt particles can also be found besides platinum in the pores of the zeolite framework.

Fig. 9. TEM images of the Pt clusters on the a) ZSM-5, b) Beta, c) Y, and d) Ferrierite zeolite surfaces, respectively. Black particles indicate the Pt clusters and the dark grey form are due to the zeolite support. Magnification: ×100 000.

Figure 10 presents an example of the EDS spectra from the 1 wt-% Pt-loaded ZSM-5 zeolite. The Cu bands are due to the Cu-gauze of the sample holder. The spectra are taken from the area as presented in Figure 9a. The bands from platinum can be detected with all the studied catalysts, which indicates that the black particles are Pt clusters.

Fig. 10. Example of the EDS spectra (1 wt-% Pt-loaded ZSM-5 zeolite catalyst).
5.2 Activity studies

The activity of a catalyst is one of its most important characteristics. Effectiveness in reducing nitrogen-containing compounds (NOX) and to oxidise unburned hydrocarbons as well as CO simultaneously is crucial in designing catalysts to meet stringent emission standards at low temperatures and in lean conditions.

In the laboratory tests the reactor outlet gas composition was measured to contain mainly nitrous oxide, nitrogen dioxide, carbon monoxide, carbon dioxide and water, in addition to the inlet reaction gases.

5.2.1 Conversions of reactants over Pt/zeolites

The conversions of NO and propene in the reaction gas mixture of NO+C3H6 balanced by nitrogen over Pt-loaded zeolite catalysts are presented in Figure 11. The conversions of NO and propene can be observed to be at their maximum at over 300°C. NO conversion is detected to be the highest with 0.8 wt-% Pt/Ferrierite zeolite, achieving conversion of over 99%, while the conversion of NO over the other studied catalysts can be detected to be around 50%. The light-off temperature of the NO reduction is lowest over the 1 wt-% Pt/Y (T_{50} = 339°C) after which comes 0.8 wt-% Pt/Ferrierite (345°C) followed by 1 wt-% Pt/ZSM-5 (565°C). Over the 1 wt-% Pt/Beta the conversion of NO did not reach the 50% value. At low temperatures hydrocarbons are adsorbed on the surface and at around 100°C desorption can be observed (negative conversions). This phenomenon is later testified by TPD measurements (Figures in Section 5.4).

In the NO+C3H6 mixture, propene is oxidised only by oxygen formed from nitric oxide. The light-off temperature of propene can be detected to be lowest over the Pt/ZSM-5 catalyst, which is the only one having the conversion of propene higher than 50%. The rather high conversions with Pt-loaded ZSM-5 and Ferrierite zeolites below 100°C are due to the adsorption of propene on the catalyst’s surface.
Fig. 11. a) NO and b) C\textsubscript{3}H\textsubscript{6} conversions and light-off temperatures of Pt-loaded zeolites with a reaction gas mixture of 1000 ppm NO, 1000 ppm propene, balanced by N\textsubscript{2}.
Fig. 12. a) NO and b) C₃H₆ conversions and light-off temperatures of Pt-loaded zeolites with a reaction gas mixture of 1000 ppm NO, 1000 ppm propene, and 5% oxygen balanced by N₂ (Paper II).
Conversions of NO and C\textsubscript{3}H\textsubscript{6}, and the maximum NO conversion reached, as well as the light-off temperatures of propene over the Pt-loaded zeolite catalysts in lean conditions (excess oxygen), are shown in Figure 12 (Paper II). The negative conversions are explained by desorption phenomenon as in the experiments without O\textsubscript{2} (Figure 11).

As reported (Paper II), NO conversions were observed to increase as a function of temperature up to 220-270\degree C. Over the 1 wt-% Pt/ZSM-5 and 0.8 wt-% Pt/Ferrierite catalysts the conversion of NO did not exceed 50%, while the highest conversions were observed over the 1 wt-% Pt-loaded Beta and Pt/Y zeolites. The maximum conversion of NO\textsubscript{x} was almost 70% over Pt-Beta and 60% over Pt/Y. NO conversions started to increase at above 150\degree C over all the catalysts except Pt/ZSM-5, over which the reaction was initiated at 250\degree C. The maximum NO conversions were measured just above the temperature at which propene had reached conversion of higher than 99%. NO conversion remained quite stable in a wide temperature window and also at temperatures above 350\degree C over the 1 wt-% Pt/ZSM-5 catalyst. The maximum conversions of NO over the 1 wt-% Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolites were achieved at 267, 245, 232, and 262\degree C, respectively. At temperatures higher than the temperature where the maximum NO conversion was reached, the observed conversion values started to decrease rapidly. This can be explained by the oxidation reaction of propene that is favoured over O\textsubscript{2} compared to NO (Peréz-Ramírez et al. 2001, Fritz & Pitchon 1997). NO conversions in the absence and presence of excess (5\%) oxygen are summarised in Figure 13.

![Figure 13](image-url)

**Fig. 13.** NO conversions in the absence and presence of excess oxygen over the Pt-loaded catalysts.
Propene is observed to reach the 50% conversion over all the studied Pt-loaded catalysts at temperatures from 200 to 253°C. High conversions of propene at low temperatures (below 100ºC) are caused by propene adsorption on the catalyst surface. The lowest light-off temperature \((T_{50})\) of propene (198ºC) can be measured over the Pt/Y zeolite catalyst. The light-off temperatures of Pt-loaded catalysts increased in the following order: Pt/Y ≤ Pt/Beta < Pt/Ferrierite < Pt/ZSM-5. The propene conversion above the light-off temperature was higher than 99% over all the studied catalysts. In the case of the parent zeolite materials propene also reached conversions of >99% at temperatures above 450°C, and the light-off temperatures of propene over the parent ZSM-5, Beta, Y, and Ferrierite zeolites were 413, 401, 421, and 391ºC, respectively. When comparing these \(T_{50}\) values to the values of Pt-loaded zeolites, the numerical values of the light-off temperature can be observed to rise in the order: Pt/Y ≤ Pt/Beta < Pt/Ferrierite < Pt/ZSM-5. Platinum loading can be detected to have the lowest effect in the case of ZSM-5 and Ferrierite-based zeolites, but it has the most significant effect on the reduction of light-off temperature over Y- and Beta-based zeolite catalysts. The smaller average pore size of Ferrierite and ZSM-5 zeolites can possibly be one reason for the smaller decrease in the light-off temperature over the Pt-exchanged Ferrierite and ZSM-5 (e.g. pore blocking, availability of active sites). The comparison of the light-off temperatures between Pt-loaded and parent zeolites is presented in Figure 14.

Fig. 14. Comparison of the light-off temperatures of propene over the parent and Pt-loaded zeolite catalysts (1000 ppm NO, 1000 ppm C\(_3\)H\(_6\), 5% O\(_2\)).

In Figure 15 (Paper III) the maximum in NO conversion was measured over ZSM-5 at 477°C \((X_{NO} = 8\%)\) and over Pt/ZSM-5 at 263°C \((X_{NO} = 32\%).\) The Pt loading can be concluded to significantly increase the conversion of NO even at low temperatures. The presence of platinum was also detected to decrease the light-off temperature of propene from 400°C to 240°C.
5.2.2 Reaction products formation over Pt/zeolites

The formations of desired products (CO$_2$, H$_2$O) as well as by-products (CO, N$_2$O, NO$_2$) during the activity experiments were detected. The formation of molecular nitrogen cannot be measured because a homonuclear diatomic species does not have an infrared adsorption band, and therefore the detection of these compounds is impossible by the FTIR technique. The maximum concentrations of the by-products formed are collected in Table 5.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO</th>
<th>N$_2$O</th>
<th>NO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c$_i$ [ppm] at T [°C]</td>
<td>c$_i$ [ppm] at T [°C]</td>
<td>c$_i$ [ppm] at T [°C]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>1080 420</td>
<td>8 –310</td>
<td>110 410</td>
</tr>
<tr>
<td>Beta</td>
<td>1560 463</td>
<td>7 –460</td>
<td>137 445</td>
</tr>
<tr>
<td>Y</td>
<td>1730 484</td>
<td>11 –530</td>
<td>107 467</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>1490 528</td>
<td>9 513</td>
<td>103 504</td>
</tr>
<tr>
<td>Pt/ZSM-5</td>
<td>115 253</td>
<td>150 275</td>
<td>207 371</td>
</tr>
<tr>
<td>Pt/Beta</td>
<td>33 214</td>
<td>156 244</td>
<td>412 280</td>
</tr>
<tr>
<td>Pt/Y</td>
<td>48 202</td>
<td>124 210</td>
<td>410 255</td>
</tr>
<tr>
<td>Pt/Ferrierite</td>
<td>43 210</td>
<td>108 243</td>
<td>228 320</td>
</tr>
</tbody>
</table>
The formation of CO$_2$ from propene was detected to be at the maxima at the light-off temperature of each catalyst. The 1 wt-% Pt/ZSM-5 zeolite seems to produce CO$_2$ just above the light-off temperature, which is most probably caused by the oxidation of adsorbed C$_3$H$_6$ species on the catalyst surface. The strongest adsorption of propene at temperatures below 70ºC was detected over the Pt/ZSM-5 catalyst. With the other samples studied, the oxidation of the carbon-containing surface species to CO$_2$ was not detected to be as strong, while more CO$_2$, than can be formed from propene was measured with all the catalysts after the light-off temperature was reached. The results correlate well with the results of Furusawa et al. (2002).

Generally only small amounts of partially oxidised hydrocarbons, mainly CO, as well as nitrogen oxides (NO$_2$ and N$_2$O) were formed around the light-off temperature of propene over all the Pt-loaded catalysts.

Carbon monoxide (CO) formation was detected with all the samples studied. With Pt-loaded samples the formation was below 50 ppm at the maximum, except with 1 wt-% Pt/ZSM-5 zeolite catalyst with which the formation was detected to be around 115 ppm. The maximum concentration can be measured at the light-off temperature of propene over all the catalysts. Over the parent zeolite samples the formation of CO was measured to be more than 30 times higher. The temperatures at which the maximum formation occurs were also much higher, being above 400ºC. The CO concentration on the parent zeolites were detected to be between 1080 ppm (ZSM-5) at temperatures around 420ºC and 1730 ppm at 484ºC (zeolite Y). On the platinum-loaded zeolites the concentration of CO decreased rapidly at the light-off temperature. (Paper III) In the complex oxidation of propene over the catalysts studied CO is formed as an intermediate (Table 5). Over the parent zeolites the oxidation of CO to CO$_2$ is probably very slow and adsorbed CO is desorbed causing an increase in the CO emissions (Petersson et al. 2005). In the presence of Pt the oxidation of CO to CO$_2$ is much faster and desorption of CO is thus reduced.

Nitrogen dioxide is observed to be formed at temperatures above the light-off temperature having maxima of 107 ppm (at 467ºC) over the Y zeolite and 412 ppm (at 280ºC) over the 1 wt-% Pt-Beta. Over the 1 wt-% loaded Beta and Y zeolites the formation of NO$_2$ are measured to be over 410 ppm, while in the case of the Pt-loaded ZSM-5 and Ferrierite the formation can be detected to be around 200 ppm. Over the parent zeolites the formation remained below 150 ppm. NO$_2$ formation is observed to decrease at temperatures above 300ºC because of the equilibrium limitation.

The formation of nitrous oxide over parent ZSM-5, Beta, Y and Ferrierite was detected to be below 10 ppm. Over the 1 wt-% Pt-loaded zeolite catalysts the maxima are measured at around the light-off temperatures, being 108 ppm, at the lowest, over Pt-Ferrierite and the highest (156 ppm) over the 1 wt-% Pt/Beta. Nitrous oxide formation can be measured at around the light-off temperature of propene over all Pt-loaded catalysts. The formation decreased rapidly at the light-off temperature and remained below the 5 ppm level.

Platinum loading can be observed to have a positive impact on the efficiency of a catalyst in oxidising hydrocarbons. The formation of CO is measured to be less than 10 per cent of the formation with the parent zeolites. The detected phenomenon can be concluded to be evidence of the hydrocarbon cracking due to the influence of platinum particles and furthermore the hydrocarbon species (CH$_x$) formed can react much more efficiently with the surface oxygen or NO species.
On the other hand, NO$_2$ formation rises to twofold in magnitude with all the Pt-loaded catalysts studied compared to the parent (H-ZSM-5, H-Beta, NH$_4$-Y and H-Ferrierite) zeolites. According to the literature, the first step in the reduction of NO in the presence of O$_2$ over the parent zeolites (Y, ZSM-5) is the oxidation of NO into NO$_2$ (e.g. Amiridis et al. 1996, Schmieg et al. 2004). This can also be seen from our results (Table 5). The presence of Pt increases the oxidation of NO considerably. Platinum can also be concluded to have an effect on O$_2$ and NO dissociation. More rapid oxidation of NO and propene can be observed over zeolites with a platinum loading.

5.2.3 Reaction products formation over Pd/Al$_2$O$_3$

The conversion of NO over the Pd/Al$_2$O$_3$-based catalyst reached over 99% in rich and stoichiometric conditions, while in lean conditions (excess oxygen or NO present) conversions up to 80% were obtained in the activity experiments. The high NO$_x$ conversion in lean exhaust gas conditions can be explained by the inlet mixture, when NO is the only oxidant. Therefore C$_3$H$_6$ reacts totally with NO in the absence of oxygen. In real exhaust gas the O$_2$/NO ratio is, however, much more than 1.0 (Paper V).

The formation of harmful by-products like ammonia (NH$_3$), carbon monoxide (CO), and nitrous oxide (N$_2$O) is not desired and therefore the amount of these compounds after the catalyst should be as low as possible. According to our experiments (Figure 16) those components were formed but the measured amounts of CO and NH$_3$ are rather small (65-120 ppm CO, 30-60 ppm NH$_3$) except in rich concentrations (1100 ppm CO, 1700 ppm NH$_3$). The formation of NH$_3$ and CO started at 200°C and the maxima were observed at the light-off temperature (~250°C). These by-products were due to incomplete oxidation of hydrocarbons. NH$_3$ is formed in reactions between hydrocarbons and nitrogen oxides. It is also possible that on γ-Al$_2$O$_3$ surface intermediates like Al-NCO and H-NCO are converted to NH$_3$ and CO$_2$. (Radtke et al. 1997, Cowan et al. 1998)

The formation of N$_2$O was observed to start at 200°C and the formation reached the maximum at around 300°C. The formation of N$_2$O was significantly smaller in rich than in lean or stoichiometric conditions. Nitrous oxide was expected to be formed in reactions between cyanides or isocyanates and nitrates or nitrites at the surface. NO can react with surface nitrogen atoms to N$_2$O. N$_2$O formation can also take place via isocyanate complexes and NO or NO$_2$. The amount of N$_2$O formation was the highest in lean conditions and it could be detected in all experiments.

The total oxidation of propene seemed to be quite effective as no evidence of lighter hydrocarbons was detected. It is possible that in rich conditions, self-poisoning of the catalyst may also occur and therefore the reduction of NO is lower than in stoichiometric conditions. (Macleod 2001)
Fig. 16. An example of the concentrations of reactants and products as a function of temperature in lean conditions, 5000 ppm NO, 400 ppm C₃H₆, over 1% Pd/Al₂O₃. The N₂ concentration is a calculated value. (Paper V)

5.3 DRIFT studies

5.3.1 Pt/zeolite catalysts

The DRIFT spectra of the NO+C₃H₆+O₂ reaction gas mixture over the Pt-loaded ZSM-5 zeolite catalyst is presented in Figure 17. The analyses of the DRIFT spectra were based on the assessment of the obtained experimental bands with the observations reported in the literature by other researchers.
The surface species were assigned to CH_x species, nitrates and nitrites, carbonates, organic nitro compounds and partially oxidised hydrocarbons such as acetates and formates as well as carbon monoxide (Gerlach et al. 1999a, Xin et al. 1997a & 1997b, Papers I-III).

Over the parent as well as 1 wt-% Pt-loaded ZSM-5, Beta and Ferrierite zeolites adsorbed propene and fragmented C_xH_y species were assigned at 3200-2900 cm^{-1}. Adsorption of propene over the parent and Pt-loaded Y zeolites was almost undetectable. A band observed at 1507 cm^{-1} was assigned to the C-H bending vibrations (Gerlach et al. 1999a) and a band at around 1650-1620 cm^{-1} to the C=C vibrations of propene (Radziszewski et al. 1996, Hoost et al. 1995a). Linearly bonded C_3H_6 can also be detected over ZSM-5 zeolite catalysts at 1470 cm^{-1}. This band was not detectable on other zeolite surfaces. The adsorption of propene can be detected to be more intensive over the Pt-loaded samples between temperatures from 100 to 250ºC. Propene was observed to adsorb on the Pt/Y zeolite at 25ºC, but no adsorption can be detected over the parent Y zeolite. It is proposed that propene is mainly adsorbed on the Pt-sites. This phenomenon can be assumed to be the same over all the Pt-loaded zeolite catalysts.

Formation and adsorption of CO can be detected at 1190 cm^{-1} over the parent and 1 wt-% Pt-loaded ZSM-5 zeolite catalysts. When increasing the temperature, the adsorption bands increased up to 250ºC. Above that temperature the adsorption bands decreased. The band detected at 1595 cm^{-1} was assigned to COO^- or CO_2^- of adsorbed acetates or formates (Xin et al. 1997a). This band was found to be much weaker with the reaction gas mixture of NO+C_3H_6+O_2 than with C_3H_6+O_2. The Pt loading had an effect on water formation over zeolite catalysts. Over all the Pt-loaded catalysts studied, except Pt/Y...
zeolite, a broad band due to adsorbed H₂O at the OH-region at 3500-3100 cm⁻¹ was observed. This can not be detected on the parent zeolite catalysts. (Papers I-II)

A broad band at around 1850 cm⁻¹ was assumed to be due to NO adsorption (Iojoiu et al. 2004). Nitrates and nitrites formed via the reaction between the adsorbed NO and surface oxygen species (O²⁻) caused multiple bands below 1900 cm⁻¹. Over the 1 wt-% Pt/ZSM-5 zeolite the band at 1696 cm⁻¹ due to adsorbed NO₂ was observed. The band at 1935 cm⁻¹ can be assigned to the adsorbed NO on the Pt-site based on the observations by Xin et al. (1997b). The broad band at around 1970-1920 cm⁻¹ and a band at 1820 cm⁻¹ were assumed to be due to NO and (NO)₂ species adsorbed on Pt and partially oxidised Pt sites. (Xin et al. 1997b, Tabata et al. 1998, Hadjiivanov et al. 1999, Paper II)

Comparising our data with the studies made by Gerlach et al. (1999a, 1999b) the bands detected at 1460 and 1414 cm⁻¹ were proposed to be caused by the propenal oxime intermediate formed in the reaction between NO and propene. Satsuma et al. (2003) have proposed the band at around 1450 cm⁻¹ on Pt/ZSM-5 to be due to the NH₄⁺ ion adsorbed on the Bronsted acid site. Organic nitro or nitrite species assigned such as C₃H₇-ONO, e.g. by Iojoiu et al. (2004), can be observed at 1662 cm⁻¹ on ZSM-5 and 1 wt-% Pt/ZSM-5.

Figure 18 shows the adsorption of propene with oxygen over the studied catalysts at 100°C. The adsorption of propene can be seen to be the most significant over the parent and 1 wt-% Pt/ZSM-5 as well as 1 wt-% Pt/Beta. The parent Beta and 0.8 wt-% Pt/Ferrierite zeolites showed a weaker adsorption of propene than the catalysts mentioned previously. Over the rest of the studied catalysts propene adsorption was determined to be almost negligible at 100°C.

The formation of intermediate species can be observed to be the strongest over the parent and Pt-loaded ZSM-5 zeolites, however, over the 1 wt-% Pt/Beta oxidised HC species such as carbonates can be detected at around 1530 cm⁻¹. (Hoost et al. 1995a)
5.3.2 Pd/Al₂O₃

Simultaneous adsorption of NO + C₃H₆ (+O₂), and NO + O₂ over the 1% Pd-catalyst at 260°C is presented in Figure 19. Formation of isocyanates can be seen at 2253-2233 cm⁻¹ when the gas mixture contains propene. This finding is in agreement with the studies reported in the literature (e.g. Bamwenda et al. 1995, Radtke et al. 1997). The amount of isocyanate species formed is small in stoichiometric conditions compared to fuel rich conditions.

The adsorption bands from partially oxidised hydrocarbons like formates (1393 and 1379 cm⁻¹) as well as acetates (1567 and 1463 cm⁻¹) are detected. These surface intermediate species are most probably interacting with aluminium (Ermini et al. 2000, Shimizu et al. 1998, Shimizu et al. 1999). In the fuel rich conditions strong adsorption bands caused by formates are found on the surface. The intensity of these bands decreases when the experiment is done in lean conditions. Formate species were observed to be more visible in the adsorption spectra when the reaction between NO and propene was done without the addition of oxygen (Figure 19).

In the beginning of the experiment the formation of nitrates and nitrites was strong in the region from 1300 to 1250 cm⁻¹. These bands disappeared in rich conditions at 260°C.
but at 260°C these bands can still be observed in lean and stoichiometric conditions. It seems quite evident that NO and oxygen react to nitrate species at the surface when the amount of reductant is very small or absent.

Hoost et al. (1995b) proposed that a band at around 1630 cm\(^{-1}\) is probably caused due to NO on palladium when the reaction gas contains propene as a reductant. In the NO + O\(_2\) reaction gas mixture, the bent NO band is also present. The observed band at 1658 cm\(^{-1}\) can be assigned to an organic nitrite compound (R-ONO) (Meunier et al. 1999, Tanaka et al. 1994). According to the literature linear NO adsorption, Pd-N=O (ca. 1750 cm\(^{-1}\)), on Pd over an oxidised catalyst is not evident. (Hoost et al. 1995a) Our experimental results are in agreement with the literature. In reducing conditions (NO + C\(_3\)H\(_6\)) it is probably adsorbed COO\(^-\) that causes the band observed at 1600 cm\(^{-1}\).

In rich reaction conditions the formation of ammonia and carbon monoxide was significant. It could be due to the reaction between isocyanates and cyanides and water to ammonia and CO or CO\(_2\).

![Fig. 19. The spectra of NO + C\(_3\)H\(_6\) reaction on 1 wt-% Pd/Al\(_2\)O\(_3\) catalysts at 260°C in fuel rich, stoichiometric, and lean conditions with excess O\(_2\) conditions. The NO+O\(_2\) spectrum is also shown. (Paper V)](image)

### 5.4 TPD studies

Temperature Programmed Desorption (TPD) measurements have been carried out to determine the adsorption of propene and NO over parent and Pt-loaded zeolite catalysts. The adsorption of propene was studied with propene and a mixture of propene plus oxygen. The adsorption of NO was studied as well. The simultaneous adsorption of a
mixture of propene, NO and oxygen was not tested because of the limitations of the mass spectrometer, and due to the many similar masses of species containing C and N atoms.

Figure 20 shows the results of the NO-TPD studies (Paper I). The desorption bands of NO can be detected at around 70°C with the parent zeolite materials, while in the case of the Pt-loaded zeolite catalysts the second band at around 120°C on Pt/ZSM-5, at around 140°C on Pt/Beta, and at 350°C on Pt/Y zeolite can be observed. This is concluded to indicate that at least two types of NO adsorption sites are available at the catalyst surface. With Ferrierite the second band can not be observed. The only desorption band can be found at 70°C on both parent and Pt-loaded Ferrierite.

![Figure 20. TPD study of NO desorption over parent and Pt-loaded zeolites. In the interior graph desorption over the parent and Pt-loaded Y and Ferrierite zeolites is presented in detail. (Paper I)](image)

Propene desorption over the zeolite catalysts studied has been observed to decrease in the following order: ZSM-5 > Pt/ZSM-5 > Pt/Beta > Beta >> Pt/Y zeolite > Y zeolite > Ferrierite ≈ Pt/Ferrierite. In the case of propene and oxygen, the order of the propene desorption is different from that of the pure propene adsorption. The order was the following: Pt/ZSM-5 > Pt/Beta >> Beta > ZSM-5 > Ferrierite ≈ Pt/Ferrierite > Pt/Y zeolite. The parent Y zeolite did not show any adsorption capacity of propene with excess oxygen (Figure 21).
Fig. 21. Propene desorption bands over the parent and 1 wt-% Pt-loaded zeolites. A C$_3$H$_6$+O$_2$-TPD study. In the interior graph desorption over the parent and Pt-loaded Y and Ferrierite zeolites is presented in detail. (Paper I)

Fig. 22. Comparison of the calculated desorption amounts of NO and C$_3$H$_6$ during the NO-, C$_3$H$_6$-, and C$_3$H$_6$+O$_2$-TPD experiments (Paper I).

In Figure 22 the comparison of calculated desorption amounts of NO and propene during the NO-, C$_3$H$_6$-, and C$_3$H$_6$ + O$_2$-TPD experiments is presented. The areas are calculated
by the SigmaPlot software using trapezoidal approximation (SigmaPlot Tutorial). It can be observed that the ZSM-5- and Beta-based zeolite catalysts adsorbed significantly higher amounts of propene than Y and Ferrierite zeolites. The 1 wt-% Pt/ZSM-5 is observed to adsorb NO most efficiently. The Y zeolite and Ferrierite showed rather small adsorption capacity of propene. All the platinum-loaded zeolite catalysts are found to adsorb more NO than the parent zeolites.

5.5 Acidity measurements

The acidic properties of zeolite catalysts have a significant role in the reduction of NOx by propene as suggested by Gerlach et al. (1999a and 1999b). In Figure 23 the pyridine adsorption over the parent and 1 wt-% Pt loaded ZSM-5, Beta and Y zeolite catalysts is presented. The first spectra of each figure (a-f) show the adsorption bands after 4 minutes of pyridine adsorption. The other spectra are taken after evacuation at 150°C for 30 minutes, 250°C for 60 minutes, and 350°C for 60 minutes. In the case of the 1 wt-% Pt/Beta and Pt/Y the spectra after the last evacuation were not recorded because pyridine was detected being desorbed after 60 minutes of evacuation at 250°C. The acidic properties of Ferrierite and 0.8 wt-% Pt/Ferrierite have not been measured.

The analyses of the spectra have been based on the comparison of the experimental bands with the observations of other research groups reported in the literature. A negative band at around 3605 cm⁻¹ can be assigned as acidic hydroxyls on the Brønsted acid site (Al-(OH)-Si). The band can be observed over ZSM-5-based zeolite catalysts. However, over the other samples the band was almost insignificant. The band caused by silanol groups at around 3740 cm⁻¹ was detected over all the catalysts studied. (Maache et al. 1991) In the case of Y and Pt/Y zeolite catalysts the hydroxyl group was detected to be the weakest. The intensity changes of the bands at the OH-region were not significant during the evacuation period over ZSM-5-based catalysts, while over the Beta-based catalysts the negative band disappeared.

The adsorption of pyridine is detected at the wavenumbers of 1545, 1490, and 1450 cm⁻¹. The band at around 1450 cm⁻¹ can be assigned as pyridine adsorbed on Lewis sites. The band at 1545 cm⁻¹ is assigned to pyridine on the Brønsted acid sites, and 1490 cm⁻¹ is due to the adsorption of pyridine on both Brønsted and Lewis sites. The Lewis sites represent the framework Al in the zeolites. (Bortnovsky et al. 2001)

The adsorption of pyridine on the Pt-loaded Y zeolite causes bands only at 1596 and 1445 cm⁻¹. The band at 1445 cm⁻¹ indicates pyridine adsorbed on weak Lewis acid sites. The very weak band at 1541 cm⁻¹ (Brønsted acid site) disappeared after evacuation at 150°C for 30 minutes. Janin et al. (1991) have obtained the same type of results in their study over the dealuminated HY zeolite.

The strongest adsorption bands are detected over the parent and 1 wt-% Pt/ZSM-5. The Beta and 1 wt-% Pt/Beta showed pyridine adsorption bands at Lewis and Brønsted acid sites at 150°C. Above 150°C the adsorption bands were insignificant. The same phenomenon can be measured over the 1 wt-% Pt/Y zeolite, however, the parent Y zeolite does not indicate any pyridine adsorption.
Fig. 23. DRIFT spectra of pyridine adsorption over the parent ZSM-5 (a), Beta (b), Y (c) and the 1 wt-% Pt-loaded ZSM-5 (d), Beta (e) and Y (f) zeolites. Spectra have been taken after (I) pyridine adsorption at 150°C for 4 minutes, (II) evacuation at 150°C for 30 minutes, (III) evacuation at 250°C for 60 minutes, and (IV) evacuation at 350°C for 60 minutes.
The adsorption of pyridine on the strong Brønsted acid sites on ZSM-5 and 1 wt-% Pt/ZSM-5 was observed to remain irreversible during heating and evacuation. It can be concluded that the interaction of pyridine with the acidic sites of the ZSM-5 is strong enough to prevent the high mobility of the adsorbed pyridine. Bludau et al. (1998) have reported similar results.

Based on the observations of the IR spectra the total amount of Brønsted acid sites was found to be equivalent between the parent and corresponding Pt-loaded ZSM-5 and Beta zeolite catalysts as reported recently also e.g. by Villegas et al. (2005) and Halász et al. (2004). In the case of Y zeolite the pyridine adsorption was observed to be very low. The acidity of the zeolite catalysts studied can be detected to decrease in the following order: Pt/ZSM-5 ≈ ZSM-5 > Pt/Beta ≈ Beta > Pt/Y > Y zeolite.
6 Reaction mechanisms and kinetics

6.1 Proposed reaction mechanisms from literature

Several proposals have been presented in the literature for the mechanism of the SCR reaction over zeolite- and Al$_2$O$_3$-based catalysts. Cu-MFI was one of the first catalysts studied for the HC-SCR of NOX. After that different mechanisms have been proposed for the SCR reaction. Reaction intermediates such as isocyanates (-N=C=O), cyanides (-CN-), nitriles, organic nitro (-ONO) and nitrite (-NO$_2$) as well as dinitrogen (-NN-) species have been introduced and studied by the IR technique. The proposed steps are 1) NO dissociation, 2) partial oxidation of hydrocarbon to C$_x$H$_y$O$_z$ species, 3) formation of organonitrogen compounds, and 4) NO oxidation to NO$_2$. (Hoost et al. 1995a, Hamada 1997, Cant & Liu 2000)

6.1.1 PGM/Al$_2$O$_3$-based catalysts

Several research groups have studied the Al$_2$O$_3$-based catalysts for the HC-SCR of NOX. Numerous reaction mechanisms and kinetic models have been proposed for NOX reduction by propene/propane over PGM-loaded catalysts. According to Burch the NO reduction by propane over Pt/Al$_2$O$_3$ goes via the dissociation of adsorbed NO. The species formed can further react to molecular nitrogen or nitrous oxide. Propane undergoes a dissociative oxidation with oxygen from NO or O$_2$ eventually producing CO$_2$ and H$_2$O. (e.g. Burch & Watling 1997, Bamwenda et al. 1995)

The reaction mechanisms over Pd/Al$_2$O$_3$ have been proposed to go via isocyanate formation, which can further react with NO, NO$_2$ or atomic oxygen. Shimizu et al. (1998) reported acetate formation over alumina catalysts. Acetate and nitrate species on the catalyst support can react and form N$_2$, CO$_2$, CO, and H$_2$O. (Shimizu et al. 1998)

The mechanistic approach by Praserthdam et al. (2002) over the Pt-loaded Al$_2$O$_3$ catalysts proposed the NO dissociation and reaction with NO to N$_2$ and N$_2$O. Organonitrogen species have also been proposed to be as intermediates in the reduction of NO. (Praserthdam et al. 2002)
6.1.2 Pt-loaded zeolite catalysts

The reaction mechanisms for NOx reduction over zeolite-based catalysts have been proposed to go via -NCO, -CN, -ONO- or -NHx intermediates formation (Hoost et al. 1995a, Amiridis et al. 2004). In the case of high-silica zeolite materials the reaction routes via the -NCO intermediate formation are not introduced so often. One reason for this can be that silica does not adsorb -NCO but alumina does, so there is a lack of evidence for -NCO species on the zeolite surfaces. (Burch et al. 2002)

Deeba et al. (1999) have proposed the platinum sites as being responsible for the NO reduction at temperatures above 250°C. The hydrocarbon mitigation at lower temperatures might be due to the storing capacity of the acidic sites of the zeolite support forming hydrocarbon species. These species are independently active for the NO reduction. (Deeba et al. 1999)

According to the study of Xin et al. (1997b), the reaction mechanism of NO reduction over Pt/ZSM-5 in the case of NO+C3H6+O2 is suggested to have three major steps: the adsorption and/or decomposition of reactants, the oxidation of surface organic compounds, and the formation of reduced products. NO and O2 are assumed to dissociate to N and O species on Pt. Pt-O can react with adsorbed propene (π-allyl) surface species forming partially oxidised hydrocarbon compounds. (Xin et al. 1997b)

Rottländer et al. (1996) have presented a similar proposition for NOx reduction over Pt/ZSM-5. They suggest that the reaction between propene and surface oxygen species form CxHy(O2) compounds. At the same time NO was proposed to react on oxidised Pt to NO2. The hydrocarbon intermediates formed react either non-selectively with O2 to CO2 or selectively with NO to the desired products (CO2, H2O, N2). (Rottländer et al. 1996)

In lean conditions NO and O2 compete for the sites of dissociative adsorption on the Pt surface. The role of hydrocarbon is proposed to be a clean-off agent by removing the atomic oxygen adsorbed on the Pt surface sites. The dissociation of NO is also reported to be slower than the dissociation of oxygen. (García-Cortéz et al. 2003a & 2003b, Burch & Scire 1994) At high temperatures the dissociation of NO on Pt is more effective, while at low temperatures only a part of NO is dissociated. The formation of N2O on the Pt-loaded catalysts can thus be explained with the reaction between adsorbed NO and formed N species. (Pérez-Ramírez et al. 2001)

Platinum-loaded Beta zeolite has been studied in the SCR of NOx in lean conditions quite recently. Pt-loaded Beta has been found to be a very effective catalyst for the SCR of NO by propene in the presence of excess oxygen. (Bueno-López et al. 2004)

The formation of NH4+ species over the Pt-loaded ZSM-5 in the excess oxygen has been introduced by Satsuma et al. (2003). They proposed that the formed NH4+ reacts with NO over acid sites. The proposition also pointed out that the formation of the undesired by-product (N2O) could be avoided.

NaY zeolites have been studied in the reduction of NO2 by propylene. Li et al. (2005) proposed that NO is oxidised to NO2 and it further reacts with hydrocarbon species. The reaction mechanism introduced suggests that the reactions between NO2 and propylene produce oxygenated hydrocarbons (e.g. C3H6O) and NO. (Li et al. 2005)
Gerlach et al. (1999a) have studied the reaction between propene and NO over H-Mordenite. They have suggested that NO reacts with zeolites’ Brønsted acid sites, producing NO$^+$ ions. The reaction of NO$^+$ with propene can furthermore produce organic nitro compounds, which can be transformed to propenal oxime and, finally, acrylonitrile.

NO reduction by hydrogen over Pt-Na/ZSM-5 has been studied by Machida et al. (2004). They reported that the Brønsted acid sites in the zeolite activate hydrogen molecules. Thus, in the reduction of NO in a NO-H$_2$-O$_2$ gas mixture the reaction between activated hydrogen and NO$_2$ produces molecular nitrogen more selectively. (Machida et al. 2004)

The coupling of nitrogen atoms is presented as a prerequisite for the molecular nitrogen N$_2$ and nitrous oxide (N$_2$O) formation. The coupling effect has been reported by isotope labelling experiments carried out by e.g. Acke & Skoglundh (1999).

DRIFT studies of adsorption of hydrocarbons on the zeolite surface have been carried out and the adsorption bands of hydrocarbon groups have been reported by e.g. Bolis et al. (1980).

6.2 Reaction mechanisms

In our study, the experimental adsorption bands (e.g. wavenumbers) were analysed and compared with similar spectra and the adsorption bands presented in the literature. The possible adsorbed surface species as well as intermediates could thus be identified. The reaction mechanistic steps were then formed based on the experimental observations and recent literature.

6.2.1 Pd/Al$_2$O$_3$-based catalyst

The data obtained over the Pd/Al$_2$O$_3$-based catalysts from DRIFT and activity experiments was used to build reaction mechanisms for the reduction of NO and for the oxidation of propene in lean to rich conditions. The possible reaction mechanisms of NO reduction by propene over the pre-oxidised Pd/alumina-based catalysts is presented in Table 6 (Paper V).

The acetates and formates detected on the catalyst surface provide evidence of the reaction mechanism that goes via the reaction between partially oxidised hydrocarbons and NO (Fritz & Pitchon 1997, Tanaka et al. 1994). The formation of isocyanate as a surface intermediate is also observed in our study. The other possible reaction route goes via the formation of isocyanate and cyanide species by the reaction with NO to N$_2$. (Fritz & Pitchon 1997, Paper V)

The most probable reaction route is initiated by the adsorption of NO and propene, and then adsorbed propene reacts with the surface oxygen to partially oxidised hydrocarbons (C$_x$H$_y$O$_z$). These compounds can then react with NO or oxygen and form organic nitro compounds, acetates, formates, and isocyanates, which were detected as surface intermediates in the DRIFT measurements. The reaction between nitrates and isocyanates or cyanides produces nitrous oxide and the desired final products (N$_2$ and CO$_2$).
Table 6. The observed reaction intermediates and products for NO, C\textsubscript{3}H\textsubscript{6}, and/or O\textsubscript{2} reactions (1 and 3% Pd-catalysts); reaction mechanism approach (Paper V).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed at/by</th>
<th>Refs in Paper V</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO adsorption and reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO + * ↔ NO*</td>
<td>1630 cm(^{-1})</td>
<td>12, 19, 20</td>
</tr>
<tr>
<td>NO* + * → N* + O*</td>
<td>n.d.</td>
<td>12, 19, 20</td>
</tr>
<tr>
<td>NO* + N* → N\textsubscript{2}O</td>
<td>Gas analysis</td>
<td>11, 12, 18</td>
</tr>
<tr>
<td>NO* + O* ↔ NO\textsubscript{2}*</td>
<td>1320-1250 cm(^{-1})</td>
<td>20</td>
</tr>
<tr>
<td>NO* + O\textsubscript{2} → NO\textsubscript{3}*</td>
<td>1300-1250 cm(^{-1})</td>
<td>4</td>
</tr>
<tr>
<td>Propene adsorption and reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} + * → C\textsubscript{x}H\textsubscript{y}*</td>
<td>3200-2900 cm(^{-1})</td>
<td>3, 21</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}* + O\textsubscript{2} / O* → C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}*</td>
<td>1565, 1395 cm(^{-1})</td>
<td>21</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}* + NO → -CH\textsubscript{2}-NO*</td>
<td>1658 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>-CH\textsubscript{2}-NO\textsubscript{2}* → -CH\textsubscript{2}-NO\textsubscript{2}*</td>
<td>1658 cm(^{-1})</td>
<td>5, 17</td>
</tr>
<tr>
<td>-CH\textsubscript{2}-NO\textsubscript{2} + NO* → -CH\textsubscript{2}-NO\textsubscript{2}*</td>
<td>1658 cm(^{-1})</td>
<td>5</td>
</tr>
<tr>
<td>Cyanide/isocyanate reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-NCO* + NO\textsubscript{x}* → N\textsubscript{2} + CO\textsubscript{2} + N\textsubscript{2}O</td>
<td>Gas analysis</td>
<td>2, 17, 20</td>
</tr>
<tr>
<td>-C≡N* + NO\textsubscript{x}* → N\textsubscript{2}O + N\textsubscript{2} + CO\textsubscript{2}</td>
<td>Gas analysis</td>
<td>21</td>
</tr>
<tr>
<td>N\textsubscript{2}O* + CO* → N\textsubscript{2} + CO\textsubscript{2}</td>
<td>Gas analysis</td>
<td>12</td>
</tr>
<tr>
<td>-NCO* + H\textsubscript{2}O → NH\textsubscript{2} + CO\textsubscript{2}</td>
<td>Gas analysis</td>
<td>17</td>
</tr>
<tr>
<td>n.d. = can not be detected by the FTIR method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X* = adsorbed species, * = vacant site</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The reaction mechanistic hypothesis for NO reduction by CO has been introduced in Table 7 (Paper IV). The formation of isocyanate species was observed experimentally to be very strong. The interaction between CO and formed nitrates as well as nitrites produced isocyanate. The reaction mechanistic model was derived and the results give evidence of the role of isocyanates in the reduction of NO.
It can be concluded that palladium on Al₂O₃-based support is a good catalyst for the reduction of NOₓ and at the same time for the oxidation reactions of propene and CO in the conditions studied.

6.2.2 Pt-loaded zeolites

In Table 8 the surface and free intermediates as well as the observed products over 1 wt-% Pt/ZSM-5 are presented (Paper III). The reaction mechanistic steps are formed by the observed surface intermediates and compared with information from recent literature (e.g. Gerlach et al. 1999, Poignant et al. 2001, Burch et al. 2002, Xin et al. 1997a & 1997b).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mechanism</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + * ⇌ NO*</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>CO + * ⇌ CO*</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>O₂ + 2 * ⇌ 2 O*</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>CO* + O* → CO₂ + 2*</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>NO* + * → N* + O*</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO* + CO* → CO₂ + N* + *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO* + N* → N₂O + 2 *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 N* → N₂ + 2*</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO* + CO* → NCO* + O*</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCO* + NO* → N₂ + CO₂ + 2*</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCO* + NO* → N₂O + CO* + *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 NO* → N₂O* + *O</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂O* ⇌ N₂O + *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂O* + N* → N₂ + O*</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 NO* → (NO*)₂</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NO*)₂ → N₂O + O* + *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 NO* → N₂O + O* + *</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*X* = adsorbed species, * = vacant site
Table 8. Identified surface and free intermediate species over 1 wt-% Pt/ZSM-5 under reaction conditions (1000 ppm NO, 1000 ppm C\textsubscript{3}H\textsubscript{6}, and 5% O\textsubscript{2}); comparison with the literature data (Paper III).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed at / by</th>
<th>Refs in Paper III</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + * → NO*</td>
<td>1820, 1935 cm\textsuperscript{-1}</td>
<td>1, 6</td>
</tr>
<tr>
<td>NO* + * → N* + O*</td>
<td>n.d.</td>
<td>7</td>
</tr>
<tr>
<td>O\textsubscript{2} + * → O\textsubscript{2}*</td>
<td>n.d.</td>
<td>7</td>
</tr>
<tr>
<td>O\textsubscript{2} + O\textsubscript{2}* → 2 O*</td>
<td>n.d.</td>
<td>7</td>
</tr>
<tr>
<td>NO* + O\textsubscript{2}* → NO\textsubscript{2}O*</td>
<td>1310-1290 cm\textsuperscript{-1}</td>
<td>2, 6</td>
</tr>
<tr>
<td>NO* + O* → NO\textsubscript{2}</td>
<td>1658, 1310-1290 cm\textsuperscript{-2}</td>
<td>2, 6</td>
</tr>
<tr>
<td>NO* + N* → N\textsubscript{2}O*</td>
<td>2234 cm\textsuperscript{-1}</td>
<td>7</td>
</tr>
<tr>
<td>NO* + NO* + O\textsubscript{2}* → N\textsubscript{2}O\textsubscript{4}</td>
<td>2234 cm\textsuperscript{-1}</td>
<td>7</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} + * → C\textsubscript{3}H\textsubscript{6}*</td>
<td>1642, 1507 cm\textsuperscript{-1}</td>
<td>1, 9</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}* + n* = n C\textsubscript{x}H\textsubscript{y}*</td>
<td>3200-2800 cm\textsuperscript{-1}</td>
<td>2</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}* + NO* → C\textsubscript{3}H\textsubscript{5}-ONO*</td>
<td>1662 cm\textsuperscript{-1}</td>
<td>9</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}* + NO* → C\textsubscript{2}H\textsubscript{4}NOH*</td>
<td>1414, 1460 cm\textsuperscript{-1}</td>
<td>1</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{4}NOH* + C\textsubscript{2}H\textsubscript{5}CN* + H\textsubscript{2}O*</td>
<td>2280 cm\textsuperscript{-1}</td>
<td>1</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{4}NOH* + O\textsubscript{2}* + C\textsubscript{2}H\textsubscript{5}O\textsubscript{2}*</td>
<td>1595 cm\textsuperscript{-1}</td>
<td>2</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{4}NOH* + C\textsubscript{2}H\textsubscript{5}O\textsubscript{2}* + CO* + H\textsubscript{2}O</td>
<td>2070-2050, 1190 cm\textsuperscript{-1}</td>
<td>8, 13</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{4}CN* + 2 H\textsubscript{2}O* → NH\textsubscript{3}* + C\textsubscript{2}H\textsubscript{5}COOH*</td>
<td>3265 cm\textsuperscript{-1}</td>
<td>1, 14</td>
</tr>
<tr>
<td>NH\textsubscript{3}* + NO* → N\textsubscript{2} + H\textsubscript{2}O</td>
<td>gaseous</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{5}* → C\textsubscript{2}H\textsubscript{5}</td>
<td>gaseous</td>
<td></td>
</tr>
<tr>
<td>NO* + NO\textsubscript{2} + *</td>
<td>gaseous</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{2}O* + N\textsubscript{2}O + *</td>
<td>gaseous</td>
<td></td>
</tr>
<tr>
<td>CO* + CO + *</td>
<td>gaseous</td>
<td></td>
</tr>
<tr>
<td>CO* + CO + 2*</td>
<td>gaseous</td>
<td></td>
</tr>
</tbody>
</table>

n.d. = can not be detected by the FTIR method

X* = adsorbed species, * = vacant site

The adsorbed reactants and the surface intermediates formed can provide information on possible reaction routes in selective catalytic reduction of NO by propene in the presence of excess oxygen at low temperatures.

Adsorbed nitrite and nitrate species, hydrocarbon species and partially oxidised hydrocarbons (C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}) can be detected over the platinum-loaded zeolite catalysts. The reactions between adsorbed species produce desired products (CO\textsubscript{2}, H\textsubscript{2}O, and N\textsubscript{2}). In addition, at around the light-off temperature the undesired by-products such as nitrogen dioxide, nitrous oxide, and carbon monoxide can be detected in the gas phase.

In the proposed reaction mechanism, it is assumed that NO is adsorbed on Pt sites, and acidic sites of ZSM-5 are active for both NO and hydrocarbons adsorption. NO and hydrocarbons are oxidised to nitrates, nitrites and partially oxidised hydrocarbons, respectively. The reaction between adsorbed NO\textsubscript{X} and cracked or partially oxidised hydrocarbon species occurs on the Pt-sites producing organic nitro- or nitroso-compounds. The reduction of NO is proposed to happen both on the acidic sites of ZSM-5 at low temperatures as well as on the Pt-sites at higher temperatures. The Pt-sites are
active in promoting NO\textsubscript{2} formation, which can have an effect on the adsorption of hydrocarbons.

The study of NO\textsubscript{X} abatement by hydrocarbon-assisted selective catalytic reduction over the Pt-loaded ZSM-5 zeolite catalyst gives guidelines for the development of more effective catalytic materials for exhaust gas purification. Furthermore, the proposed reaction mechanism gives the possibility to derive the mechanistic kinetic model for the C\textsubscript{3}H\textsubscript{6}-SCR of NO over the zeolite catalysts.

In Table 9 the reactions that are probably present in the reaction mechanism of C\textsubscript{3}H\textsubscript{6}-SCR of NO over Pt-loaded zeolite catalyst have been introduced. Three different hypotheses for the possible reaction mechanism have been derived. Hypothesis A contains only the reactions between NO or propene with O\textsubscript{2}. In hypothesis B the reactions between NO and C\textsubscript{3}H\textsubscript{6} have been included and in hypothesis C the NO\textsubscript{2} as an oxidant has also been considered. In the table the C\textsubscript{x}H\textsubscript{y}-species are marked as C\textsubscript{3}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, and CH\textsubscript{2} to make the reaction mechanism atom balance equal. Thus, CH\textsubscript{2} can be assigned as CH\textsubscript{3} species as well. The reactions (e.g. H\textsuperscript{+} addition) which can be due to the acidic properties of the zeolitic support are also neglected. To keep the mechanism as simple as possible, the formation of carbocations is not included in the reaction. The author is, however, aware that e.g. C\textsubscript{3}H\textsubscript{7}-ONO surface intermediates are reported to be formed over e.g. ZSM-5 zeolite catalysts.
Table 9. The possible mechanistic steps for the C3H6-SCR of NO over Pt-zeolite catalysts.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + * =&gt; NO*</td>
<td>Hyp. A: +, Hyp. B: +, Hyp. C: +</td>
</tr>
<tr>
<td>C3H4 + * =&gt; C3H5*</td>
<td></td>
</tr>
<tr>
<td>NO2* + N2 + 2*</td>
<td></td>
</tr>
<tr>
<td>CO* + NO2* =&gt; CO2 + NO* + 2*</td>
<td>Hyp. A: +, Hyp. B: +, Hyp. C: +</td>
</tr>
<tr>
<td>X* = adsorbed species, * = vacant site</td>
<td></td>
</tr>
</tbody>
</table>
The reactants adsorbed on the catalyst surface and these adsorbed species were detected by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The desired gaseous (e.g. CO₂, H₂O) and other reaction by-products and/or intermediates (e.g. CO, NO₂, and N₂O) were detected by the gas FTIR technique. Homonuclear diatomic molecules like molecular nitrogen (N₂) cannot, however, be detected by the IR technique. The experimental observations used to build a plausible reaction mechanism for the C₃H₆-assisted selective catalytic reduction (SCR) of NOₓ over platinum-based zeolite catalysts can be presented as shown in Figure 24 (Paper III).

![Fig. 24. A plausible reaction mechanism for the C₃H₆-SCR of NOₓ over Pt-loaded zeolite catalysts (Paper III).](image)

The results reported in the literature were used as reference data in the analysis of the observed adsorption bands. The inlet gas components (NO, C₃H₆, and O₂) were first adsorbed on the catalytic active sites. The adsorbed species were then reacting with each other, forming partially oxidised hydrocarbons, nitrate, and nitrite species. Furthermore, partially oxidised hydrocarbons and nitrogen species can form organic nitro compounds (R-ONO and R-NOH). These organic nitro species in turn can produce e.g. ammonium ions, which can react with NOₓ to form N₂ and H₂O. Nitrogen oxides were assumed to desorb or react with N* atoms or organic nitro species, forming N₂, N₂O, CO₂, and H₂O. All of the mechanistic steps are not presented in Figure 24 because of the multiple reaction pathways and complexity of the reactions between various adsorbed surface species as well as the reactions between gaseous and adsorbed molecules.

### 6.3 Kinetic studies

The reaction kinetic model based on the activity and DRIFT studies has been derived for NO reduction by CO over Pd/Al₂O₃-based (Paper IV) and by propene over Pt/zeolite catalysts. A pseudo steady-state one-dimensional plug-flow (fixed bed) reactor model was
used (Monnerat et al. 2003, Maunula et al. 2000). A steady-state operation was assumed. A non-linear regression analysis was used for the parameter estimation. The Nelder-Mead simplex and the Levenberg-Marquardt algorithms were used in the parameter estimation (Nelder & Mead 1965, Marquardt 1963). The system of ordinary differential equations was solved by a stiff ODE solver (LSODE) using the backward difference method (Hindmarsh 1980). The axial dispersion was neglected and the reactor was assumed to operate in isothermal steady-state conditions. External and internal heat transfer was also neglected.

### 6.3.1 NO reduction by CO over Pd/Al₂O₃-based catalysts

Three different mechanisms were compared: direct decomposition (A), bimolecular reaction (B) and N₂O formation via isocyanate complex formation (C). The mechanisms are presented in Table 7, Chapter 6.2.1 (Paper IV). The first mechanism, A, presents the regenerative mechanism in which CO reacts with adsorbed oxygen on the surface formed in NO decomposition (steps marked in Table 7). Mechanism B is an example of a coupled mechanism, in which NO decomposition is assisted with CO. Mechanism C is a combination of the two previous mechanisms.

The frequently used presumption of dissociative adsorption of O₂ was used based on the low desorption rate of oxygen at temperatures below 400°C on the catalyst (Harmsen et al. 2001, Mukadi & Hayes 2002, Oh et al. 1986). The steady-state kinetic model is derived and reported in detail in Paper IV.

In principal, reaction rate parameters are temperature dependent by the Arrhenius law and the temperature dependence of the equilibrium constants follows the Gibbs-Helmholtz equation. The assumption that the reaction enthalpies are temperature independent results in the fact that the same functional form (exponential function) for temperature dependence of all the parameters can be used. In addition, the mean temperature reaction rate constants and equilibrium constants were used instead of pre-exponential coefficients, and the standard re-parameterisation was applied.

The calculated parameter values are presented in Table 10 (Paper IV). The maximum number of adjustable parameters was 16, but several of the parameters could be ignored. The neglected parameters are expectedly the ones that describe the temperature dependence or the adsorption limitations. The estimated parameters are in the physically meaningful domain and the magnitude of the parameters is typical for the type of catalyst, e.g., adsorption enthalpies are non-positive and the activation energies of the catalytic reactions are tens of kJ. However, the activation energy of oxygen adsorption was relatively high (approx. 20 kJ/mol). The mass transfer limitations were not taken into account in the reactor model.
Table 10. The calculated parameters for the kinetic models of NO reduction by CO in the three mechanisms studied (see Table 7).

<table>
<thead>
<tr>
<th>Param.</th>
<th>Value</th>
<th>Std. error</th>
<th>Param.</th>
<th>Value</th>
<th>Std. error</th>
<th>Param.</th>
<th>Value</th>
<th>Std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_6$</td>
<td>2.30 m$^3$/kgs</td>
<td>12.6</td>
<td>$k_{69}$</td>
<td>380 m$^3$/kgs</td>
<td>10.3</td>
<td>$k_6$</td>
<td>0.79 m$^3$/kgs</td>
<td>0.3</td>
</tr>
<tr>
<td>$E_{a,6}$</td>
<td>22.7 kJ/mol</td>
<td>16.3</td>
<td>$E_{a,10}$</td>
<td>46.2 kJ/mol</td>
<td>2.8</td>
<td>$E_{a,6}$</td>
<td>21.0 kJ/mol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>$k_{11}$</td>
<td>14.1 m$^3$/mol/kgs</td>
<td>13.3</td>
<td>$k_{610}$</td>
<td>0.260 mol/kgs</td>
<td>18.4</td>
<td>$k_{112}$</td>
<td>3.15 m$^3$/mol/kgs</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>$k_{22}$</td>
<td>13.0 m$^3$/mol/kgs</td>
<td>13.6</td>
<td>$E_{a,210}$</td>
<td>20.8kJ/mol</td>
<td>10.0</td>
<td>$E_{a,212}$</td>
<td>1.75 kJ/mol</td>
<td>73.8</td>
</tr>
<tr>
<td>$E_{a,22}$</td>
<td>46.9 kJ/mol</td>
<td>4.4</td>
<td>$k_{27}$</td>
<td>254 m$^3$/mol$^4$/kgs</td>
<td>10.4</td>
<td>$k_{222}$</td>
<td>4.69 m$^3$/mol/kgs</td>
<td>0.1</td>
</tr>
<tr>
<td>$K_{a2}$</td>
<td>5.98 m$^3$/mol</td>
<td>50.0</td>
<td>$E_{a,b7}$</td>
<td>31.2 kJ/mol</td>
<td>5.5</td>
<td>$E_{a,222}$</td>
<td>49.7 kJ/mol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>$H_{a2}$</td>
<td>-37.5 kJ/mol</td>
<td>15.7</td>
<td>$K_{a0}$</td>
<td>0.24 m$^3$/mol</td>
<td>19.7</td>
<td>$K_{a1}$</td>
<td>1.5 m$^3$/mol</td>
<td>15.8</td>
</tr>
<tr>
<td>$K_{a0}$</td>
<td>45.0 m$^3$/mol</td>
<td>15.8</td>
<td>$K_{c0}$</td>
<td>205 m$^3$/mol</td>
<td>5.6</td>
<td>$H_{a1}$</td>
<td>-17.9 kJ/mol</td>
<td>39.0</td>
</tr>
<tr>
<td>$H_{a0}$</td>
<td>-9.31 kJ/mol</td>
<td>12.8</td>
<td>$K_{a1}$</td>
<td>115 m$^3$/mol</td>
<td>22.8</td>
<td>$K_{a2}$</td>
<td>1.0 \times 10^4</td>
<td>0.4</td>
</tr>
<tr>
<td>$K_{c0}$</td>
<td>7.0 m$^3$/mol</td>
<td>30.2</td>
<td>$K_{a2}$</td>
<td>0.043</td>
<td>32.0</td>
<td>$K_{a3}$</td>
<td>22.0 m$^3$/mol</td>
<td>0.1</td>
</tr>
<tr>
<td>$H_{a2}$</td>
<td>11.7 kJ/mol</td>
<td>17.5</td>
<td>$H_{a2}$</td>
<td>-16.6 kJ/mol</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Std. error = standard error (%) 

Pore diffusion has slight, if any, effect within the temperature range used because of the thin (20 $\mu$m) washcoat layer of the monolith catalyst. However, as the temperature, and reaction rate, increase, the influence of mass transfer increases rapidly (Massing et al. 2000, Duprat 2002). Only minor differences exist between the model and the gas phase concentrations measured between the three models. The evaluation is made by comparing the simulated concentration curves with the experimental values and deriving the $R^2$ values of the estimations. An example of the calculated (direct decomposition model) vs. experimental gas-phase concentrations is shown in Figure 25. The data was taken from the experiments performed in lean conditions. Model A predicts the observed experimental data quite well.
By comparing the simulated surface coverages to the semi-quantitative adsorption amounts (Paper IV), it can be postulated that the bimolecular reaction mechanism is not the main reaction pathway. The coverage predicted by the direct decomposition reaction (A) and reaction via isocyanate (C) includes the same kind of features as the measured adsorption values. Neither mechanism can predict the increase in NO coverage in the absence of CO, because NO decomposition is proposed to be irreversible. The other parts of the NO coverage are predicted correctly by the direct decomposition model. The isocyanate measured by DRIFT is adsorbed on the support rather than on platinum group metal clusters. Thus, it is postulated that it is advantageous to construct models on NO reduction over the Pd-containing catalysts based on direct decomposition mechanisms (A). The kinetic model can be modified by considering the equilibrium limitation of NO decomposition, which takes into account the increase in the NO coverage in addition to the increase in the oxygen coverage, when the amount of CO is insufficient. However, it
should be considered in each application if the benefits of the equilibrium limited NO decomposition step is greater than the drawbacks of the increasing model complexity.

The results of the modelling give evidence that the most probable NO reduction route over the Pd-containing catalysts goes via the direct decomposition mechanism (mechanism A, Table 7). The main role of the reductant was to regenerate the oxygen-covered surface. The evidence of isocyanate as an intermediate to nitrous oxide was not found based on the modelling done. However, strong isocyanate formation on the surface of the support material was detected. The formation causes slow transient effects above the light-off temperature, which might reduce emissions during the catalyst warm-up. DRIFT measurements did not give a complete structural guidance for the reaction steps, but knowledge of surface intermediates facilitates the model construction and discrimination. However, more activity data (e.g. isotopic labelling and transient experiments) is still needed to support the plausible kinetic model.

6.3.2 Hydrocarbon-assisted NO reduction

The activation energies, \( E_a \), for the NO reduction and propene oxidation in the lean conditions over the 1 wt-% Pt-loaded ZSM-5, Beta, Y, and 0.8 wt-% Pt-Ferrierite were calculated by the Arrhenius equation. The light-off curves i.e. conversion versus temperature plots of the NO and propene were used as the data source for the calculations. The NO reduction rates were calculated from measurements of differential NO conversions by the equation (1) (Duprat 2002, Massing et al. 2000, Captain et al. 1998, Roberts and Amiridis 1997)

\[
\text{r}_{\text{NO}} = \frac{F_{\text{NO}} x_{\text{NO}}}{m_{\text{cat}}},
\]

where the NO reduction rate is \( \text{r}_{\text{NO}} \) (mol/g s), \( F_{\text{NO}} \) is the molar inlet rate of NO (mol/s), \( x_{\text{NO}} \) is the fractional conversion of NO and the mass of the catalyst in the reactor is denoted as \( m_{\text{cat}} \) (g). The logarithmic reduction and oxidation rates versus temperature were drawn. The regression lines were fitted in the range below the maxima of the NO reduction. The determination coefficient (\( R^2 \)) of the regressions was good in all cases but two. For the propene oxidation the average activation energies (\( E_{a, \text{C}_3\text{H}_6} \)) were 165±7, 115±3, 114±9, 134±20 kJ/mol over the 1 wt-% Pt-loaded ZSM-5, Beta, Y, and Ferrierite zeolite catalysts, respectively. The average activation energies for the NO reduction (\( E_{a, \text{NO}} \)) were 104±8, 105±9, 136±1 and 154±15 kJ/mol, respectively. The calculated values are in line with the activation energies reported in the recent literature over several catalysts i.e. for propene oxidation 107-151 kJ/mol and for NO conversion in the range of 72-182 kJ/mol (e.g. Bueno-Lopez et al. 2006 Botas et al. 2001, Ioan et al. 2005).

The reaction mechanism of the NO reduction by propene in excess oxygen over zeolite-based catalysts has been derived (see Table 9 proposed reaction mechanisms from A to C) and the kinetic modelling will be done in the next research step. The mechanistic models still need assumptions to be done to facilitate the kinetic modelling. Discrimination between the importance of each mechanistic step can further be supported by data from transient and isotopic labelled experiments.
7 Discussion

The reduction of NO by propene over the parent and 1 wt-% Pt-loaded zeolite and the 1 and 3 wt-% Pd/Al₂O₃-based catalysts have been studied and compared. For the reaction mechanisms the DRIFT technique was used to detect the surface species that were adsorbed and formed. The gaseous products were analysed in the activity experiments by gas FTIR.

The EFTEM experiments of the Pt-loaded zeolite catalysts give evidence of the large (5-10 nm) extraframework platinum particles. These Pt clusters can be assumed to act as one type of the active sites of the catalysts. The Pt dispersions of the catalysts were detected to be around 12%, except for 0.8 w-% Pt/Ferrierite around 33% (see Table 4). The small platinum particles inside the pores were not detected, but they have an effect on catalytic activity because the pores of the zeolite materials used are large enough for the inlet gas molecules to enter into the pores and for the product molecules to exit. This was testified by the N₂ adsorption experiments and the mean pore sizes of the zeolite materials.

In the activity tests propene reached a conversion of >99% over all the Pt-loaded zeolite catalysts with the inlet gas mixture containing excess oxygen. The light-off temperatures of propene over the 1 wt-% Pt-loaded ZSM-5, Beta, Y, and Ferrierite were 253, 208, 198, 227°C, respectively. When comparing the \( T_{50} \) values of propene conversions over the parent zeolites and the 1 wt-% Pt-loaded zeolites, the reverse order of the materials can be observed. Platinum can be detected to have a minor effect on propene oxidation in the case of ZSM-5 and Ferrierite-based zeolites, but the most significant effect on the light-off temperature of Y- and Beta-based zeolite catalysts. This phenomenon can possibly be due to the smaller average pore size of Ferrierite and ZSM-5 zeolites resulting in a smaller decrease in the light-off temperature of propene over the Pt-loaded Ferrierite and ZSM-5.

Nitric oxide did not exceed 50% conversion over the 1 wt-% Pt/ZSM-5 and Pt/Ferrierite catalysts, while the best conversions were observed over the 1 wt-% Pt/Beta and Pt/Y zeolites in the lean conditions with excess O₂. The maximum conversion of NOₓ was almost 70% over Pt/Beta and 60% over Pt/Y. NO started to react at above 150°C over all the catalysts except Pt/ZSM-5, which had the ignition temperature at 250°C. In the case when O₂ was absent the NO conversion reached values of 71, 48, 59, and 98% over
The 1 wt-% loaded Pt/ZSM-5, Pt/Beta, Pt/Y, and Pt/Ferrierite, respectively. The maximum NO conversions were measured just above the temperature at which propene had reached conversion of higher than 99% in the case of excess O₂. In the absence of O₂ the maxima in the NO conversions were detected at the temperatures above 500°C, expect in the case of the 1 wt-% Pt/Beta (390°C). The activities of the catalysts for the reduction of NO decreased in the order: Pt/Beta > Pt/Y > Pt/Ferrierite > Pt/ZSM-5 in the conditions with excess O₂.

The platinum loading can be observed to have a positive impact on catalyst efficiency in oxidising hydrocarbons. The observed phenomenon can be concluded to be evidence of the hydrocarbon cracking on the platinum surfaces. Further, the small hydrocarbon species (CHₓ) formed can more efficiently react with the surface oxygen and/or NO species. However, NO₂ formation was observed to rise twofold in magnitude with all the studied Pt-loaded catalysts compared to the parent zeolites. Platinum can be concluded to have an effect on O₂ and NO dissociation. Oxidation reactions of NO to NO₂ and propene to CO₂ can be observed to be more intense over the platinum-loaded zeolites than over the parent zeolites at lower temperatures.

The TPD studies of the adsorption of NO, propene as well as propene plus O₂ on the parent and Pt-loaded zeolite catalysts were done. The adsorption of NO indicates that NO can be adsorbed on at least two different sites on the catalyst surface, except in the case of Ferrierite-based catalysts. One adsorption site is concluded to be on the supporting zeolite and the other site on Pt. Propene is detected to adsorb the strongest on the ZSM-5- and Beta-based catalysts, while on the Y and Ferrierite zeolites propene adsorption is almost negligible. With the inlet gas mixture of propene and O₂ the Pt-ZSM-5 and Pt-Beta zeolites showed major adsorption capacities. Propene adsorption was observed to decrease in the following order: Pt/ZSM-5 > Pt/Beta >> Beta > ZSM-5 > Ferrierite ≈ Pt/Ferrierite > Pt/Y zeolite > Y zeolite.

The acidities of the parent and Pt-loaded zeolite catalysts show that pyridine was adsorbed on the ZSM-5-based catalysts via the most irreversible bonds. The adsorption of pyridine on the Brønsted and Lewis acid sites can be observed over all the catalysts studied. The acidity was determined to decrease in the following order: Pt/ZSM-5 ≈ ZSM-5 > Pt/Beta ≈ Beta > Pt/Y > Y zeolite. The acidic properties of the parent and Pt/loaded Ferrierite were not determined.

The average activation energies for NO reduction and propene oxidation were calculated. The activation energies for NO reduction decreased in the following order: Pt/Ferrierite > Pt/Y > Pt/Beta ≈ Pt/ZSM-5 and for propene oxidation the activation energies decreased in the order: Pt/ZSM-5 > Pt/Ferrierite > Pt/Y ≈ Pt/Beta.

The comparison of the activity studies, adsorption properties and acidities of the zeolite catalysts gives a guideline for the interaction of acidic surface sites and the behaviour of catalysts in the reduction of NO in excess oxygen. It is significant that the most acidic zeolites (ZSM-5 and Pt/ZSM-5) did not show the best activities for the NO reduction or propene oxidation in excess O₂. In addition, zeolite Y and Pt/Y omit good activities for the HC-SCR of NO, though their acidities and adsorption capacities were observed to be almost negligible.

The reaction mechanisms over the 1 wt-% Pt-loaded zeolite catalysts and the Pd/Al₂O₃-based catalysts are found to have differences in the formation of reaction intermediates. Over the Pd/Al₂O₃-based catalysts the main intermediates observed were
nitrates, nitrites, isocyanates and formates, while various organonitrogen species were considered to be formed as intermediates over the Pt-loaded zeolite catalysts. Over the Pt-loaded zeolite catalysts the main reaction intermediates on the surface are concluded to be organonitrogen species such as CₓHᵧ-NO₂ and CₓHᵧ-ONO. The plausible reaction mechanism has been derived and the NO oxidation to NO₂ has been considered to be one of the crucial mechanistic steps for the formation of organonitrogen species. These species can further react with NO to desired products (N₂, CO₂, and H₂O). However, the well-known disadvantage of the Pt-loaded catalyst is the formation of N₂O at the light-off temperature. The formation of dinitrogen containing species on zeolite catalysts as intermediates has also been reported in the literature. These species were, however, not identified.

Palladium loaded Al₂O₃ catalysts have been studied widely and several reaction mechanisms have been proposed in the literature. In this study, the Pd-loaded catalyst was used as a reference for the mechanistic studies because of the detailed information in the literature and our own earlier research and experience as well. The formation of nitrates, nitrites, formates, acetates, and isocyanates was observed by the DRIFT technique in the reduction of NO by propene over the Pd/Al₂O₃-based catalysts. The reaction mechanism of HC-SCR of NO is proposed to go via these intermediates over the Pd/Al₂O₃ catalysts. Our experimental studies of NO reduction by propene and CO over Pd-loaded Al₂O₃-based catalysts also give convincing evidence of the reaction mechanism that goes via -NCO and partially oxidised hydrocarbon species formation.

The DRIFT technique together with activity experiments is found to be a useful and effective tool for the derivation of the reaction mechanism. The techniques used allow for the detection of the main differences between the adsorbed surface species and the possible intermediates formation over Pt-loaded zeolite and the Pd-loaded Al₂O₃-based catalysts. In addition, while the determination of the surface species on the zeolite-based materials is more difficult than on the alumina-based materials, the DRIFT technique was proved to be a reliable research method in the case of zeolite materials as well. Furthermore, the experimental data obtained by DRIFT and activity experiments can be used to derive the kinetic model for the NO reduction by propene.

The reaction mechanisms of the HC-SCR of NOₓ over supported noble metal catalysts are, however, very complicated and deriving a simple kinetic model that could describe the phenomena on the catalyst surfaces with sufficient precision is very demanding and even impossible. Thus, transient and isotopic labelling experiments can provide further support to discriminate between the importance of the mechanistic steps inside each mechanism proposed and also when comparing the different mechanisms. This could very much facilitate the kinetic modelling.
8 Conclusions

In this study the parent and 1 wt-% Pt/zeolite and the 1 wt-% Pd/Al₂O₃-based catalysts were studied in the NO reduction by hydrocarbon and CO. The Pd-based catalyst has been used as a reference material for Pt-loaded zeolite catalysts because the examination of the zeolite materials is more demanding than that of alumina-based materials. The main goal of the work was to gain new knowledge on the mechanisms of NO reduction by propene over Pt-loaded zeolite catalysts. The second target was to study the IR techniques and their applicability and reliability for investigating and identifying the intermediates and adsorbed surface species in heterogeneous catalysis. The third goal was to derive the reaction mechanism for NO reduction by propene in excess oxygen by using only a few present-day experimental techniques and data from recent supporting literature. Finally, the derived reaction mechanistic routes for propene-assisted NO reduction over Pt/zeolites and Pd/Al₂O₃-based catalysts were compared.

Platinum-loaded zeolite catalysts are observed to oxidise hydrocarbons to CO₂ as well as NO to NO₂ much more effectively than the parent zeolites. It can be concluded that hydrocarbons are activated by platinum, and small reactive hydrocarbon species (CₓHᵧ) are formed. These hydrocarbon species can be oxidised more efficiently with surface oxygen and/or nitric oxide. The platinum loading is also detected to have a significant effect on the catalyst activity by lowering the light-off temperature (T₅₀) of propene and, furthermore, the conversions of NO reach the maximum values at lower temperatures than with the parent zeolites.

The excess oxygen in the inlet gas mixture is observed to lower the light-off temperature of the catalysts. Propene reached over 99% conversion with all the Pt-loaded catalysts. In addition, the maxima at the conversions of NO were reached at lower temperatures. However, the conversions were smaller than with the inlet gas mixture of NO+C₃H₆.

Another goal was to study the applicability of the IR techniques. The techniques were found to be valid tools providing a good basis for the mechanistic evaluation and, furthermore, for the creation of the kinetic models for the HC-SCR reactions of NO. The DRIFT spectra of the intermediates and the adsorbed surface compounds under the reaction provide a clear difference on the reaction intermediates over the Pt-loaded
zeolites and Pd/Al$_2$O$_3$-based catalysts. Activity studies also give the guidelines for the catalysts’ functioning in the reduction of NO by propene over the catalysts examined.

The comparison of the DRIFT spectra of the Pt-loaded zeolite and Pd/Al$_2$O$_3$-based catalysts offers significant evidence of different reaction intermediates on the catalyst surface during the two cases. Over the Pd/Al$_2$O$_3$-based catalysts the NO reduction was concluded to go via isocyanates, nitrates and partially oxidised hydrocarbon intermediates formation. In the case of the 1 wt-% Pt/zeolite catalysts the isocyanate formation was not detected. However, the formation of organonitro species was observed. Thus, the reaction mechanisms of NO reduction by propene over Pt/zeolites and Pd/Al$_2$O$_3$-based catalysts can be concluded to be dissimilar based on the experimental results obtained by DRIFT.

The most effective catalysts for the NO reduction by propene were found to be the 1 wt-% Pt/Beta and Pt/Y zeolite catalysts. However, the temperature windows for the maximum reduction were observed to be quite narrow, smaller than 50°C. It can be concluded that the Pt-loaded zeolite catalysts are good materials for the C$_3$H$_6$-assisted SCR of NO in the conditions studied. The reaction mechanistic approaches give the bases for the kinetic modelling that will be done in the future. Further studies will be performed in kinetic modelling as well as in the use of isotope-labelled molecules for making more detailed analyses of the mechanistic routes.

In this thesis, IR techniques have been used as a tool for deriving the reaction mechanisms for the propene-assisted SCR of NO. The Pt-loaded zeolite catalysts were found to be effective simultaneously in NO mitigation and propene oxidation. It can be concluded that the IR techniques can be used to derive the precise reaction mechanistic model. The adsorbed and formed surface species can be identified by DRIFT and the reaction products can be measured by gas FTIR in activity tests. The possibility that with only a small number of present-day experimental techniques, i.e. simultaneous DRIFT and FTIR, catalytic properties can be studied and reliable reaction mechanisms can be derived makes these techniques useful for reactor design. Kinetic modelling can, however, be facilitated by e.g. transient experiments, which give evidence of the importance of each mechanistic step and can thus make the simplifications in the kinetic models easier. The reaction routes for the NO reduction over the Pt-loaded zeolite and Pd/Al$_2$O$_3$-based catalysts were concluded to go mainly via the organonitrogen and isocyanate intermediates formation, respectively.
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ZEOLITE CATALYSTS IN THE REDUCTION OF NOX IN LEAN AUTOMOTIVE EXHAUST GAS CONDITIONS

BEHAVIOUR OF CATALYSTS IN ACTIVITY, DRIFT AND TPD STUDIES