Selective catalytic reduction of NOx over Ag/alumina

Dissertation

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2005
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Dissertation

Selective catalytic reduction of NOx over Ag/alumina

Scientific field – Inorganic Technology

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2005
I declare that I worked out this Dissertation myself and the aid of other person is clearly stated.
All data, used from literature given in the Dissertation are cited.
This Dissertation was carried out at the Department of Catalysis of the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic through 2001-2005 years.

It is a great pleasure for me to acknowledge Dr. Blanka Wichterlová’s supervision and kind support during my PhD studies. I also would like to thank to other colleagues for creating an inventive and friendly atmosphere during my studies.
Summary

The air pollution by nitrogen oxides remains a serious environmental problem in urban area. The conventional three-way catalysts used at stoichiometric engines are completely un-effective for NO reduction to N₂ under oxidizing atmosphere of lean-burn combustion at diesel engine exhausts. Selective catalytic reduction of nitrogen oxides (SCR-NOₓ) into harmless nitrogen by hydrocarbons is believed to be the simplest and friendly to environment way to eliminate nitrogen oxides in diesel engine exhausts. However, the catalysts with sufficient activity, selectivity and durability under real conditions of automotive exhausts are still far from application. The silver/alumina is one of the most active and relatively stable catalysts. It exhibits high SCR-NOₓ activity at high temperature region but at low temperatures it needs to be improved for practical application.

The object of the research work was analysis of the structure and operation of the most active Ag/alumina catalyst in SCR-NOₓ by decane and that co-assisted by hydrogen. The study was focused on elucidation of the state of silver in Ag/Al₂O₃ catalyst and the effect of hydrogen in the enhancement of the rate of decane-SCR-NOₓ reaction as well as the individual reactions steps. For that purpose a combination of reaction kinetic experiments and UV-Vis spectroscopy monitored at in-situ condition of the catalytic reactions was employed supplemented by ex-situ FTIR and TPR-H₂ techniques.

Ag⁺ ions were supported on γ-Al₂O₃ and ion exchanged into MFI zeolite with Ag loadings 1.3 - 2.88 wt.% and 1.41 - 5.91 wt.% respectively. Silver alumina possessed much higher SCR-NOₓ activity than Ag-MFI catalyst. SCR-NOₓ by decane and decane + O₂ and NO - NO₂ reaction steps over Ag/Al₂O₃ are greatly enhanced by hydrogen co-assistance. The effect is completely reversible. The NOₓ conversion varied with reaction temperature, silver content of the catalysts, water vapor presence or absence in reactant stream, space velocity and decane, oxygen, nitrogen monoxide and nitrogen dioxide concentration in synthetic exhaust gas.

It has been concluded that Ag⁺ ions in highly active Ag/Al₂O₃ catalyst are active site in SCR-NOₓ, stabilized by strong interaction with alumina support. Only a very small part of Ag⁺ is reduced to metallic charged Agₙ⁺⁺⁺ clusters (n ≤ 8) during both the decane- and H₂/decane-SCR-NOₓ reactions. The amount of the Agₙ⁺⁺⁺ clusters is related to NOₓ conversion, regardless the increase of NOₓ is achieved by increasing concentration of hydrogen, decane and oxygen, but they do not represent the active sites. Acceleration of the SCR-NOₓ reaction by hydrogen has
been shown to originate mainly from the increased rate of oxidation of hydrocarbons and reaction intermediates, but not from the increased rate of the NO-NO$_2$ reaction. Hydrogen function in the C$_{10}$H$_{22}$-SCR-NOx reaction is suggested to proceed via a radical reaction pathway. It is supposed that hydrogen dissociates, forms Ag-hydride, and then hydperoxy and hydroxy radical species. Addition of H$_2$O$_2$ into the reactant stream, as source of radicals, has been shown to enhance also decane-SCR-NOx over Ag/Al$_2$O$_3$. The requirement for the highly active and durable Ag/alumina is high dispersion of Ag$^+$ ions stabilized on alumina surface with ability to be again re-dispersed if metallic Ag clusters are formed.

The high activity of silver alumina in C$_{10}$H$_{22}$-SCR-NOx activated by hydrogen or H$_2$O$_2$ at low temperatures and short contact times provide promising results for further development of this catalytic system for its application at real diesel engine exhausts.

Keywords: Ag/alumina; Ag-MFI zeolite; SCR-NOx; Hydrogen effect; Ag clusters; In situ UV-Vis
Souhrn
Znečištění vzduchu oxidy dusíku v městských aglomeracích zůstává závažným ekologickým problémem. Třícestné katalyzátory, které jsou používány pro motory se stehiométrickým spalováním, jsou zcela neefektivní pro redukci oxidů dusíku na dusík v oxidační atmosféře chudého spalování dieselových motorů. Selektivní katalytická redukce oxidů dusíku na dusík (SCR-NOx) uhlouvodíky je považována za nejvýhodnější a ekologicky šetrnou metodu pro odstranění oxidů dusíku z výfukových plynů dieselových motorů. Nicméně, katalyzátor s dostatečnou aktivitou, selektivitou a životností v podmínkách automobilových exhalátorů není dostupný. Stříbro nanesené na alumině (Ag/Al2O3) je jeden z nejvíce aktivních a relativně stabilních katalyzátorů. Vykazuje vysokou aktivitu v oblasti vysokých teplot, ale pro praktické použití je nutné podstatně zvýšit aktivitu v nízkoteplotní oblasti.

Předmětem této práce byla analýza struktury a funkce vysoce aktivního Ag/Al2O3 katalyzátoru v selektivní katalytické redukci oxidů dusíku dekanem a analýza vlivu vodíku na tuto reakci. Práce byla zaměřena na objasnění stavu stříbra v Ag/Al2O3 katalyzátoru a vysvětlení efektu vodíku na dramatické urychlení SCR-NOx i jednotlivých reakčních kroků. Pro tento účel byl použit kompletní přístup, který zahrnoval studium kinetiky reakce a současně stavu stříbra v katalyzátoru za reálných podmínek pomocí in-situ UV-Vis spektrometrie doplněný ex-situ FTIR, NIR a TPR-H2 technikami.

1.3 až 2.9 hm.% stříbra bylo naneseno v Ag⁺ formě na γ-Al2O3 a 1.4 až 5.9 hm.% stříbra bylo iontově vyměněno v zeolitu MFI. Katalyzátor Ag/Al2O3 vykazovaly mnohem vyšší aktivitu v SCR-NOx než AgMFI katalyzátor. Konverze NOx se mění s reakční teplotou, obsahem stříbra v katalyzátoru, přítomností vody v reakční směsi, zatížením katalyzátoru a koncentraci dekanu, kyslíku oxidu dusnatého a oxidu dusičitého v syntetických výfukových plynách. SCR-NOx dekanem a oxidace dekanu a NO byly významně podporovány přítomností vodíku v reakční směsi. Tento efekt je zcela reverzibilní.

Aktivními centry ve vysoce aktivním Ag/Al2O3 katalyzátoru jsou Ag⁺ ionty stabilizované silnou interakcí s povrchem aluminu. Pouze malá část velmi aktivních Ag⁺ iontů je redukována na kovové nabité klastry Agₙ⁺⁺ (n ≤ 8) během SCR-NOx dekanem nebo dekanem za přítomnosti vodíku. Množství Agₙ⁺⁺ (n ≤ 8) přítomných na katalyzátoru je spojeno s NOx konverzí, nezávisle na tom zda je vyšší konverze dosažena zvýšenou koncentrací vodíku, dekanu nebo kyslíku, ale tyto klastry nereprezentují aktivní centrum pro SCR-NOx. Efekt vodíku na SCR-NOx má původ
zejména v propagaci oxidačních reakcí uhlovodíku a reakčních intermediátů, ale ne ve zvýšené oxidaci NO na NO2. Je navržena funkce vodíku v mechanismu SCR-NOx spočívající v propagaci radikálových reakcí. Předpokládáme, že vodík disocituje, tvoří Ag-hydríd a hydroperoxy a peroxy radikály. Dávkování peroxidu vodíku, jako zdroj radikálů, do reakční směsi také významně podporuje SCR-NOx dekanem.

Podmínkou pro katalyzátor s vysokou a trvalou aktivitou je vysoká disperzita Ag+ iontů stabilizovaných na povrchu aluminy se schopností zpětné redispersace, jestliže vznikají kovové klastry.

Vysoká aktivita Ag/Al2O3 katalyzátoru v SCR-NOx dekanem aktivované za nízké teploty nebo krátké doby zadržení přítomnosti vodíku nebo peroxidu vodíku poskytuje slibný výsledek pro další vývoj tohoto katalytického systému pro jeho aplikaci pro dieselové motory.

**Klíčová slova:** Ag/alumina; Ag-MFI zeolit; SCR-NOx; Efekt vodíku; Ag klastry; In situ UV-Vis
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1 Introduction

1.1 Nitrogen oxides

Nitrogen has six different oxides NO, N₂O, NO₂, N₂O₃, N₂O₄, and N₂O₅. The most populated nitrogen oxides are nitric oxide (NO) and nitrogen dioxide (NO₂). The generic term nitrogen oxide/s (NOx) is usually used to refer to NO and NO₂ or a mixture of them [1].

The source of NOx in exhaust gases of combustion processes is oxidation of molecular nitrogen from air at high temperature (thermal NOx) and of nitrogen compounds present in fuel (fuel NOx), i.e. in the coal and oil. The rate of formation of NOx is primary function of temperature and the residence time. During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N₂ or NO. Fuel NOx can contribute as much as 50% of total emissions when combusting oil and as much as 80% when combusting coal [2].

The primary manmade sources of NOx are motor vehicles, electric utilities, and other industrial, commercial, and residential sources that burn fuels. Mobile sources are responsible for more than half of all nitrogen oxide emissions in the United States [2]. Chemical industry particularly nitric acid plants are also significant sources of NOx emission.

NOx causes a wide variety of health and environmental impacts. It is one of the main ingredients involved in the formation of ground-level ozone, nitrate particles and acid aerosol, which can trigger serious respiratory problems. It also contributes to atmospheric particles that cause visibility impairment and formation of acid rain [2,3].

While there are strong limits for NO and NO₂ emissions there is no limit for N₂O; N₂O₃, N₂O₄ and N₂O₅ are unstable [2]. Therefore, various processes have been developed to abate NOx and further advanced processes are under development.

1.2 NOx abatement

1.2.1 NOx abatement in reducing atmosphere

A three-way catalytic converters are now standard equipment in cars with stoichiometric gasoline engine. A three-way catalytic converter has three simultaneous tasks:

- Oxidation of carbon monoxide to carbon dioxide.
- Reduction of nitrogen oxides to nitrogen.
- Oxidation of hydrocarbons (unburned fuel) to carbon dioxide and water.
These three processes are most balanced at the stoichiometric point, where there is a balanced amount of oxygen to fuel in the engine. When there is more oxygen than required, then the system is said to be running lean, and the system is in oxidizing conditions. The above two oxidation reactions (of CO and hydrocarbons) are favoured at this conditions, but reduction of nitrogen oxides to nitrogen becomes uneffective. When there is more fuel than oxygen (stoichiometrically), then the engine is running at rich conditions and the reduction of NOx is favoured [4].

1.2.2 NOx abatement in oxidising atmosphere

Nitric acid tail gas

Waste gas from nitric acid plants downstream from the absorption column typically contains 200 – 3,000 ppm NOx, 1,000 – 2,000 ppm N2O and 1 – 4% O2. Since the mid-seventies, selective catalytic reduction of NOx by ammonia has been installed at nitric acid plants for NOx abatement [2]. But as there is no limit for N2O, no one takes care for N2O pollution, although N2O is more dangerous greenhouse gas compared to NOx. NOx at selective catalytic reduction reacts with ammonia, which is provided as a reducing agent. NH3 is adsorbed on the catalyst and reacts with NO2 and NO to give N2 and H2O. The majority of commercial installations use the V2O5/TiO2 or V2O5-WO3/TiO2 catalyst as extruded monoliths. Same installations use a Cu-zeolite catalyst technology [5], advantage of which is operation at much lower temperature. The main reactions of the SCR-NOx with ammonia are

\[
\begin{align*}
4\text{NH}_3 + 4\text{NO} + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
4\text{NH}_3 + 4\text{NO} + \text{NO}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
4\text{NH}_3 + 3\text{NO}_2 & \rightarrow 7/2\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

These reactions implies 1:1 stoichiometry for NH3 and NO and a participation of oxygen.

Exhaust from power plants

The NOx emissions are primarily reduced by advanced system of fuel burning [6]. There are also installations where selective catalytic reduction systems selectively reduce NOx by ammonia to form molecular nitrogen and water using V2O5/TiO2 catalyst.

Exhaust from lean burn engines

Lean burning is an internal combustion of lean air-fuel mixtures. It occurs at high air-fuel ratio (typically 22:1), so the mixture has considerably less amount of fuel in comparison to
stoichiometric combustion ratio (14.6:1 for gasoline engines). The engines with lean burning provide much better performance with respect to efficiency of fuel use and thus low exhaust emissions of carbon oxides than those in conventional gasoline engines. The diesel engine operating at lean conditions is one of the most efficient energy converters of today, with up to 50% of the chemically bound fuel energy transformed into kinetic energy. Its high efficiency results in a low emission of carbon dioxide, nevertheless others emission characteristics such as emission of nitrogen oxides are high. The main drawback of lean burning is large amount of NOx being generated, so a complex catalytic converter system is required (see Chapters 1.3 and 1.4). The three-way catalyst cannot remove nitrogen oxides in lean-burn engine exhausts containing oxidizing atmosphere [2,3,4].

1.3 NOx emission from lean burn engines

There are two types of applications of lean burn engines - stationary and mobile diesel engines.

Stationary sources

A stationary diesel engine such as power generators or irrigation pumps is operated at constant load and there is actually no restriction concerning of the size of the SCR catalyst. That allows high values of contact time, simple control for the dosage of reducing agents and thus achievement of high NOx conversions at very low slip. A well-established technology where ammonia is used as a reducing agent for abatement of NOx from stationary sources could be applied [5,7,8].

Mobile sources

The requirements for NOx abatement in a mobile diesel engine in a personal car or truck are completely different to the stationary sources of NOx emissions. Firstly, load and engine speed vary often and abruptly, and this cause permanent changes of flow and temperature of the exhaust gas. A sophisticated control for the dosage of reducing agent is therefore necessary. In addition a catalyst has to be effective at broad temperature region. Moreover, the space available for a mobile De-NOx system is very limited; therefore, typical space velocities (GHSV) are being
high, ranging from 30,000 to 60,000 h\(^{-1}\), in short period to 120,000 h\(^{-1}\). Further problems are represented by high concentration of water vapour (up to 12%) and presence of sulphur oxides in exhaust gases, which both by strong interaction with the catalyst causes its deactivation [1,2,7,8].

1.4 NO\(_x\) emission control for lean burn engines

The desire to reduce NO\(_x\) emission has been driven by legislation [3]. An indication of the extent to which legislation has been tightened in recent years is given by the fact that since the uncontrolled emissions level in 1966 the NO\(_x\) emissions have had to be reduced by more than 95\%, of which the final most difficult part has came since the early 1990s (Table 1-1) [7].

In principle, there might be several possible ways from chemical viewpoint how eliminate nitrogen oxides from exhaust of diesel engines: Decomposition of NO to N\(_2\) and O\(_2\), NO\(_x\) storage with subsequent NO\(_x\) reduction in reducing atmosphere, selective catalytic reduction of NO\(_x\) by urea and selective catalytic reduction of NO\(_x\) by hydrocarbons in oxidizing atmosphere.

One of the main problems of diesel emissions is also particulate matter (PM). To eliminate the PM from exhaust gases various types of filter are used with high efficiency. The filters can contain Pt and/or Pd to oxidise trapped soot particles as well as NO. Provided NO\(_2\) is much more effective oxidant than O\(_2\), so it removes PM with high efficiency [7].

The opportunities of approaches for NO\(_x\) abatement at diesel exhaust by catalytic processes are described in the following paragraphs.
Table 1-1 Development of European emissions requirements [2,3,7].

Gasoline engine vehicles

<table>
<thead>
<tr>
<th>Year</th>
<th>Mass CO g.km(^{-1})</th>
<th>Mass HC g.km(^{-1})</th>
<th>Mass HC + NO(_x) g.km(^{-1})</th>
<th>Mass NO(_x) g.km(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996 (EURO II)</td>
<td>2.2</td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2000 (EURO III)</td>
<td>2.3</td>
<td>0.20</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>2005 (EURO IV)</td>
<td>1.0</td>
<td>0.10</td>
<td></td>
<td>0.08</td>
</tr>
</tbody>
</table>

Light duty diesel engine vehicles

<table>
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<th>Year</th>
<th>Mass CO g.km(^{-1})</th>
<th>Mass HC + NO(_x) g.km(^{-1})</th>
<th>Mass NO(_x) g.km(^{-1})</th>
<th>Particulates g.km(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996 (EURO II)</td>
<td>1.00</td>
<td>0.7</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>2000 (EURO III)</td>
<td>0.64</td>
<td>0.56</td>
<td>0.50</td>
<td>0.05</td>
</tr>
<tr>
<td>2005 (EURO IV)</td>
<td>0.50</td>
<td>0.30</td>
<td>0.25</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Heavy duty diesel vehicles

<table>
<thead>
<tr>
<th>Year</th>
<th>Mass CO g.kWh(^{-1})</th>
<th>Mass HC + NO(_x) g.kWh(^{-1})</th>
<th>Mass NO(_x) g.kWh(^{-1})</th>
<th>Particulates g.kWh(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996 (EURO II)</td>
<td>4.00</td>
<td>1.10</td>
<td>7.0</td>
<td>0.25</td>
</tr>
<tr>
<td>2000 (EURO III)</td>
<td>2.10</td>
<td>0.66</td>
<td>5.0</td>
<td>0.10</td>
</tr>
<tr>
<td>2005 (EURO IV)</td>
<td>1.50</td>
<td>0.46</td>
<td>3.5</td>
<td>0.02</td>
</tr>
<tr>
<td>2008 (EURO V)</td>
<td>1.50</td>
<td>0.46</td>
<td>2.0</td>
<td>0.02</td>
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</table>
1.4.1 Decomposition of NO to $N_2$ and $O_2$

Nitrogen monoxide is the simplest thermally stable odd-electron molecule and it is well known that NO decomposition to $N_2$ and $O_2$ is thermodynamically feasible at temperatures below 1200 K. Catalytic NO decomposition would be the simplest and most elegant method for its removal. However, the rate of decomposition is very low due to very high activation energy, therefore, highly efficient catalyst would be necessary [9]. Cu-MFI catalyst developed by Iwamoto [10] provides relatively high decomposition activity. But to-date, however, no catalyst with durable high activity in oxidizing atmosphere has been developed. This is due to fact that oxygen contained in the feed or produced in the decomposition of NO, oxidizes the active sites and competes with NO for adsorption sites. Also water vapor present in the exhaust gases decreases substantially the activity. As a result, high temperature and/or reducing agents are required to remove surface oxygen and regenerate catalytic activity [9].

1.4.2 NOx Storage catalysts

A commercial NOx storage-reduction (NSR) catalyst system first appeared in the marketplace in Japan in 1994 [7]. The air/fuel ratio (A/F) in an engine feed is alternated between the stoichiometric value and lean value. NOx is trapped when the engine is running lean, through the conversion of surface barium carbonate to nitrate, and it is transferred back when the engine is running rich by the reverse reaction coupled with NOx reduction through a conventional TWC reaction. A typical NSR catalyst comprises Pt, to oxidize NO to NO2 in order to enhance the efficiency of the trapping reaction, barium, which is present as a carbonate because the high levels of CO2 in the normal exhaust, is used to trap NO2, and frequently Rh is added to facilitate the reduction of NO, mainly by CO, under rich regeneration conditions [7]. A problem of NSR catalyst is its poisoning by SO2. SO2 in exhaust is readily oxidized to SO3 on Pt component of the NSR catalyst and this SO3 reacts rapidly with barium compounds to form a sulphate that is much more stable than either nitrate or carbonate. Regeneration of sulphate-poisoned catalyst requires very high temperature (with an associated fuel penalty).

1.4.3 Selective catalytic reduction of NOx by urea

Selective catalytic reduction of NOx using urea as reducing agent (urea-SCR-NOx) is commercially accessible technology, which can fulfil present NOx emission limit. The standard
catalyst systems are based on V₂O₅-WO₃ or V₂O₅-MoO₃ supported on TiO₂ similar to that used in NH₃-SCR-NOx technology. If urea is used instead of ammonia the de-NOx chemistry involves isocyanic acid as an intermediate.

\[
\text{NH}_2 - \text{CO} - \text{NH}_2 \rightarrow \text{NH}_3 + \text{HNCO} \tag{5}
\]

\[
\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \tag{6}
\]

The emission of isocyanic acid may occur producing ammonia slip at low temperature. In addition, isocyanic acid may react to higher products like biuret, melamine, cyanuric acid etc. [8]. Possible formation of all these compounds is the reason why the EPA in USA in 2002 has not approved the urea technology for applications at diesel engines [2].

### 1.4.4 Selective catalytic reduction of NOx by hydrocarbons

In selective catalytic reduction of NOx by hydrocarbons (HC-SCR-NOx), hydrocarbon is used as the reducing agent and is injected into the flue gas stream, passing over a catalyst. Overall reactions of the SCR-NOx process are

\[
\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 \tag{7}
\]

\[
\text{NOx} + \text{hydrocarbons} \rightarrow \text{N}_2 + \text{COx} + \text{H}_2\text{O} \tag{8}
\]

\[
\text{hydrocarbons} + \text{O}_2 \rightarrow \text{COx} + \text{H}_2\text{O} \tag{9}
\]

The temperature window in the diesel engine exhaust is usually between 473 and 723 K. The non-selective oxidation of hydrocarbons by oxygen causes loses of reducing the agent [3].

Research of HC-SCR-NOx for lean NOx after-treatment system began in the early 1980s. So far there is no catalyst, which could fulfill the requirements for NOx abatement at lean-burn conditions. Thus, HC-SCR-NOx in the oxygen-rich exhaust stream of lean-burn engines remains one of the major challenges for environmental catalysis.

### 1.4.4.1 Reducing agents for selective catalytic reduction of NOx by hydrocarbons

Efficiency of HC-SCR-NOx depends markedly on the nature of the reducing agent. Academic studies have tended to focus on the use of C1–C3 alkenes and alkanes as reductants [11,12,13,14]. Longer chain hydrocarbons (e.g. C8-C10), like those typically found in diesel fuels already on board, have attracted less attention [15,16]. The long chain alkanes usually give higher conversion of NO to N₂ at low temperatures. The greater enthalpy of adsorption of the longer
alkane chains and the weaker C-H bond strength of their methylene groups explain their higher reactivity and thus ability to react at lower temperature [3].

The oxygenated molecules as reducing agents have also been investigated. Alcohols and esters appear to give advantageously high conversion of NO at low temperatures [17,13]; however, the need for an additional on-board supply tank is the reason for which these substances are not considered as reductants of NOx at exhaust gases of diesel engines [3].

1.4.4.2 Catalysts for selective catalytic reduction of NOx by hydrocarbons

The first catalysts for HC-SCR-NOx under oxidizing conditions were reported Cu-MOR and Cu-MFI [7]. Among various metal zeolite catalysts investigated the Cu-MFI was tolerant to water vapor but at long-term hydrothermal conditions it exhibited decline in activity. Low activity or a severe decline in the NO conversion was observed on chromium, iron, manganese, vanadium, cobalt, nickel ion exchanged several types of zeolites. Introduction of noble metals (platinum, rhodium, iridium) into MFI zeolite gave catalysts with low conversion in a rather narrow temperature range, with formation of N₂O and NO₂ [7]. Many others zeolite based catalyst have been found to catalyse the SCR-NOx reaction. Nevertheless, all these catalyst proved to be inferior in comparison to Cu-MFI.

An alternative to the zeolite-based catalysts is development of non-zeolite based catalysts with high activity and durability for lean-NOx reduction. Alumina is widely used as support in current automotive catalysts and is naturally the first choice as a support. Various alumina-supported metal oxide catalysts has been studied. However, the addition of Sn, Ga, Co, Ni oxides supported on alumina did not lead to high activity [15]. Pt/Al₂O₃ catalysts exhibited high activity for the NOx reduction but only in the low-temperature range (473–523 K). Moreover, all the platinum-based catalysts present a serious drawback, i.e. formation of N₂O as a by-product. In 1993, Miyadera [18] found that an alumina-supported silver (Ag/Al₂O₃) catalyst is highly effective for SCR-NO by C₃H₆ and C₂H₅OH. Ag/Al₂O₃ exhibited considerably higher activity for the SCR-NOx than Cu/Al₂O₃, especially at high temperature region [19].

At present, it is recognized that Ag/Al₂O₃ is one of the most active alumina-based catalyst for NOx reduction with hydrocarbons or oxygenated hydrocarbons. It exhibits high activity at the conditions of real exhaust gas from diesel engine at temperatures above 620 K. But this catalyst
needs to be substantially improved at low temperatures (470-620 K), which is important for diesel engine exhaust.

1.4 Selective catalytic reduction of NOx by hydrocarbons over silver catalysts

After more than 10 years of research on the Ag/alumina system, a breakthrough has not yet been achieved proving the significance of a silver-containing catalyst for commercial exhaust gas cleaning of gasoline or diesel engines under road conditions [20]. The complex process of the SCR-NOx reaction over Ag/Al$_2$O$_3$ is not completely understood from the viewpoint of the reaction mechanism as well as the structure of active sites. The potential of silver-based supported catalysts for the selective catalytic reduction (SCR) of nitrogen oxides to nitrogen has recently been reviewed by Burch et al. [3] and Satsuma and Shimizu [21] summarized the present knowledge on mechanistic details of NO reduction over alumina-based catalysts.

1.4.1 Supports for silver catalysts

It has been recognized that silver on γ-Al$_2$O$_3$ alumina or located in MFI zeolite represent the most active silver catalysts for NO reduction with hydrocarbons or oxygenated hydrocarbons at lean conditions [3,21].

γ-Al$_2$O$_3$

Among various requirements, an effective automotive catalyst for lean NOx reduction must be able to withstand both high temperatures and high concentrations of water vapor. As γ-Al$_2$O$_3$ can be prepared in a hydrothermally stable form, a γ-Al$_2$O$_3$-supported metal or metal oxide may be a practical lean NOx reduction catalyst [14]. The γ-Al$_2$O$_3$ has a spinel-like structure; the oxygen lattice is built up by a cubic close-packed staking of anions and aluminum atoms occupy both octahedral and tetrahedral sites. The surface of γ-Al$_2$O$_3$ can be regarded as an extended defect and therefore can be easily covered by various types of adsorbed species [22]. The alumina surface has acid-base character, however, the basicity is rather low. In general, alumina provides possibility for stabilization of small metal particles and/or metal ions [23].
**MFI zeolite**

Among high silica zeolites, rather stable at hydrothermal conditions, a zeolite of MFI structure exhibits advantageous pore architecture, more stable structure and well accessible cationic sites. MFI zeolite is crystalline aluminosilicates with well-defined crystallographic 10-member ring intersecting channels with distinct size of pores. This provides large inner surface area and low atomic density of the unit cell. Chemical composition can be represented as:

\[ M_{2n} \text{Al}_2\text{O}_3 \times \text{SiO}_2 \times y\text{H}_2\text{O} \]  

(1-1)

Where \( M \) is a cation of valency \( n \); \( x \) has value equal to or greater than ca 25. The aluminosilicates consist of \( \text{SiO}_4 \) tetrahedra in which each silicon is joined to four oxygen situated at the corners of a tetrahedron. The \( \text{SiO}_4 \) tetrahedra are linked to the other tetrahedra through shared oxygen atoms forming three dimensional framework structures. The framework structure of MFI is depicted in Fig. 1-1 [24,25].
Fig. 1-1 Structure of zeolite MFI with the indication of pore diameter (Å).
1.4.2 Preparation of silver catalysts

Silver can be loaded into alumina and zeolite by various methods, the most widely used being impregnation, ion exchange, sol-gel method and co-precipitation.

Silver zeolite catalysts

The channels within the zeolite structure are large enough for the Ag⁺ ions to diffuse through. The Ag⁺ ion exchanges ion (e. g. Na⁺, NH₄⁺), which neutralise the negative framework charge in the zeolite.

When impregnation is used, the metal-support interaction in zeolites is weaker, and large metal particles are obtained, which can affect secondary reactions, namely those that are structure-sensitive. On the other hand, the ion-exchange technique normally brings about a strong metal-support interaction [26].

Silver alumina catalysts

The Ag/Al₂O₃ catalysts can be prepared by impregnating of Al₂O₃ by solution of silver nitrate or by sol-gel method [15,27,28]. The improved catalytic performances of sol-gel-prepared Ag/Al₂O₃ was assigned to a better dispersion of the metal cations.

The loading method has an influence on characteristics of the catalysts as metal dispersion, size and location of the metal particles and metal-surface interactions. All of them are important parameters, affecting the resulting catalyst activity.

1.4.3. Activity of the silver catalysts at SCR-NOx by hydrocarbons

Silver alumina

The activity of Ag/Al₂O₃ catalysts with various loading were compared for lean NO reduction with C₃H₆ and others hydrocarbons as reducting agent [14,18,29,28]. The effectiveness of the Ag/Al₂O₃ catalyst in the reduction of NO with C₃H₆ was a strong function of the Ag loading [18,29,28]. High conversions of NO to N₂ were obtained over Ag/Al₂O₃ with loadings of 2 – 3 wt.% Ag. In contrast, the NO conversions to N₂ were much lower over highly loaded Ag/Al₂O₃ (~6 wt.%), and this catalyst formed a substantial amount of N₂O [14]. Jen [30] has shown that the de-NOx efficiency for Ag/Al₂O₃ varies significantly with the type of Al₂O₃ support used. In some case high activity was observed for silver loading up to ca 5 wt.% Ag [27,30]. Surface area as well as narrow distribution of pore-size appears to be important [30]. The
methods of introduction of silver into Al₂O₃ have also an effect on activity of Ag/Al₂O₃ (see chapter 1.4.2).

Silver zeolite catalysts

The conversion of NOx to N₂ at CH₄-SCR-NOx over Ag-MFI catalysts increases with silver loading up to 11 wt.%. Further increase in loading (>11 wt.%) decreased the NO conversion [31]. Silver ions in the zeolite cation sites are inevitable necessary for the SCR-NO by methane. Without presence of isolated silver ions (only nano-sized silver particles exist on the outer surface of zeolite), the catalyst showed much lower activity and selectivity in the SCR reaction. Nevertheless, the activity was significantly enhanced by the nano-sized silver particles, besides isolated Ag⁺ ions, if methane was used as reducing agent [31].

Among Ag/Al₂O₃, Ag-MFI and Ag-MOR studied in Ref. [32], the Ag/Al₂O₃ catalyst showed superior activity in comparison with the Ag-MOR and Ag-MFI catalysts in the temperature range 623-723 K. Within zeolite based catalysts Ag-MFI displays higher activity compared with Ag-MOR [47].

1.4.4 Reducing agents at selective catalytic reduction of NOx over silver catalysts

The efficiency of HC-SCR-NOx strongly depends on the reductant type. In general using more reactive reductants yields higher NOx conversion at low temperatures. Especially C₃H₆ as a reducing agent has been investigated at selective catalytic reduction of NOx over silver catalysts [27,28,32]. E.F. Iliopoulou at al. [33] tested C₂H₄, C₂H₆, C₃H₆, C₄H₁₀, 1-C₄H₈ and 1,3-C₄H₆ as reducing agents. 1-C₄H₈ was the most efficient reductant not only increasing the maximum NOx conversion, but exhibiting the lower and wider active temperature window as well. Miyadera reported [18] that also oxygen-containing organic compounds such as ethanol and acetone were more effective than propene in reducing nitric oxide over Ag/Al₂O₃ in the presence of water and excess oxygen. The most suitable reductant from practical viewpoint would be Diesel fuel. The high activity and durability of the Ag/Al₂O₃ catalyst for the NOx reduction could be achieved by using the fuel injected before the catalyst [34].
1.4.5 State of silver on silver/alumina catalysts

Data concerning the electronic states of silver on surfaces of oxide supports are important for obtaining a insight into the nature of active sites for the catalytic reactions at the SCR-NOx process. The state of silver was studied by various methods, FTIR [35], XRD [35,36], ESR [37, 38], $^1$H MAS NMR and $^{129}$Xe NMR [39, 40], XPS [41], UV-Vis [42,43,44,45]. The results of these studies show that silver can be supported on Ag/Al$_2$O$_3$ at different states: silver ions Ag$^+$, silver charged clusters Ag$_n$,$^{5+}$ and silver metallic particles.

Stabilization of Ag$^+$ ions on γ-alumina depends on silver loading. Highly dispersed Ag$^+$ ions are dominant Ag species on the low loading samples (ca 2 wt.%) [14,16,34,42,43,44,45, 46,47]. However, the local structure of species, containing Ag$^+$ ions has not been ascertained. Supported Ag$_2$O clusters [20] or silver aluminate [29, 34] were observed in high active Ag/Al$_2$O$_3$. The formation of silver aluminate was confirmed by EXAFS and X-ray diffraction [29, 34].

In generally, reduction of silver ions in Ag/Al$_2$O$_3$ yields metallic silver with particle diameters of several nanometers. When a partial reduction is carried out oligomeric silver charged clusters Ag$_n$,$^{5+}$ various nuclearity and charge could be formed. These Ag$_n$,$^{5+}$ clusters could be stabilized in Ag/Al$_2$O$_3$ [14,16,45]. Crystalline Ag phases and large silver clusters are detectable in highly loaded Ag/Al$_2$O$_3$ ($\geq$ 6 wt.% Ag) catalysts [14,16, 29,45,46] at the reaction conditions of the SCR process. The 2 wt.% Ag/Al$_2$O$_3$ was supposed to contain silver in the +1 oxidation state under reaction conditions, while the 6 wt.% Ag/Al$_2$O$_3$ catalyst contained Ag$^0$ particles.

Bethke and Kung [14] showed that the oxidation states of Ag in Ag/Al$_2$O$_3$ were different under reaction conditions. The structure of a silver catalyst is very dynamic and readily transforms among Ag$^+$, Ag$_n$,$^{5+}$ clusters and metallic particles when changing the oxidative and reductive environment over the catalyst. As a consequence, ex-situ studies of the catalyst structure are of small relevance for elucidating the active site and the catalysts should be characterized under relevant catalytic conditions. To fulfill this condition, i.e. to find optimal conditions for measuring at the same conditions the catalyst performance and spectroscopic data, is not easy task. This experimental gap has led, in some cases, to contradictory or, at least, confusing conclusions on the type and nature of active sites (see chapter 1.4.6). The appropriate approach is therefore to study silver catalysts inside a reactor by spectroscopic means at the same conditions, i.e. temperature, contact time, pressure and reactor design.
1.4.6 Active sites at selective catalytic reduction of NO\textsubscript{x} by hydrocarbons over silver/alumina

\textit{Ag\textsuperscript{+} ions}

High dispersion of Ag\textsuperscript{+} ions, preserved as a result of a strong interaction with alumina support has been suggested to be indispensable for HC-SCR-NO\textsubscript{x} to N\textsubscript{2} [14,16]. The difference in de-NO\textsubscript{x} activity of the 2 wt.% and 6 wt.% Ag/Al\textsubscript{2}O\textsubscript{3} were attributed to the much higher Ag dispersion for the 2 wt.% than the 6 wt.% of Ag, where also metallic particles were formed.

However, nature of active species, which contain Ag\textsuperscript{+} ions, has not been yet ascertained. Small Ag-aluminate “clusters” [14,34,45] or Ag\textsubscript{2}O clusters of appropriate size [20] were suggested as the active sites.

\textit{Metallic silver}

The low NO\textsubscript{x} conversion during SCR-NO\textsubscript{x} was reported over the highly loaded samples of Ag/Al\textsubscript{2}O\textsubscript{3} [14,16,45,46]. Therefore, it was suggested that metallic silver is not active site for SCR-NO\textsubscript{x}. The presence of Ag\textsuperscript{0} resulted in a high rate of C\textsubscript{3}H\textsubscript{8} combustion at the expense of NO\textsubscript{x} reduction [14]. The presence of Ag\textsuperscript{0} in the catalyst resulted also in formation of a substantial amount of N\textsubscript{2}O [14].

\textit{Silver clusters - Ag\textsubscript{n}^{\delta+}}

In recent work [48] Satokawa and co-workers suggested that the active sites are small silver clusters. They observed same structure–activity relationship and supposed that the small silver clusters, probably the Ag\textsubscript{4}\textsuperscript{2+}, are responsible for the selective reduction of NO by C\textsubscript{3}H\textsubscript{8} [49].

It can be concluded that the definite conclusion on the structure of active site in Ag/Al\textsubscript{2}O\textsubscript{3} at SCR-NO has not been made.
14.7 Reaction mechanism of selective catalytic reduction of NOx by hydrocarbons over silver/alumina

The reaction mechanism of HC-SCR-NOx over Ag/Al₂O₃ catalyst, including several reaction steps, is extremely complex. Much attention has been devoted to elucidation of the reaction mechanisms but so far it is not completely understood.

The in-situ FTIR spectroscopy investigations under the HC-SCR-NOx reaction were used to try to identify key reaction intermediates [16,50,51,52]. From these extensive studies, it is clear that several intermediates are present under reaction conditions – nitrates and nitrites, cyanides and isocyanates, carboxylates and acetates and organo-nitrogen species. However, it is less clear which species are true intermediates or spectator species in the NO reduction to N₂. Shimizu et al. [16] on the basis of their results, and those given in the literature proposed a set of reaction steps (not elementary) for SCR-NO by hexane. They suggested that the reaction starts with formation of adsorbed nitrates via NO oxidation by O₂ (7) and formation of acetates by partial oxidation of a hydrocarbon with O₂ (8).

\[
\begin{align*}
\text{NO} + 1/2\text{O}_2 &\rightarrow \text{NO}_2^- \text{ (NO}_2 \text{ on O}_2^-) \\
n\text{C}_6\text{H}_{14} + \text{O}_2 &\rightarrow \text{CH}_3\text{COO}^- + \text{CO}_x
\end{align*}
\]

(7) (8)

The acetate, which acts as a surface reductant, reduces nitrates via several steps to N₂. N-containing hydrocarbon species, Ag⁺ -NCO and -CN adspecies, are formed, possibly via organo-nitrogen species (9,10) [12,50]. Ag⁺ -NCO and -CN adspecies react with nitrates and O₂ to produce N₂, (12) [51,52].

\[
\begin{align*}
\text{NO}_2^- + \text{CH}_3\text{COO}^- &\rightarrow \text{organo-N species} \\
\text{organo-N species} &\rightarrow \text{NCO and/or CN} \\
\text{NCO and/or CN + NO}_2 \text{ or } \text{O}_2 &\rightarrow \text{N}_2
\end{align*}
\]

(9) (10) (11)

NH₃ may be easily produced through hydration of NCO⁻ and CN⁻ species (12) [12,53] and can further react with NO₂ to produce N₂ (13) [12,53,54].

\[
\begin{align*}
\text{NCO and/or CN + H}_2\text{O} &\rightarrow \text{NH}_3 \\
\text{NH}_3 + \text{NO}_2 &\rightarrow \text{N}_2
\end{align*}
\]

However He et al. [55] showed that C₃H₆ at C₃H₆-SCR-NO over Ag/Al₂O₃ and Cu/Al₂O₃ can be partially oxidized into enolic species and acetate species on the catalysts. The enolic species is more reactive intermediate for the formation of NCO species via the reaction with NO + O₂ than acetate species. However, the C₃H₆ can only be partially oxidized into acetate species
and then CO₂ on the Cu/Al₂O₃ catalyst. This has been indicated as the main reason why the activity of the Cu/Al₂O₃ catalyst for NO reduction is much lower than that of the Ag/Al₂O₃ catalyst.

In addition to the clearly surface reactions, Eränen et al. [56] showed that the formation of a part of N₂, might take place in the gas phase in a short distance after the catalyst bed [56,57]. They showed that gas-phase reactions are initiated on the catalyst surface and proceeds in the free gas volume in the reactor behind the catalyst. Matrix isolation combined with EPR and FTIR technique at low temperature revealed formation of radicals of low molecular weight at the gas phase involved in SCR-NOx over a highly active Ag/Al₂O₃ catalyst.

It should be emphasis that the details of the reaction mechanism depend on gas composition, loading of silver, choice of reductant, choice of support and can vary with temperature.

1.5 Enhancement of decane-SCR-NOx over silver catalyst by hydrogen.

In 2000 was discovered that the NO reduction by C₃H₈ over Ag/Al₂O₃ could be dramatically increased by adding H₂ into the feed in the presence of excess of oxygen and water vapor [58]. The positive effect of hydrogen on NOx conversion was predominantly observed at lower temperature region (590–760 K). Since NOx reduction to N₂ by H₂ was negligible in the absence of hydrocarbons, H₂ should act as a promoter of the NO reduction by hydrocarbons over Ag/Al₂O₃ [58]. NOx conversion at the low temperature region increased with increasing concentration of H₂ [58]. This discovery has not attracted attention in scientific community until 2003. Later, during performance of this study, this positive hydrogen-effect has invoked a high interest [20,49,59,60,61,62,63,64,65,66,67,68]. There have been proposed a mechanism and reason for the increase in the rate of NOx reduction and individual reaction steps of SCR-NOx. However, up to now there has not been given a definite conclusion.
Aim of the study

The aim of the study has been understanding of the structure and operation of silver alumina catalyst in transformation of NOx to N₂ in exhaust gases of diesel engines by using selective catalytic reduction of NOx with decane, as main component of diesel fuel, and under co-assistance of hydrogen.

To analyse the state and behaviour of silver species in Ag/alumina catalyst at the SCR-NOx process and the dramatic positive effect of co-fed hydrogen, the individual reaction steps, i.e. oxidation of NO, decane and H₂ were also investigated. The purpose of co-feeding of carbon monoxide and hydrogen peroxide was to bring about an additional insight into the function of hydrogen in the SCR-NOx process.

FTIR, UV-Vis-NIR and TPR by H₂ techniques were used to obtain relevant information on the state of silver. Of high importance was performance of the in-situ UV-Vis study carried out at the H₂/C₁₀H₂₂-SCR-NOx reactions and it steps, monitoring real behaviour of silver species on alumina at true reaction conditions.

The study was a part of the European project “Advanced nanostructured metal/metal-oxo/matrix catalysts for redox processes. Application for NOx reduction to nitrogen” carried out through 2001-2004 to solve abatement of NOx in exhausts of diesel engines.
2 Experimental

2.1 Catalysts preparation

2.1.1 Silver zeolite catalysts

A MFI zeolite provided by IIC (Na\(^+\) form, Si/Al = 12.5, crystal size 0.5 \(\mu\)m) was used for preparation of silver zeolite catalysts. To obtain an NH\(_4\)\(^+\) form, the zeolite was ion exchanged repeatedly (4x) with 1 M NH\(_4\)NO\(_3\) solution at RT for 12 h\(^{-1}\) (1,000 ml of solution per 20 g of zeolite), washed several times with distilled water, filtered and dried in open air at room temperature. Silver zeolite catalysts were prepared by ion exchange of the MFI zeolite with a solution of AgNO\(_3\) (100 ml of solution per 1 g of zeolite). The Na\(^+\) and NH\(_4\)\(^+\) forms of the MFI zeolite were used to prepare AgNa-MFI and AgNH\(_4\)-MFI catalysts, respectively. After the Ag\(^+\) ion exchange the silver zeolites were filtered, washed several times by distiller water and dried in open air at RT. The conditions of preparation and composition of silver zeolite catalysts are given in Tab. 2-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conditions of preparation</th>
<th>Composition of Ag-zeolites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of AgNO(_3) solution (mol.dm(^{-3}))</td>
<td>Time (h)</td>
</tr>
<tr>
<td>AgNH(_4)-MFI-1.4</td>
<td>0.002</td>
<td>24</td>
</tr>
<tr>
<td>AgNH(_4)-MFI-4.2</td>
<td>0.01</td>
<td>24</td>
</tr>
<tr>
<td>AgNa-MFI-5.9</td>
<td>0.01</td>
<td>24</td>
</tr>
</tbody>
</table>

2.1.2 Silver alumina catalysts

Alumina supported silver catalysts were supplied by Laboratory of Industrial Chemistry, Abo Akademi University, Turku. The catalysts were prepared by impregnation of a commercial alumina support (< 250 \(\mu\)m, LaRoche, specific surface area 289 m\(^2\)g\(^{-1}\)) with aqueous silver nitrate solution. The conditions of preparation and composition of the catalysts are given in Tab. 2-2.
Table 2-2 Preparation and composition of silver alumina catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of AgNO₃ solution (mol dm⁻³)</th>
<th>Time (h)</th>
<th>Concentration of Ag (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Al₂O₃-1.3</td>
<td>0.011</td>
<td>24</td>
<td>1.28</td>
</tr>
<tr>
<td>Ag/Al₂O₃-1.8</td>
<td>0.022</td>
<td>24</td>
<td>1.76</td>
</tr>
<tr>
<td>Ag/Al₂O₃-2.9</td>
<td>0.033</td>
<td>24</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Chemical analysis of all the above catalysts was carried out after their dissolution by Atomic Absorption Spectrometry at the Institute of Inorganic Chemistry Academy of Sciences, CR.

2.2 Catalyst testing in the C₁₀H₂₂-SCR-NOₓ reactions, and NO, H₂ and C₁₀H₂₂ oxidation

2.2.1 Catalytic apparatus

The silver based catalysts were tested in selective catalytic reduction of NO and NO₂ with decane (C₁₀H₂₂-SCR-NO, C₁₀H₂₂-SCR-NO₂). Decane as a main component of diesel fuel, considered as a model hydrocarbons reductant. A fixed-bed through-flow quartz reactor placed in a catalytic apparatus (Fig. 2-1) was used to investigate the catalyst activity in C₁₀H₂₂-SCR-NO and C₁₀H₂₂-SCR-NO₂ and in oxidation of NO, H₂ or C₁₀H₂₂ by molecular oxygen. The effect of additional components (H₂, H₂O₂ and CO) in gas stream was also investigated.

The feed consists of helium and concentrations of NO, NO₂, n-C₁₀H₂₂, O₂, H₂O, H₂O₂, H₂, CO in He, in the range 0 - 1000 ppm NO, 0 - 1000 ppm NO₂, 0 – 1200 ppm n-C₁₀H₂₂, 0 – 12 vol. % O₂, 0 or 12.0 % H₂O, 0 - 7200 ppm H₂, 0 or 7200 ppm CO and 0 or 2000 ppm H₂O₂. The typical composition of gases in the inlet of the reactor with the C₁₀H₂₂-SCR-NOₓ reaction was 1000 ppm NO, 300 ppm n-C₁₀H₂₂, 6% O₂, 12 % H₂O and 0 or 2000 ppm H₂. Feed compositions for the individual experiments are given in Chapter 3. The flow rates of gases were controlled by gas mass-flow controllers (Elmet, C gas 02). Water and decane vapor were dosed by saturators, kept by thermostats (GRANT, thermostat GD 120) at constant temperature corresponding to the equilibrium decane or water vapor pressure necessary for obtaining appropriate concentrations in the gas inlet. Vapour of hydrogen peroxide was dosed directly into the reactor by linear dosing.
device (Institute of Scientific Instruments, LD 2) equipped with 'home-made' Teflon-coated evaporator. The weight of the catalyst (grains 0.3-0.5 mm) was 26 - 210 mg and the flow rate of 150 cm$^3$.min$^{-1}$, which corresponded to GHSV of 30,000 – 240,000 h$^{-1}$. Temperature of the catalyst was kept in the range 323 – 723 K controlled by an oven equipped by temperature-controller (Eurotherm 2216). The catalysts were calcined in a stream of oxygen at 723 K for 1 h prior to each catalytic test.

2.2.2 Product analysis

NO, NO$_2$, N$_2$, N$_2$O, H$_2$, CO, CO$_2$ and C$_{1-10}$ hydrocarbons were analysed. Concentrations of NO and NO$_2$ (NOx) were monitored by a NO/NOx chemiluminescence analyser (Horiba CLA-355K), enabling determination of NOx in the presence of high concentration of water vapor. The concentrations of N$_2$, N$_2$O, H$_2$, CO, CO$_2$ and C$_{1-10}$ hydrocarbons were determined by an on-line connected gas chromatograph (GC Hewlett Packard 6090). For GC analysis two gaseous samples were simultaneously injected using two 10-th port valves. In one branch with thermal conductivity detector (TCD), Haysep column was used for retention and removal of organic compounds and water, and columns of Poraplot Q (30 m x 0.53 mm, d$_f$ = 40 μm) and two Molecular sieve 5A (30 m x 0.53 mm, d$_f$ = 25 μm) were used for separation of H$_2$, O$_2$, N$_2$, CO$_2$, CO and N$_2$O. Poraplot Q column separated CO$_2$ from H$_2$, O$_2$, N$_2$, CO and N$_2$O. The 6-th port valve was used to by-pass Molecular sieve 5A columns during the analysis of CO$_2$ on TCD. After the analysis of CO$_2$, mixture of H$_2$, O$_2$, N$_2$, CO and N$_2$O was separated with column Molecular sieve 5A and monitored on TCD. In the second branch DG-200 column was used for retention and removal of inorganic compounds and water. C$_{1-10}$ hydrocarbons were separated on a non-polar HP-5 column (50 m x 0.53 mm, d$_f$ = 15 μm) and monitored by flame ionisation detector (FID). Accuracy of measurement for this experimental set up was < 5% expressed as relative error of measurement ($\delta_{(X)}$). $\delta_{(X)} = 100 \cdot \Delta x / X_{(m)}$, where $X_{(m)}$ is measured value and $\Delta x$ is absolute error of measurement.
<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oven</strong></td>
<td>Constant temperature 313 K for 21.5 min, ramp 40 K.min(^{-1}) up to 473 K and constant temperature for 44 min</td>
</tr>
<tr>
<td><strong>Branch with FID detector</strong></td>
<td>Column DG-200, Column HP-5 Al(_2)O(_3) &quot;M&quot; deactivated (50 m x 0.53 mm, (d_f = 15 \mu m))</td>
</tr>
<tr>
<td></td>
<td>Loop volume 0.250 ml, Load Time 0.5 min, Pressure 10 psi, Total flow 90 ml.min(^{-1}), Flow in columns 8.2, Split 1:10</td>
</tr>
<tr>
<td></td>
<td>Rinsing of DG-200 column from 15 min, flow of He at constant pressure 10 psi</td>
</tr>
<tr>
<td></td>
<td>Valves at 423 K, Auxiliaries at 453 K, Split at 423 K</td>
</tr>
<tr>
<td></td>
<td>FID detector: (T = 523) K, 40 ml.min(^{-1}) (H_2), 400ml.min(^{-1}) Air, 10 ml.min(^{-1}) He (Make up gas flow)</td>
</tr>
<tr>
<td><strong>Branch with TCD detector</strong></td>
<td>Column Haysep, Poraplot Q (30 m x 0.53 mm, (d_f = 40 \mu m)), 2x Molecular sieve 5A (30 m x 0.53 mm, (d_f = 25 \mu m))</td>
</tr>
<tr>
<td></td>
<td>Loop volume 1 ml, Load Time 0.5 min, Pressure 20 psi, Splitless, By-pass of Molecular sieve 5A at 5.1-10.0 min</td>
</tr>
<tr>
<td></td>
<td>Rinsing of Haysep column from 13.5 min, flow of He at constant pressure 15 psi</td>
</tr>
<tr>
<td></td>
<td>Valves at 423 K, Auxiliaries at 453 K, Split at 423 K</td>
</tr>
<tr>
<td></td>
<td>TCD detector: (T = 523) K, Makeup gas flow: 6 ml.min(^{-1}) He, Reference gas flow: 25 ml.min(^{-1}) He</td>
</tr>
</tbody>
</table>
### Table 2-4 Retention time for the individual inorganic compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Columns</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Haysep and Poraplot Q</td>
<td>8.1</td>
</tr>
<tr>
<td>H₂</td>
<td>Haysep, Poraplot Q, 2x Molecular sieve 5A</td>
<td>11.1</td>
</tr>
<tr>
<td>O₂</td>
<td>Haysep, Poraplot Q, 2x Molecular sieve 5A</td>
<td>12.8</td>
</tr>
<tr>
<td>N₂</td>
<td>Haysep, Poraplot Q, 2x Molecular sieve 5A</td>
<td>14.0</td>
</tr>
<tr>
<td>CO</td>
<td>Haysep, Poraplot Q, 2x Molecular sieve 5A</td>
<td>16.4</td>
</tr>
<tr>
<td>N₂O</td>
<td>Haysep, Poraplot Q, 2x Molecular sieve 5A</td>
<td>28.2</td>
</tr>
</tbody>
</table>

### Table 2-5 Retention time for the individual organic compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Columns</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>DG-200, HP-AL/M</td>
<td>2.1</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>DG-200, HP-AL/M</td>
<td>2.8</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>DG-200, HP-AL/M</td>
<td>4.2</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>DG-200, HP-AL/M</td>
<td>9.5</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>DG-200, HP-AL/M</td>
<td>12.4</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>DG-200, HP-AL/M</td>
<td>14.8</td>
</tr>
<tr>
<td>n-C₁₀H₂₂</td>
<td>DG-200, HP-AL/M</td>
<td>58</td>
</tr>
</tbody>
</table>
Conversion of the reactants i, i.e. NO, NO$_2$, C$_{10}$H$_{22}$, H$_2$ was defined as
\[ x_i = \left( (c^0_i - c_i)/c^0_i \right) \times 100 \text{ (\%)} \]  
(2-1)
where $c^0_i$ is the concentration (ppm) of the reactant i before inlet of the reactor and $c_i$ is the concentration of the reactant i after outlet of the reactor.

Yields of N$_2$ and N$_2$O related to NO or NO$_2$ and yields of CO, CO$_2$ related to C$_{10}$H$_{22}$ were defined as
\[ y_j = \left( v_j \cdot c_j/c_i \cdot c^0_i \right) \times 100 \text{ (\%)} \]  
(2-2)
where $c_j$ is the concentration (ppm) of the product j i.e. N$_2$, N$_2$O, CO, CO$_2$, in the reactor outlet and $v_j$ is the number of C or N atoms in the corresponding molecule, $c^0_i$ is the concentration (ppm) of the reactant i, i.e. NO or C$_{10}$H$_{22}$, in the reactor inlet and $v_i$ is the number of C or N atoms in the corresponding molecule.

The conversion values were calculated from the product compositions obtained at the steady-state conditions of the reaction, corresponding to a constant product composition obtained at about 60-120 min of time on stream (TOS). In selected cases NOx transformation was followed depending on TOS.

Selectivity of reductant utilization is given by the parameter $s$ that relates the oxygen atoms supplied by NO to all oxygen atoms reacted with decane theoretically to CO$_2$ and H$_2$O at SCR-NOx process.

\[ s = \left( x_{\text{NOx}} \cdot c^0_{\text{NO}} \cdot 31 \right)/(100 \cdot x_{\text{decane}} \cdot c^0_{\text{decane}}) \text{ (\%)} \]  
(2-3)
where $x_{\text{NOx}}$ is the conversion of NOx to N$_2$, $c^0_{\text{NO}}$ and $c^0_{\text{decane}}$ is the concentration (ppm) of NO and decane before inlet of the reactor, respectively and $x_{\text{decane}}$ is the conversion of decane to COx.

Turnover frequencies (TOF), i.e. molecules of NO converted to N$_2$ or N$_2$O per Ag atom per second, was calculated from equation

\[ \text{TOF} = \left( F \cdot c^0_{\text{NO}} \cdot y_{N_2+N_2O} \cdot M(\text{Ag}) \right) \times 10^5/(V_m \cdot w \cdot m) \text{ (s}^{-1} \)  
(2-4)
where $F$ is the total flow of the reaction mixture (dm$^3$. s$^{-1}$), $V_m$ is the gas molar volume (22.4 dm$^3$), $c^0_{\text{NO}}$ is the concentration of NO (ppm) in the inlet of the reactor, $y_{N_2+N_2O}$ is the yield of N$_2$ and N$_2$O (\%), $w$ is content of Ag in a silver alumina catalyst (wt.\%), $m$ is weight of catalyst and $M(\text{Ag})$ is an atomic weight of Ag (g.mol$^{-1}$).
Fig. 2-1. Arrangement of the catalytic tests apparatus.

1. Gas mass flow controllers (Elmet, C gas 02)
2. Water saturators heated by thermostat (GRANT, GD 120)
3. Decane saturators heated by thermostat (GRANT, GD 120)
4. Linear dosing device (Institute of Scientific Instruments, LD 2) equipped with teflon-coated evaporator
5. Fixed-bed through-flow quartz reactor
6. Oven equipped by temperature controller (Eurotherm 2216)
7. Gas chromatograph (Hewlett Packard 6090)
8. NO/NOx chemiluminescence analyser (Horiba, CLA-355K)
2.3 H₂-TPR

The reducibility of silver supported on alumina and in a zeolite was measured by temperature-programmed reduction (H₂-TPR). H₂-TPR profiles were obtained on a Zeton Altamira AMI-200 under conditions of sample weight 0.1 g, heating rate of 20 K.min⁻¹ (from 308 to 723 K), flow rate 30 cm³.min⁻¹, water formed at the H₂-TPR was removed by cooling trap and the hydrogen consumption was monitored by thermal conductivity detector (TCD).

2.4 FTIR spectroscopy

The FTIR spectra were recorded on a thin self-supporting wafer (ca 10 mg/cm²) of alumina and silver alumina catalyst. The wafers were placed in an IR cell equipped with KBr windows and connected to vacuum/adsorption apparatus. Alumina and silver alumina were at first dehydrated in air at increasing temperature of 3 K.min⁻¹ up to 723 K, than kept at constant temperature and than evacuated to reach a final vacuum of 10⁻⁵ Pa. Then the alumina and silver alumina were cooled to RT and d₃-acetonitrile was adsorbed (20 min, RT, 10³ Pa) followed by evacuation at RT for 20 min. Spectra were collected at RT prior and after d₃-acetonitrile adsorption. FTIR spectra were measured in the interval from 1,000 to 4,000 cm⁻¹ with a resolution of 2 cm⁻¹ on the Nexus 670 FTIR spectrometer (Thermo Nicolet Co.) equipped with DTGS KBr detector.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral range</td>
<td>1,000 to 4,000 cm⁻¹</td>
</tr>
<tr>
<td>No. of scans</td>
<td>128</td>
</tr>
<tr>
<td>Aperture</td>
<td>69</td>
</tr>
<tr>
<td>Gain</td>
<td>2</td>
</tr>
<tr>
<td>Beamsplitter</td>
<td>KBr</td>
</tr>
<tr>
<td>Detector</td>
<td>DTGS KBr</td>
</tr>
<tr>
<td>Windows</td>
<td>KBr</td>
</tr>
</tbody>
</table>
2.6 **Diffuse reflectance UV-Vis-NIR spectroscopy**

The state of Ag on alumina and in a zeolite was monitored by UV-Vis-NIR spectroscopy. The diffuse reflectance UV-Vis-NIR spectra were collected on a Perkin Elmer UV-Vis-NIR spectrometer Lambda 19 using diffuse reflectance attachment with an integrating sphere. The sphere was coated with BaSO₄ and as a reference BaSO₄ powder was used. The spectra were recorded in the range from 4,000 to 50,000 cm⁻¹ at a speed of 480 nm.s⁻¹, scanning step 1 nm and slit width 5 nm. The $F(R_{∞})$ function was calculated from the Schuster-Kubelka-Munk equation

$$ F(R_{∞}) = \frac{(1 - R_{∞})^2}{2R_{∞}} $$

where $R_{∞}$ is the diffuse reflectance from a semi-infinite layer. $F(R_{∞})$ is proportional to the concentration of absorbing species in solids.

2.4.1 **Ex-situ diffuse reflectance UV-Vis-NIR spectroscopy**

Granulated silver alumina or silver zeolite samples (300 – 600 μm) were activated in an oxygen stream at 723 K for 1 h in a quartz reactor and cooled to 423 K in an oxygen atmosphere, followed by evacuation at 423 K using a pressure of $7 \times 10^{-2}$ Pa for 15 min. Such treated Ag-samples were transferred under vacuum into the quartz cell (QC, SUPRASIL) of 5 mm thickness and their spectra were recorded.

2.4.2 **In-situ diffuse reflectance UV-Vis-NIR spectroscopy**

Heated home-made through-flow quartz optical cell (Fig. 2-2) was constructed and used to obtain the spectra under the conditions of the catalytic reactions. The optical cell, placed in the oven with a window for a beam pathway, was attached to the surface of the integrating sphere. *In-situ* UV-Vis-NIR measurements carried out at conditions of the catalytic reaction were run at the reaction temperature of 473 and 523 K and at the identical conditions of reactant compositions and GHSV values as the catalytic tests in the standard micro-reactor set up. Reactant feed was mixed by a mixing station consisting of dosing system for gases, gas mass-flow controllers and saturators for water and decane. The arrangement is similar to that used for the catalytic tests (Fig. 2-1).
Fig. 2-2. Scheme of experimental arrangement of in-situ UV-Vis-NIR spectroscopy (A) and the UV-Vis-NIR heated through-flow optical quartz cell (B).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start wavelength</td>
<td>2,500 nm</td>
</tr>
<tr>
<td>End wavelength</td>
<td>190 nm</td>
</tr>
<tr>
<td>Data interval</td>
<td>1.0 nm</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>1</td>
</tr>
<tr>
<td>Scan speed</td>
<td>480 nm.min⁻¹</td>
</tr>
<tr>
<td>Slit</td>
<td>5 nm</td>
</tr>
<tr>
<td>Lamp change</td>
<td>320 nm</td>
</tr>
<tr>
<td>Detector change</td>
<td>860 nm</td>
</tr>
</tbody>
</table>
3 Results

Silver alumina catalysts with silver loading around 2 wt.% have been shown as highly active in CH-SCR-NOx, while higher silver content led to catalysts much less effective [14]. Thus in this study silver alumina catalysts with silver loadings in the 1.28–2.88 wt.% Ag range have been analysed with respect to the activity in SCR-NOx and state of silver. The catalytic performance and structural analysis of Ag-MFI zeolite as the most active silver zeolite based catalyst [31] has also been investigated especially with purpose to explain same structural and catalytic features of Ag/Al₂O₃ catalyst.

3.1 Characterisation of the silver catalyst structure

3.1.1 UV-Vis spectra of silver alumina

Fig. 3-1 shows UV-Vis spectra of Ag/Al₂O₃ catalysts oxidized and dehydrated at 723 K followed by evacuation at 423 K for 15 min. According to the literature the UV-Vis bands can in general be ascribed as follows: (i) the bands above 40,000 cm⁻¹, including also the absorption bands above 50,000 cm⁻¹ (out of the accessible spectral range here), belong to the electronic transitions of Ag⁺ cations [43], (ii) the bands in the range 27,000 – 40,000 cm⁻¹, can be attributed to small metallic Agₙ⁺⁺ clusters (n ≤ 8) [43] (with the increasing number of Ag atoms in the cluster decreases the wavenumber [43]), and (iii) the bands below 27,000 cm⁻¹ can be ascribed to large or oxide-like silver particles (for details of UV-Vis bands attribution see the Discussion).

The investigated Ag/Al₂O₃ catalysts with Ag content ranging from 1.28 to 2.88 wt.% treated in an oxygen stream exhibit the bands at 41,600 and 46,000 cm⁻¹ assigned to single Ag⁺ ions. A small intensity observed as a shoulder at 30,000 – 38,000 cm⁻¹ was found and it increased with metal content of the catalyst. This finding indicates that the shoulder could be ascribed to small metallic Agₙ⁺⁺ clusters formed during the procedure of catalyst evacuation. Same increase in the absorbance intensity around and above 50,000 cm⁻¹ might indicate presence of additional band, but this spectral region is out of the measurements of our and all-standard UV-Vis spectrometers.
Fig. 3-1. UV-Vis spectra of Ag/Al₂O₃ catalyst calcined in an oxygen at 723 K followed by evacuation at 423 K for 15 min.

3.1.2 UV-Vis spectra of silver MFI

Two bands centred at 42,400 and 46,400 cm⁻¹ are observed in UV-Vis spectral region for all the investigated Ag zeolites (Fig. 3-2). The bands are ascribed to the single Ag⁺ ions. AgNH₄-MFI-4.2 and AgNa-MFI-5.9 catalysts show well-distinguished maxima of the bands. The spectrum of AgNH₄-MFI-1.4 shows only a broad profile due to low concentration of silver and due to weak absorption bands at 28,000 – 44,000 cm⁻¹ of iron impurities (0.1 wt.% Fe). The third strong band with maximum at 37,500 cm⁻¹ appeared in the spectrum of the AgNa-MFI zeolite. The position of the band indicates that it corresponds to small Agₙ⁺⁺⁺ intrazeolitic clusters (n ≤ 8). Presence of the Agₙ⁺⁺⁺ clusters for AgNa-MFI-5.9 could be explained by lower mobility of Ag⁺ in Na-form of zeolite. Hence Agₙ⁺⁺⁺ clusters present in channels of Na⁺ zeolite after catalyst preparation can hardly be dispersed during calcination in a dry O₂ stream. Formation of Agₙ⁺⁺⁺ clusters in AgNa-MFI compared to AgNH₄-MFI could be also explained by easier reducibility of Ag⁺ ions in Na-form zeolite compared to H-forms as the presence of H⁺ cations shifts the equilibrium to the Ag⁺ ions.
Fig. 3-2. UV-Vis spectra of Ag/zeolite calcined in oxygen at 723 K followed by evacuation at 423 K for 15 min. AgNa-MFI-5.9 (---), AgNH$_4$-MFI-4.2 (----) and AgNH$_4$-MFI-1.4 (-----).

3.1.3 \textit{H}_2\text{-TPR of silver catalysts}

All Ag/Al$_2$O$_3$ samples contain reducible Ag$^+$ ions as follows from H$_2$-TPR experiments after the \textit{in-situ} pre-treatment in O$_2$ for 1 h at 723 K (Fig. 3-3, Table 3-1). The position of the temperature maxima of hydrogen consumption over Ag/Al$_2$O$_3$ samples is slightly shifted to lower temperatures with increasing Ag loading. This indicates easier formation of metallic silver clusters at higher silver loading. The degree of Ag reduction was calculated according to the stoichiometry that 1 mol Ag$^+$ requires 1/2 mol H$_2$. The values of the blank H$_2$-TPR run with the alumina support shows hydrogen consumption of 5.2 \textmu mol of H$_2$ g$^{-1}$ below 723 K (well below 10\% of that for Ag/Al$_2$O$_3$), taken into account for the quantitative analysis. As all silver is in the monovalent state in the calcined Ag/Al$_2$O$_3$ (Fig. 3-1), the reduction degree indicates that a part of Ag$^+$ ions was not reduced under hydrogen flow below 723 K. A continuous hydrogen consumption above 870 K was reported with Ag/Al$_2$O$_3$ [18].

The H$_2$-TPR curve of AgNH$_4$-MFI-4.2 after treatment in O$_2$ for 1 h at 773 K (Fig. 3-3) shows three temperature maxima of hydrogen consumption at around 410, 475 and 605 K. It
clearly indicates that Ag⁺ ions in the zeolite are much more easily reducible than that in alumina. The amount of H₂ uptake by the AgNH₄-MFI-4.2 catalyst corresponded to the reduction of all Ag⁺ ions to Ag⁰ (Table 3-1).

![Graph showing H₂-TPR profiles of silver catalysts.]

**Fig. 3-3.** H₂-TPR profiles of silver catalysts.

**Table 3-1.** H₂-TPR data of silver catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag content (wt.%)</th>
<th>H₂ consumption* (µmol.g⁻¹)</th>
<th>Ag content (µmol.g⁻¹)</th>
<th>Reduction degree b (%)</th>
<th>Peak maximum T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Al₂O₃-1.3</td>
<td>1.28</td>
<td>51.2</td>
<td>118.6</td>
<td>86.3</td>
<td>595</td>
</tr>
<tr>
<td>Ag/Al₂O₃-1.8</td>
<td>1.76</td>
<td>72.5</td>
<td>163.0</td>
<td>89.0</td>
<td>589</td>
</tr>
<tr>
<td>Ag/Al₂O₃-2.9</td>
<td>2.88</td>
<td>71.6</td>
<td>266.8</td>
<td>53.6</td>
<td>576</td>
</tr>
<tr>
<td>AgNH₄-MFI-4.2</td>
<td>4.20</td>
<td>192.2</td>
<td>389.0</td>
<td>98.8</td>
<td>409, 474, 605</td>
</tr>
</tbody>
</table>

* H₂ consumption up to 723 K  
  b 2Ag⁺ + H₂ → 2Ag⁰ + 2H⁺
3.1.4 Interaction of silver with the support at the silver catalysts

3.1.4.1 NIR spectra of silver MFI

The coordination of Ag\(^+\) ions to bridging oxygen atoms can be observed by changes in OH groups after introduction of the cation into the zeolite. To detect OH groups in silver zeolites diffuse reflectance spectroscopy in the NIR region was used. An advantage of this technique is simultaneous monitoring of vibrations of OH groups and electronic transitions of Ag species. The diffuse reflectance measurements have been performed over the working range from 4,000 to 50,000 cm\(^{-1}\) (2,500 to 200 nm). Thus both the electronic state of silver (Fig. 3-2) and the OH groups (Fig. 3-4) can be evaluated on the sample at the same conditions. This is especially important for the systems exhibiting high versatility of the metal redox state.

Two regions of NIR spectra of oxidized and dehydrated AgNa-MFI-5.9, AgNH\(_4\)-MFI-4.2 and AgNH\(_4\)-MFI-1.4 catalysts and parent NH\(_4\)MFI are shown in Fig. 3-4. In the first region (4,000-5,000 cm\(^{-1}\)) the bands are ascribed to combination vibrations of hydroxyl groups (\(v_{0-\delta}\) + \(\delta\)). The bridging hydroxyl groups (Brönsted acids sites), originated from NH\(_4^+\) ions by their thermal decomposition to H\(^+\) (bridging OH groups) and NH\(_3\), are shown by the bands with maxima at 4,660 cm\(^{-1}\) (\(v_{0-\delta}\),OH (3.610 cm\(^{-1}\)) + \(\delta_{0-\delta}\),OH (1.050 cm\(^{-1}\))) [70]. The intensity of the band of the bridging hydroxyl groups linearly decreases with increasing loading of silver cations for AgNH\(_4\)-1.4 and AgNH\(_4\)-MFI-4.2 samples. With AgNa-MFI-5.9 a negligible intensity of Brönsted site is present. The absorption bands with maximum at 4,530 cm\(^{-1}\) (\(v_{0-\delta}\),SiOH (3.745 cm\(^{-1}\)) + \(\delta_{0-\delta}\),SiOH (785 cm\(^{-1}\))) [70] demonstrate the terminal Si-OH bands. Their intensities are the same for all the samples. It indicates that terminal Si-OH groups are not exchanged by Ag\(^+\) ions. The absence of the band at 5,280 cm\(^{-1}\) confirms complete dehydration of the investigated samples, but for brevity it is not depicted.

In the second region there is a group of partially overlapping bands corresponding to overtone vibrations of hydroxyls (\(v_{0-\delta}\)). The bands at 7,310 cm\(^{-1}\) represent the first overtone vibrations of terminal SiOH groups with fundamental vibration (\(v_{0-\delta}\),SiOH (3.745 cm\(^{-1}\)) [70]. The well-defined bands with maxima at 7,070 cm\(^{-1}\) are assigned to the first overtone vibrations of bridging hydroxyl groups (fundamental vibrations \(v_{0-\delta}\),OH (3.610 cm\(^{-1}\))). The intensity of the bands at 7,070 cm\(^{-1}\) decreases after Ag\(^+\) and Na\(^+\) introduction into a zeolite with the same extent as the intensity of the bands at 4,660 cm\(^{-1}\). The low intensity broad band (around 7,200 cm\(^{-1}\)) occurring between the vibrations of terminal and bridging hydroxyl groups are assigned to first
overtone vibrations of Al-OH species (fundamental vibrations \( v_{0\rightarrow1}\text{OH} \) (3,650 – 3,660 cm\(^{-1}\)). This low intensity band indicates only low number of defects in the zeolite.

Fig. 3-4. NIR diffuse reflectance spectra of Ag-zeolites calcined in oxygen at 723 K followed by evacuation at 423 K for 15 min. H-MFI (——), Ag\( \text{NH}_4\)-1.4 (---), Ag\( \text{NH}_4\)-MFI-4.2 (-----) and Ag\( \text{Na}\)-MFI-5.9 (----).

3.1.4.2 NIR spectra of silver alumina

The comparison of the spectra of zeolites and alumina allows attribution of the absorption bands of alumina in the NIR region to hydroxyl groups (Fig. 3-5). The absorption bands at 7,000 – 7,400 cm\(^{-1}\) represent first overtone of the hydroxyl-stretching mode and at 4,300 – 4,700 cm\(^{-1}\) combination stretching and deformation mode of hydroxyl groups. The overlapping bands of parent alumina exhibit maxima at 4,450, 4,500 and 4,560 cm\(^{-1}\) and at 7,200, 7,290 and 7,320 cm\(^{-1}\) in the first and second region, respectively. Ag/\( \text{Al}_2\text{O}_3\)-1.3 exhibited a decrease in the intensity of the bands at 7,200 and 7,320 cm\(^{-1}\). Higher silver loading did not lead to any further change in the intensity of the hydroxyl bands.
Busca et al. [71] described OH structures on alumina by FTIR spectra; two types of terminal OH bound to tetrahedral aluminium (v = 3,800 cm\(^{-1}\) and v = 3,770 cm\(^{-1}\)), terminal OH bound to octahedral aluminium (v = 3,740 cm\(^{-1}\)), bridged OH (v = 3,690 cm\(^{-1}\)) and tri-bridged OH (v = 3,590 cm\(^{-1}\)) were indicated. With superposition conservation of the absorption bands of the individual hydroxyl groups at fundamental and first overtone mode the bands at the NIR region can be tentatively assigned hereby: absorption with maximum 7,200 cm\(^{-1}\) to the bridged and/or tri-bridged hydroxyl groups, absorption with maximum 7,290 cm\(^{-1}\) to the terminal OH bound to octahedral aluminium and absorption with maximum 7,320 cm\(^{-1}\) to OH bound to tetrahedral aluminium.

This implies that a part of Ag\(^+\) species preferably interacts with bridged and/or tri-bridged hydroxyl groups and with terminal OH bound to tetrahedral aluminium. From the intensity of residual hydroxyl groups we can deduce that only a small part of hydroxyl groups could be exchangeable with Ag\(^+\) ions and that a substantial part of silver in higher loading samples interacts with alumina by a different manner.

![Graph](image)

**Fig. 3-5.** NIR diffuse reflectance spectra of Al\(_2\)O\(_3\) and Ag/Al\(_2\)O\(_3\) catalysts calcined in an oxygen stream at 723 K followed by evacuation at 423 K for 15 min. (a) Al\(_2\)O\(_3\), (b) Ag/Al\(_2\)O\(_3\)-1.3, (c) Ag/Al\(_2\)O\(_3\)-1.8, (d) Ag/Al\(_2\)O\(_3\)-2.9.
3.1.4.2 FTIR spectra of $d_3$-acetonitrile

To describe the interaction of silver with Lewis sites and/or basic sites of alumina adsorption of $d_3$-acetonitrile was used as a probe. Figure 3-6 shows difference FTIR spectra of Al$_2$O$_3$ and Ag/Al$_2$O$_3$-1.8 after $d_3$-acetonitrile adsorption (20 min, RT, $10^3$ Pa) and evacuation at RT. The bands at 2,255 and 2,110 cm$^{-1}$ exhibit the same positions as the bands for liquid CD$_3$CN [71] and thus correspond to the $\nu$(CN) and $\nu_2$(CD$_3$) modes of physisorbed CD$_3$CN on alumina [73, 74]. The second derivative mode of the spectrum in the region of 2,270 – 2,370 cm$^{-1}$ (absorbance around 2,320 cm$^{-1}$) and its decomposition to the Gaussian bands yields two bands with maxima with 2,313 and 2,327 cm$^{-1}$ (Fig. 3-7). The bands correspond to the $\nu$(CN) mode of CD$_3$CN interacting, through the N lone-pair, with strong (2,327 cm$^{-1}$) and weak (2,313 cm$^{-1}$) Lewis sites [73]. The intensities of the bands are substantially higher for Al$_2$O$_3$ than those for Ag/Al$_2$O$_3$-1.8. It evidences that silver interacts with both types of Lewis acid sites. Figure 3-7 and Table 3-2 show a higher decrease in the band intensity of strong Lewis sites. Only rough estimate of the number of interacting Lewis sites on the alumina support is possible. As silver species on alumina could also play a role of weak Lewis sites quantitative analysis cannot be done. The absence of the $\nu$(CN) bands shifted upward by 10-35 cm$^{-1}$ with respect to the liquid phase shows the absence of Bronsted acid centers of medium strength.

Absorption bands observed at 1,425, 1,515 and 1,575 cm$^{-1}$ (see Fig. 3-6) could be attributed to surface acetamide species, formed by a hydrolytic process and the component at 2,180 cm$^{-1}$ to physisorbed CD$_3$CN or to the polymerisation product(s) of CD$_2$CN$^-$ carbanion [73]. In Ref. [73] it is supposed that those species originate from acetonitrile interaction with basic sites. We also observed a new band at 2,715 cm$^{-1}$, which is ascribed to stretching band of OD groups [75]. A deuterium atom of CD$_3$ group in acetonitrile is eliminated with formation of the observed OD group and CD$_2$CN$^-$ carbanion. The bands are present on both alumina and silver alumina samples. The intensity of the band at 2715 cm$^{-1}$ is substantially higher on alumina than on silver alumina catalyst. The appearance of the products of basic catalysed reactions on alumina surface is also higher than that on silver alumina (cf. bands intensities at 1575, 1515, 1425 cm$^{-1}$).

It can be concluded that the introduction of Ag$^+$ ions leads to a decrease of both Lewis acid site and basic sites on alumina.
Fig. 3-6. Differential FTIR absorbance spectra of CD$_3$CN onto Al$_2$O$_3$ (A) and Ag/Al$_2$O$_3$-1.8 (B). The spectra were collected at RT on Al$_2$O$_3$ and Ag/Al$_2$O$_3$-1.8 (both calcined in air at 723 K) prior and after CD$_3$CN adsorption for 20 min at RT and 10$^3$ Pa followed by evacuation at RT for 20 min.

Fig. 3-7. Decomposition of the spectra of CD$_3$CN coordinated to Lewis sites to Gaussian curves in range 2,270 – 2,370 cm$^{-1}$, (Al$_2$O$_3$ (a) and Ag/Al$_2$O$_3$ (b)).
<table>
<thead>
<tr>
<th></th>
<th>Peak area at 2327 cm⁻¹</th>
<th>Peak area at 2313 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>4.04</td>
<td>4.85</td>
</tr>
<tr>
<td>Ag/Al₂O₃-1.8</td>
<td>1.47</td>
<td>3.44</td>
</tr>
</tbody>
</table>

3.2 Activity of silver catalysts in selective catalytic reduction of NOₓ

3.2.1 Selective catalytic reduction of NOₓ by decane over silver alumina catalyst

The activity of Ag/Al₂O₃ catalysts in the decane-SCR-NOₓ was tested at high value of GHSV (240,000 h⁻¹) and high concentration of reductant agent (600 ppm) to avoid complete conversion for highly active samples. The conversion values represent those at steady-state conditions, usually attained within 90 min.

Figs. 3-8a and 3-9a show general trends of conversions of both NOₓ and decane, which increase with temperature. At low conversion NO-N₂ values the dependence of conversions on temperature follows Arrhenius plot approx. up to the temperature of 623 K. Above 623 K the increase in NOₓ to N₂ conversion with temperature decline for Ag/Al₂O₃-1.8 and Ag/Al₂O₃-2.9, but not for Ag/Al₂O₃-1.3. The silver loading has a large effect on the NOₓ to N₂ conversion, which substantially increases with increasing loading of Ag in the catalysts from 1.3 to 1.8 wt.% Ag. Further increase of silver loading does not show promotion of NOₓ conversion in the whole temperature interval studied. To clarify the strong relationship between NOₓ to N₂ conversion and the Ag content in Ag/Al₂O₃ catalysts, turnover frequencies (TOF) for the SCR-NO at 573 and 673 K were depicted as a dependence on silver loading (Fig. 3-8b). The TOF for NO to N₂ reduction increases with increasing Ag loading up to ca 1.8 wt.% Ag and then decreases. That is, there is an optimum Ag loading for SCR-NOₓ activity.

All silver catalysts show high yield of N₂ (3-8a). Nevertheless, values of N₂O and N₂ yields at low temperatures reflected indispensable selectivity of NOₓ reduction to N₂O. At higher temperatures (> 620 K) increased only N₂ formation and the yield of N₂O become insignificant compared to the yield of N₂.

A part of NO was oxidized to NO₂ at the complex decane-SCR-NOₓ reaction. The conversion of NO to NO₂ increased with temperature up to 573 K. At 723 K conversion of NO to NO₂ become negligible for Ag/Al₂O₃-1.3, while it is significant for Ag/Al₂O₃-1.8.
Decane at C_{10}H_{22}-SCR-NOx was converted mostly to carbon oxides (Fig. 3-9a) and hydrocarbon-like products (Fig. 3-9b). Fig 3-9a shows that conversion of C_{10}H_{22} to CO and CO_{2} increases with temperature in the temperature interval of 523 - 723 K for Ag/Al_{2}O_{3}-1.8 and Ag/Al_{2}O_{3}-2.9, while with Ag/Al_{2}O_{3}-1.3 is rather low up to 673 K. This decane conversion corresponds to the NOx conversions. Yields of CO_{2} and CO shows that CO production is a drawback of all Ag/Al_{2}O_{3} catalyst studied. The quantitative analysis of decane and CO and CO_{2} showed that decane is converted predominantly to COx and only <10% of decane to hydrocarbon-like products. Fig. 3-9b depicts chromatograms of hydrocarbon-like products at C_{10}H_{22}-SCR-NO at 623 K. A spectrum of products was detected. Among them were low chain hydrocarbons (CH_{4}, C_{2}H_{6}, C_{2}H_{4}, C_{3}H_{8}, C_{3}H_{6}) other peaks might correspond to other hydrocarbons and their oxo/nitro-derivates. The GC signal intensity of the hydrocarbon-like products is highest over Ag/Al_{2}O_{3}-1.8, lower over Ag/Al_{2}O_{3}-2.9 and negligible over Ag/Al_{2}O_{3}-1.3 at 623 K it corresponds roughly to the conversion values of NOx conversion. The complexity of product composition disables analysis of all the products by GC equipped only with FID. The gaseous hydrocarbon-like products were analysed at the Laboratory of Industrial Chemistry AAU Turku, Finland within the EU cooperative research project. They detected by GC-MS minute concentrations of various hydrocarbons, oxygenates, amines and other N-containing hydrocarbons products over Ag/Al_{2}O_{3}-1.8 at C_{8}H_{10}-SCR-NOx. These products are involved in gas-phase reactions initiated on the catalyst surface and proceeding in the free gas volume of the reactor behind the catalyst bed. The contribution of gas phase reactions at SCR-NOx over Ag/Al_{2}O_{3} was also studied at Laboratory of Industrial Chemistry AAU [14], and this subject is not a matter of this study.

Fig. 3-9c shows the decane utilization that relates the oxygen atoms supplied by NO to all oxygen atoms reacted with the decane to CO_{2} and H_{2}O at the complex SCR-NOx process over Ag/Al_{2}O_{3} catalysts. The NOx conversions are negligible at 473 K, and thus selectivity values cannot be either estimated. It should be noted that a comparison of selectivity of various catalyst is correct if the conversion values over individual samples are similar. This condition cannot be fulfilled due to the high complexity of SCR-NOx process over Ag/Al_{2}O_{3}. However, the selectivity utilization of decane at SCR-NOx appears to be a parameter that describes non-selective consumption of decane by oxygen occurred at SCR-NOx. The values of selectivity
utilization show that Ag/Al₂O₃ catalysts exhibit the highest selectivity between 523 and 723 K and the selectivity decrease at higher temperature.

Fig. 3-8a. Conversion of NOx to N₂ and N₂O and yield of N₂ and N₂O at C₁₀H₂₂-SCR-NO over Ag/Al₂O₃ depending on temperature. Reaction conditions: 1,000 ppm NO, 600 ppm C₁₀H₂₂, 6% O₂, 12% H₂O, GHSV = 240,000 h⁻¹.
Ag/Al₂O₃-1.3 (-----), Ag/Al₂O₃-1.8 (——) and Ag/Al₂O₃-2.9 (-----).
Fig. 3-8b. TOF for NOx conversion at $C_{10}H_{22}$-SCR-NO over Ag/Al$_2$O$_3$ depending on silver content. Reaction conditions as for 3-8a.

Fig. 3-8c. Conversion of NO to NO$_2$ at $C_{10}H_{22}$-SCR-NO over Ag/Al$_2$O$_3$ depending on temperature. Reaction conditions as for 3-8a. Ag/Al$_2$O$_3$-1.3 (-----), Ag/Al$_2$O$_3$-1.8 (-----) and Ag/Al$_2$O$_3$-2.9 (-----).
Fig. 3.9a. Conversion of decane to COx and yield of CO₂ and CO at C₁₀H₂₁-SCR-NO over Ag/Al₂O₃ depending on temperature. Reaction conditions as for 3-8a. Ag/Al₂O₃-1.3 (-----), Ag/Al₂O₃-1.8 (——) and Ag/Al₂O₃-2.9 (——).
Fig. 3-9b. Chromatograms of GC analysis (FID signal) of gaseous products at C_{10}H_{22}-SCR-NO over Ag/Al_{2}O_{3}. Reaction conditions as for 3-8a.

Fig. 3-9c. Selectivity of decane utilization at C_{10}H_{22}-SCR-NO over Ag/Al_{2}O_{3} depending on temperature. Ag/Al_{2}O_{3}-1.3 (-----), Ag/Al_{2}O_{3}-1.8 (———) and Ag/Al_{2}O_{3}-2.9 (— — —). Reaction conditions as for 3-8a.
3.2.2 Selective catalytic reduction of NOx over silver alumina catalyst by decane and hydrogen

The results reported in the previous paragraph showed that the conversion of NOx is low at temperatures $< 623$ K, which is the region of temperatures important for NOx abatement in exhaust gases of diesel engines. It has been reported that hydrogen added to the feed substantially increases NOx conversions [58]. We attempt to analyse this effect. It is clearly seen that the conversion values at decane-SCR-NOx are much higher if hydrogen is added as a co-reactant into the reactant stream (cf. Fig. 3-10a,b and 3-11a with Fig. 3-8a,b and 3-9a). High values of NOx conversions were reached already at 573 K and were nearly constant up to 723 K for Ag/Al2O3-1.8. In the low temperature region the conversion of NO to N2O was slightly increased at hydrogen presence. N2O is mainly produced at temperatures 523-573 K. Turnover frequencies for the SCR-NO at 573 and 673 K indicate high increase in efficiency of NOx reduction at hydrogen presence in the reactant mixture (cf. Fig. 3-10b with 3-8b). Values of TOF show that ca 2 wt.% is an optimum Ag loading for C10H22-SCR-NOx co-assisted by hydrogen.

Presence of hydrogen in the reactant stream yielded also high activity in oxidation of NO to NO2 at SCR-NOx particularly at low temperatures (473-523 K). Conversion of NO to NO2 had a decreasing tendency at higher temperature (Fig. 3-10c).

The promotion effect of hydrogen was accompanied by the increase of decane conversion (cf. Fig. 3-11a with 3-9a). The decane conversion was significant already at temperatures of 473 - 523 K at hydrogen presence, whereas at hydrogen absence the conversion is negligible. Addition of hydrogen also induced an increase in concentration of the CHx-products over all the catalysts (Fig. 11b); nevertheless, decane was converted mostly to carbon oxides and only $< 10\%$ to hydrocarbon-like products.

Fig 3-11c shows that the H2 co-assistance at decane-SCR-NOx modifies the selectivity of decane utilization. H2 co-fed improves the selectivity particularly at low temperature region and the selectivity decreases with increasing temperature, as increases NOx conversion.
Fig. 3-10a. Conversion of NOx to N\textsubscript{2} and N\textsubscript{2}O and yield of N\textsubscript{2} and N\textsubscript{2}O at C\textsubscript{16}H\textsubscript{32}-SCR-NO co-assisted by hydrogen over Ag/Al\textsubscript{2}O\textsubscript{3} depending on temperature. Reaction conditions: 1,000 ppm NO, 600 ppm C\textsubscript{16}H\textsubscript{32}, 2,000 ppm H\textsubscript{2}, 6% O\textsubscript{2}, 12% H\textsubscript{2}O, GHSV = 240,000 h\textsuperscript{-1}.
Ag/Al\textsubscript{2}O\textsubscript{3}-1.3 (----), Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 (-----) and Ag/Al\textsubscript{2}O\textsubscript{3}-2.9 (--.--).
Fig. 3-10b. TOF for NOx conversion at H2/C10H22-SCR-NO over Ag/Al2O3 depending on silver content. Reaction conditions as for 3-10a.

Fig. 3-10c. Conversion of NO to NO2 at C10H22-SCR-NO over Ag/Al2O3 depending on temperature. Reaction conditions as for 3-10a. Ag/Al2O3-1.3 (-----), Ag/Al2O3-1.8 (---) and Ag/Al2O3-2.9 (--.--).
Fig. 3-11a. Conversion of decane to COx and yield of CO₂ and CO at C₁₀H₂₂-SCR-NO over Ag/Al₂O₃ depending on temperature. Reaction conditions as for 3-10a. Ag/Al₂O₃-1.3 (-----), Ag/Al₂O₃-1.8 (——) and Ag/Al₂O₃-2.9 (-----).
Fig. 3-11b. Chromatograms of GC analysis (FID signal) of gaseous products at H$_2$/C$_{10}$H$_{22}$-SCR-NO over Ag/Al$_2$O$_3$. Reaction conditions as for 3-10a.

Fig. 3-11c. Selectivity of decane utilization of C$_{10}$H$_{22}$-SCR-NO over Ag/Al$_2$O$_3$ depending on temperature. Reaction conditions as for 3-10a. Ag/Al$_2$O$_3$-1.3 (---), Ag/Al$_2$O$_3$-1.8 (---) and Ag/Al$_2$O$_3$-2.9 (-----).
It can be concluded that among Ag/Al₂O₃ catalysts the Ag/Al₂O₃-1.8 exhibits the highest NOx conversion, moreover, long-term performance in SCR-NOx (Fig 3-16) and thus it was selected for further analysis of the state of Ag at real conditions of the decane-SCR-NOx reaction.

3.2.3 Selective catalytic reduction of NOx over silver zeolite catalyst by decane and co-assisted by hydrogen

The conversions of NOx to N₂ at decane-SCR-NOx over silver zeolite catalyst AgNH₄-MFI-4.2 were close to zero at very high value of GHSV = 240,000 h⁻¹ at temperature region 473 – 673 K (not plotted). To reach reasonable conversion values, the activity of the silver zeolite catalysts at decane-SCR-NOx and H₂/decane-SCR-NOx were tested at lower values of GHSV (30,000 h⁻¹), (Fig. 3-12). Conversion of NOx increased with increasing temperature up to 673 K and declined at higher temperatures due to complete conversion of decane. Addition of hydrogen caused a slight increase in both conversion of NOx and decane. It is to be pointed out that the activity of Ag-MFI decreased in time due to coke formation [77] and steady-state conversions in this study were achieved within several hours. NO was reduced predominantly to N₂ as only trace concentrations of N₂O (up to 15 ppm) were detected in the products (not depicted). It is clearly seen that catalytic activity of silver zeolite catalyst is substantially lower than that of silver alumina catalysts (cf. conversion values in Figs. 3-12 and 3-9a, 3-10a and GHSV values).
Fig. 3-12. Conversion of NOx to N₂ and decane to COx at C₁₀H₂₂-SCR-NO and H₂/C₁₀H₂₂-SCR-NO over AgNH₄-MFI-4.2 depending on temperature. Feed: 1,000 ppm NO, 450 ppm C₁₀H₂₂, 6% O₂, 12% H₂O and 0 ppm H₂ (●) or 2,000 ppm H₂ (●). GHSV = 30,000 h⁻¹. Hydrogen conversion (●).
3.3 Effect of hydrogen on selective catalytic reduction of NOx over silver alumina catalyst

To obtain an insight into hydrogen function as a co-reactant to hydrocarbons, effect of hydrogen on decane-SCR-NOx, oxidation of NO to NO₂ and decane to CO and CO₂ by molecular oxygen over the most active Ag/alumina (Ag/Al₂O₃-1.8) catalyst was investigated in detail.

3.3.1 Effect of hydrogen concentration on selective catalytic reduction of NOx

Fig. 3-13 demonstrates high promotion effect of hydrogen on the C₁₀H₂₂-SCR-NO reaction over Ag/Al₂O₃-1.8 particularly at low reaction temperature range, i.e. below 623 K. But hydrogen alone, i.e. at decane absence, did not yield any molecular nitrogen. The positive effect of hydrogen if co-fed with decane on NOx conversion was increased with the increasing concentration of hydrogen in the feed from 1,000 to 4,000 ppm. This hydrogen-effect on C₁₀H₂₂-SCR-NO was also reflected in a higher conversion of decane to carbon oxides, but without changing the yield of CO. In the low temperature region (473-573 K) the conversion of NO to N₂O was slightly increased at hydrogen presence, where at 573 K the N₂O yield increased from ca 3 to 10%. At higher temperatures (>600 K) the increase in N₂O formation compared to the reaction without added hydrogen was negligible and has a decreasing tendency. Hydrogen addition also enhances formation of NO₂ at low temperatures (not depicted). The experiments were performed at GHSV of 30,000 h⁻¹ and with lower concentration of decane (300 ppm) than that depicted in Figs. 3-9, 3-10. Hence the conversion values in Fig. 3-13 are substantially higher at low temperatures. Conversions of NOx at higher temperatures are lower due to limitation of decane concentration.
3.3.2 Reversibility of the hydrogen effect on selective catalytic reduction of NOx

A time response of the NOx consumption to the addition and removal of hydrogen into the reactant stream at C_{10}H_{22}-SCR-NOx is shown in Fig. 3-14. The NO consumption sharply increased (within seconds, being limited by the response of the NO/NOx analyser to concentration changes) showing a sharp peak in the NOx conversion followed by stabilization of NOx concentration. Switching off of hydrogen caused an opposite response in NOx concentration, again with a temporary higher NOx concentration than that stabilized within
several minutes. These experiments showed complete reversibility of NOx conversion values depending on the absence and presence of hydrogen in the feed. Existence of a sharp peak of NOx consumption at hydrogen addition and, on the other hand, a peak of increased level of NOx concentration at hydrogen switching off (but much lower and wider compared to that at hydrogen addition) is explained by the fast oxidation of NO to NO₂ and its enhanced adsorption due to hydrogen co-assistance.

![Graph showing NOx conversion over time with hydrogen on and off events.]

**Fig. 3-14.** Effect of hydrogen switching on and off in C₁₀H₂₂-SCR-NO over Ag/Al₂O₃-1.8. Feed: 1,000 ppm NO, 300 ppm decane, 6% O₂ and 0 or 2,000 ppm H₂, 12% H₂O. GHSV = 30,000 h⁻¹. T = 523 K.

### 3.3.3 Effect of hydrogen on selective catalytic reduction of NOx as a function of GHSV

The effect of hydrogen on C₁₀H₂₂-SCR-NO at 523 K as a function of reciprocal contact time (GHSV) is also remarkable (Fig. 3-15). While without hydrogen the conversion of NOx in C₁₀H₂₂-SCR-NO at GHSV > 60,000 h⁻¹ was close to zero, under hydrogen presence the increase of GHSV from 30,000 to 60,000 h⁻¹ resulted in a decrease in NOx conversion from 100% only to 80%. At extremely high GHSV values of 120,000 and 240,000 h⁻¹ the NOx conversions were still ca 50 and 30%, respectively. Nitrogen was a major product of NO reduction in both the absence
and presence of hydrogen in the whole range of GHSV values investigated. NO₂ was also found in the products and the yield of N₂O was only slightly increased under the presence of hydrogen, i.e. from 0 to 2% and from 2 to 6% at GHSV values of 240,000 and 30,000 h⁻¹, respectively. Understandably, both the hydrogen and decane conversions considerably decreased with increasing GHSV values. As for decane, it was mostly converted to CO₂. The yield of CO was only slightly higher at hydrogen presence compared to the C₁₀H₂₂-SCR-NOₓ reaction.

Fig. 3-15. Effect of hydrogen on C₁₀H₂₂-SCR-NO at 523 K over Ag/Al₂O₃-1.8 as a function of GHSV. Feed: 1,000 ppm NO, 600 ppm C₁₀H₂₂, 6% O₂, 12% H₂O and 0 ppm H₂ (■, □), 2,000 ppm H₂ (●, ○). Hydrogen conversion (●).
3.3.4 Effect of water vapour on selective catalytic reduction of NOx by decane and hydrogen

The effect of water vapour on H₂/C₁₀H₂₂-SCR-NO over Ag/Al₂O₃ was also investigated. If water vapor was not fed at the H₂/C₁₀H₂₂-SCR-NOx reaction, slow but substantial deactivation of the catalyst took place (Fig. 3-16). After 300 min, the NO conversion decreased to the values similar to those obtained in the reaction carried out without hydrogen as a co-reactant. Thus, a concentration of water vapor of 12% in the stream (like that present in the real exhausts of diesel engines) is valuable, as it prevents catalyst deactivation. This implies that water vapor suppresses the adsorption of various hydrocarbons and their derivates and thus “cleans” the catalyst surface.

\[ \text{Fig. 3-16. Effect of hydrogen and deactivation in the water absence in } H₂/C₁₀H₂₂-SCR-NO \text{ over Ag/Al₂O₃-1.8. Feed: } 1,000 \text{ ppm NO, } 300 \text{ ppm decane, } 6\% O₂, \ 0\% H₂O, \ 2,000 \text{ ppm H}_₂ \ (● \text{ or } ○) \text{ or } \ 0 \text{ ppm H}_₂ \ (■), \ GHSV = 30,000 \text{ h}^{-1}. \]

3.5 Oxidation of hydrogen, and effect of hydrogen on oxidation of NO and decane

Fig. 3-17 shows that the oxidation of hydrogen with molecular oxygen over Ag/Al₂O₃-1.8 started below 373 K and was complete at ca 470 K. If water vapor was added (12%) it only slightly decreased hydrogen conversion at low temperature region, but complete conversion of
hydrogen was reached at the same temperature of 470 K. As the decrease of hydrogen conversion is found at temperature below 450 K it can be caused by water molecules adsorption on active sites. If decane and water vapour were added into the (H$_2$+O$_2$+He) stream, oxidation of hydrogen was shifted to higher temperatures (depending on the feed composition), and complete hydrogen oxidation was obtained for a given reactant concentrations at about 570 K. It follows that the rate of hydrogen oxidation is primarily affected by the presence of hydrocarbons.

![Graph showing hydrogen conversion vs temperature](image)

Fig. 3-17. Effect of water vapor and decane on hydrogen oxidation over Ag/Al$_2$O$_3$-1.8. Feed: 2,000 ppm H$_2$ and 6%O$_2$ (▲), 2,000 ppm H$_2$, 6%O$_2$ and 12% H$_2$O (●), 2,000 ppm H$_2$, 6%O$_2$, 12% H$_2$O and 600 ppm decane (■). GHSV = 30,000 h$^{-1}$. 
The contribution of hydrogen to decane oxidation by molecular oxygen is shown in Fig. 3-18. At low temperature region decane conversion to CO₂ was enhanced by hydrogen added, but the yield of CO was not changed, like at the SCR-NOx reaction. In the absence of water vapour in the (decane+O₂+H₂) stream a considerable catalyst deactivation in T-O-S occurred (Fig. 3-19), analogously to the catalyst deactivation at H₂/decane-SCR-NO carried out in the absence of water vapour in the reactant feed. This again indicates that water vapor suppresses adsorption of reaction intermediates and oligomeration processes leading to catalyst coking and deactivation.

Oxidation of NO to NO₂ by molecular oxygen over Ag/Al₂O₃ catalyst was strongly enhanced by hydrogen addition in the same temperature range and comparable conditions as the SCR-NOx reaction, i.e. up to ca 670 K (Fig. 3-20). This positive effect of hydrogen on the rate of NO-NO₂ reaction has already been reported in Ref. 58. The hydrogen-effect was observed regardless high concentration of water vapor (12%) was present or absent in the reactant feed. In both cases no decrease in NO conversion with T-O-S was observed.

![Graph](image.png)

Fig. 3-18. Effect of hydrogen on the oxidation of C₁₀H₂₂ to CO (○, ○) and CO₂ (■, □) over Ag/Al₂O₃-1.8, 1% O₂, 300 ppm n-C₁₀H₂₂ and 0 ppm H₂ (solid symbols) or 2,000 ppm H₂ (open symbols). GHSV = 3,000 h⁻¹.
Fig. 3-19. Deactivation of the catalyst at hydrogen + decane oxidation on Ag/Al₂O₃-1.8 in the absence of water vapor. Conversion of hydrogen (●), and yield of CO (■) and CO₂ (▲). Feed: 300 ppm decane, 2,000 ppm H₂ and 6% O₂. GHSV = 30,000 h⁻¹. T = 523 K.

Fig. 3-20. Effect of hydrogen on the oxidation of NO to NO₂ over Ag/Al₂O₃-1.8. Feed: 1,000 ppm NO, 6% O₂ and 0 ppm H₂ (■), 1,000 ppm H₂ (▲), 2,000 ppm H₂ (●). GHSV = 30,000 h⁻¹.
3.3.6 **Effect of NO vs. NO\textsubscript{2} on selective catalytic reduction of NO\textsubscript{x} by decane and hydrogen**

To elucidate the effect of NO\textsubscript{2} on the C\textsubscript{10}H\textsubscript{22}-SCR-NO\textsubscript{x} reaction and the reaction co-assist by hydrogen (both reactions were carried out in 12\% of water vapour), NO was partly or completely replaced by NO\textsubscript{2} in the reactant feed (Table 3.3). It is clearly seen that the higher concentrations of NO\textsubscript{2} at low temperatures decreased the conversion of NO\textsubscript{x} to N\textsubscript{2} for SCR-NO using both decane and decane co-assisted by hydrogen. It is also shown that hydrogen enhanced the rate of the SCR-NO\textsubscript{2} reaction.

**Table 3-3.** Effect of NO/NO\textsubscript{2} composition and hydrogen on conversion of NO\textsubscript{x} and C\textsubscript{10}H\textsubscript{22} at C\textsubscript{10}H\textsubscript{22}-SCR-NO\textsubscript{x} over Ag/Al\textsubscript{2}O\textsubscript{3}-1.8.

Feed: 1,000 ppm NO\textsubscript{x}, 500 ppm C\textsubscript{10}H\textsubscript{22}, 6\% O\textsubscript{2}, 12\% H\textsubscript{2}O and 0 and 2,000 ppm H\textsubscript{2}.

GHSV = 60,000 h\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>NO\textsubscript{x} composition</th>
<th>473 K</th>
<th>523 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 ppm H\textsubscript{2}</td>
<td>2,000 ppm H\textsubscript{2}</td>
</tr>
<tr>
<td>NO\textsubscript{x} (%)</td>
<td>C\textsubscript{10}H\textsubscript{22} (%)</td>
<td>NO\textsubscript{x} (%)</td>
</tr>
<tr>
<td>1,000 ppm NO</td>
<td>0</td>
<td>18.4</td>
</tr>
<tr>
<td>500 ppm NO + 500 ppm NO\textsubscript{2}</td>
<td>~1</td>
<td>13.0</td>
</tr>
<tr>
<td>1,000 ppm NO\textsubscript{2}</td>
<td>~1</td>
<td>8.6</td>
</tr>
</tbody>
</table>

3.3.7 **Effect of H\textsubscript{2} vs. CO as a co-reactant on selective catalytic reduction of NO\textsubscript{x} by decane**

The effect of CO or H\textsubscript{2} on the SCR-NO\textsubscript{x} with decane was compared with the feed containing of 4.3\% O\textsubscript{2} and 720 ppm NO on the Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 catalyst sample. The addition of hydrogen resulted in a marked improvement in the catalyst activity over the temperature range 473 - 673 K (Fig. 3-21). On the other hand, the addition of CO (being also a reductant) to decane had practically no effect on the SCR-NO\textsubscript{x} activity of the catalyst.
Fig. 3-21. NOx conversion as a function of temperature for the C_{10}H_{22}-SCR-NOx by decane over Ag/Al_2O_3-1.8 that with CO or H_2 added. With decane (■), 0.72% CO added (♦) and with 0.72% H_2 added (○). Conditions: 720 ppm NO, 4.3% O_2, 435 ppm C_{10}H_{22}, 4.3% H_2O. GHSV = 240,000 h^{-1}.

3.4 State of silver at silver alumina catalyst at the conditions of the catalytic process

UV-Vis spectra were used to monitor the state of silver in the 1.8-Ag/Al_2O_3 catalyst under real the condition of the reactions.

3.4.1 Reduction of Ag/alumina by hydrogen

Reduction of silver in Ag/Al_2O_3 occurred already under very mild conditions at RT. At this experiment the UV-Vis spectra were measured after calcination of the sample in an oxygen stream at 723 K, cooled down to RT, and after replacement of oxygen by a helium stream and hydrogen (Fig. 3-22a,b). Due to some low extent of hydration the spectra of Ag/Al_2O_3 exhibited a change in intensities of the bands of Ag^{+} ions. The low intensity bands at ca 28,000 and 34,000 cm^{-1}, which increased in intensity after introduction of hydrogen into the system, indicate development of small Ag_{n}^{+} clusters. As the position of the both bands did not significantly
change with time, the nuclearity of $\text{Ag}_n^{6+}$ clusters can be expected to was not changed but increase their concentration. It indicates that define nuclearity of $\text{Ag}_n^{6+}$ clusters might be preserved during the reduction of $\text{Ag/Al}_2\text{O}_3$ catalyst.

Fig. 3-22a,b. Ag clusters formation at 2,000 ppm $\text{H}_2$ in He over $\text{Ag/Al}_2\text{O}_3$-1.8 at RT.

a) Evolution of the in-situ diffuse reflectance UV-Vis-NIR spectra of $\text{Ag/Al}_2\text{O}_3$ at hydrogen

b) Difference spectrum between that under reaction conditions and the spectrum in flow of $\text{O}_2$. 
To obtain a rough estimation of the intensity of the spectral bands corresponding to Ag$_n^{5+}$ clusters the UV-Vis spectra were measured at the experimental conditions simulating H$_2$-TPR experiment. Thus the amount of Ag$^+$ reduced to Ag$^0$ was known from the amount of H$_2$ consumption. Fig. 3-23 depicts in-situ UV-Vis spectra of Ag/alumina calcined in an oxygen stream at 723 K for 1 h and reduced at 520 K in hydrogen. According to the hydrogen consumption, obtained by H$_2$-TPR experiments, roughly a quarter of silver was reduced at this temperature. While the oxidized sample exhibited the bands at 41,600 and 46,600 cm$^{-1}$ assigned to the electronic transition of isolated Ag$^+$ ions, after its reduction with hydrogen at 520 K an intensive broad band centered at 26,000 cm$^{-1}$ appeared. This absorption reflects formation of various metallic charged Ag$_n^{5+}$ clusters and Ag particles (see the Discussion). The high intensity of the absorption band indicates very high extinction coefficient for these metallic silver species compared to those of Ag$^+$ ions. But as clusters of various nuclearity and particles of various dimensions were formed, the overall intensity of the broad band about 26,000 cm$^{-1}$, cannot be used for quantitative analysis of concentration of the individual clusters or metallic silver particles.
Fig. 3-23. *In-situ* UV-Vis-NIR spectra of reduced Ag/Al₂O₃-1.8 in H₂ flow at 523 K, when ¼ of Ag⁺ content was reduced to metal. Spectrum of oxidized (---) and reduced (-----) Ag/Al₂O₃. Difference spectrum (------).

3.4.2 Oxidation of H₂ and CO by oxygen

Fig. 3-24a shows *in-situ* UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 in a stream of oxygen and at oxidation of hydrogen by oxygen at 473. The complete conversion of H₂ is just attained at 473 K (cf. Fig. 3-17). If only oxygen was present in the feed the bands at 41,600 and 46,600 cm⁻¹ assigned to electronic transitions of isolated Ag⁺ ions were found. When hydrogen was added into the feed an intensive broad band centered at ca 31,000 cm⁻¹ appeared immediately, indicating formation of small charged Agₙ⁺⁺ clusters. The intensity of the band around 31,000 cm⁻¹ increased fast, and more than 80% of the intensity was attained after ca 25 s; a delay-time in which hydrogen reached the catalyst bed was ca 3 s (see Fig. 3-24b). After a fast increase of the absorbance intensity with maximum at 31,000 cm⁻¹, the intensity increase was much slower, but without changing the shape of the complex band. Surprisingly, when considerable absorption at
31,000 cm$^{-1}$ was developed, the bands of Ag$^+$ ions at 41,600 and 46,600 cm$^{-1}$ did not change their intensities (see the abstracted spectrum). It is to be pointed out that at hydrogen oxidation at 50 K higher, i.e. at 523 K, when the hydrogen conversion was already complete, no Ag clusters with absorption around 31,000 cm$^{-1}$ were observed; only the bands at 41,600 and 46,600 cm$^{-1}$ were present in the spectrum. Thus, no significant amount of Ag$_n^{5+}$ clusters was present in the catalyst at conditions when all hydrogen was converted in the oxidation reaction. This indicates easy reoxidation of Ag$_n^{6+}$ species. The absence of a decrease in intensity of the bands of Ag$^+$ ions when Ag$_n^{6+}$ clusters are formed can be explained by high extinction coefficient for the metallic Ag$_n^{6+}$ clusters compared with those of Ag$^+$ ions and by a low degree of reduction of these ions.
Fig. 3-24a. In-situ diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 in a stream of O₂ (-----) and under reaction conditions: 2,000 ppm H₂ and 6% O₂ (-----). Difference spectrum between that under reaction conditions and the spectrum in flow of O₂ (⋅⋅⋅⋅⋅). T = 473 K.

Fig. 3-24b. Rate of growth of silver clusters, expressed as absorbance intensity at 31,000 cm⁻¹, after hydrogen (2,000 ppm) addition. In-situ diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8.
Fig. 3-25a shows UV-Vis spectra of silver alumina catalyst under streams of O₂, H₂ + O₂ and CO + O₂ at 473 K at similar concentrations to those of the catalytic test analysing of the effect of CO on SCR-NOx (Fig. 3-21). With Ag/Al₂O₃-1.8 exposed to a stream of oxygen, bands at 41,600 and 46,600 cm⁻¹, corresponding to the electronic transitions of isolated Ag⁺ ions, and very low intensity absorption around 28,000 – 30,000 cm⁻¹ were observed. The spectrum obtained during catalyst exposure to O₂ was subtracted from those obtained during the H₂+O₂ and CO+O₂ reactions (Fig. 3-25b). For the H₂+O₂ reaction the absorption maxima observed at ca 24,000, 29,000, 31,000 and 34,000 cm⁻¹ (see Fig 3-25a) were attributed to Agₙ⁶⁺ clusters, for n ≤ 8 [see the Discussion]. The tail below 24,000 cm⁻¹ indicates the presence of some larger metallic Ag particles. For the CO + O₂ reaction the maxima of absorbance due to Agₙ⁶⁺ clusters were located at ca 29,000, 31,000 and 34,000 cm⁻¹. The intensities of the bands due to Agₙ⁵⁺ clusters for the CO + O₂ reaction were substantially lower when compared to those obtained during the H₂ + O₂ reaction. It is evident from the difference spectra for both reactions that the intensity of the bands of Ag⁺ ions did not change significantly, when Agₙ⁶⁺ clusters were formed. This is in agreement with the very high absorbance of Agₙ⁵⁺ clusters compared to Ag⁺ ions.
Fig. 3-25a. *In-situ* diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 at hydrogen or CO oxidation over Ag/Al₂O₃-1.8 at 473 K. Feed: 7 200 ppm H₂ or 7 200 ppm CO, 4.3% O₂, rest He.

Fig. 3-25b. Difference spectra to that of Ag/Al₂O₃-1.8 in flow of O₂.
3.4.3 Oxidation of NO to NO\textsubscript{2} by molecular oxygen and the effect of hydrogen presence

Oxidation of NO by molecular oxygen to NO\textsubscript{2} is highly promoted by hydrogen addition as reported in the literature [58] and described for the Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 sample (Fig. 3-20). In an oxygen stream at 473 K, the spectrum of Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 showed only the bands at 41,600 and 46,600 cm\textsuperscript{-1} attributed to Ag\textsuperscript{+} ions. At the NO + O\textsubscript{2} reaction carried out at 523 K (with the yield of NO\textsubscript{2} in the products below 1\%, see Fig. 3-20) an increase in absorption intensity at 46,600 cm\textsuperscript{-1} was observed (with a slight shift to higher wavenumbers), while only a very small increase in absorbance intensity was monitored in the range 25,000 – 30,000 cm\textsuperscript{-1} (Fig. 3-26). The intensity increase of the band at 46,600 cm\textsuperscript{-1} was more pronounced, when hydrogen was added into the reaction mixture. As addition of hydrogen at 473 K caused an increase in conversion of NO to NO\textsubscript{2} up to 21\%, and thus induced higher concentration of NO\textsubscript{2} in the gaseous products, we ascribed the intensity increase at 46,600 cm\textsuperscript{-1} to adsorbed NO\textsubscript{2}, i.e. NO\textsubscript{2}\textsuperscript{-} and/or NO\textsubscript{3}\textsuperscript{-} species.

![Graph showing F(R) vs. Wavenumber (cm\textsuperscript{-1})](image)

Fig. 3-26. Effect of hydrogen on the oxidation of NO to NO\textsubscript{2} over Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 at 523 K. In-situ diffuse reflectance UV-Vis spectra of Ag/Al\textsubscript{2}O\textsubscript{3}-1.8 in flow of O\textsubscript{2} (——) and under reaction conditions: 1,000 ppm NO, 6% O\textsubscript{2}, without H\textsubscript{2} (-----) and with 2,000 ppm H\textsubscript{2} (-----).
3.4.4 Adsorption of NOx species on silver alumina catalyst

Pre-treated Ag/Al₂O₃-1.8 in oxygen flow at 523 K was contacted with a gas stream of 1,000 ppm NO₂ (Fig. 3-27a,b). First, a band centered around 26,600 cm⁻¹ grew in the first 20 min. Subsequently, this band eroded while a new band around 33,400 cm⁻¹ appeared. The spectra displayed an isosbestic point around 30,300 cm⁻¹, evidencing that the species responsible for the band around 26,600 cm⁻¹ is converted into the species that absorbs around 33,400 cm⁻¹. The intensity of the bands at 26,600 and 33,400 cm⁻¹ grow only up to F(Rₑ) = 0.1. Thus extinction of these bands can be estimated to be several times lower than those of silver clusters. An intensive band after NO₂ adsorption was found above 40,000 cm⁻¹ due to NO₂⁻ and NO₃⁻ adsorbed species.

An intensive broad band appeared after subsequent addition of hydrogen to the stream. This band reflects formation of silver clusters and metallic silver particles. The intensity of this bands show that the presence of NO₂ substantially suppresses reduction of Ag⁺ ions (cf. reduction of Ag/Al₂O₃-1.8 at the presence and the absence of NO₂ in the stream).
Fig. 3-27a. *In-situ* diffuse reflectance UV-Vis spectra of Ag/Al$_2$O$_3$-1.8 in flow of O$_2$ (---) and in a stream of 1,000 ppm NO$_2$ (rest of He) in 5 min (-----), 15 min (----), 30 min (------), 60 min (-----) and after subsequent addition of 2,000 ppm H$_2$ to the stream of NO$_2$ for 20 min (-------). T = 473 K.

Fig. 3-27b. Difference spectra to that of Ag/Al$_2$O$_3$-1.8 in flow of O$_2$. 
3.4.5 Selective catalytic reduction of NOx depending on \( H_2/C_{10}H_{22}/O_2 \) compositions

3.4.5.1 Effect of hydrogen concentration

Fig. 3-28 shows in-situ UV-Vis-NIR spectra of Ag/Al\(_2\)O\(_3\)-1.8 at 473 K in an oxygen stream and at the C\(_{10}\)H\(_{22}\)-SCR-NO\(_x\) reaction and that with added hydrogen as a co-reactant. Under the stream of the C\(_{10}\)H\(_{22}\)-SCR-NO reaction, where at the same conditions of the experiment with standard micro-reactor kinetic test no conversion to molecular nitrogen was monitored in the gas phase (cf. Fig 3-13), a negligible intensity increase of the absorbance at ca 27,000 and 38,000 cm\(^{-1}\) was found. This absorbance indicates formation of very low amount of small Ag\(_n^{\delta^+}\) clusters. At the same time an increase of the absorption intensity ranging from 44,000 to 50,000 cm\(^{-1}\) indicating adsorption of NO\(_x\) was observed (Fig. 3-28a and 3-28b). Addition of hydrogen (1,000 and 2,000 ppm) to the reaction mixture caused a substantial increase in the conversions of NO\(_x\) to nitrogen and decane to CO\(_3\), predominantly to CO\(_2\), which values increased with the increasing concentration of hydrogen. The conversion of NO to N\(_2\)O was slightly increased with hydrogen presence. With increasing hydrogen concentration increases a part of unreduced NO converted to NO\(_2\) (not depicted). The spectra clearly indicate that the positive effect of hydrogen on the conversion of NO and decane was accompanied by a dramatic increase of the spectrum intensity in the region from ca 20,000 to 38,000 cm\(^{-1}\) with a broad maximum centred at 31,000 cm\(^{-1}\) and a small intensity increase in the region 44,000 - 50,000 cm\(^{-1}\). Positions of the individual bands forming the envelope of the broad band at 31,000 cm\(^{-1}\) have been estimated from the derivation mode of the subtracted spectra (Fig. 3-28b) to be at ca 27,000 and 38,000 cm\(^{-1}\) and at 31,000 - 33,000 cm\(^{-1}\). With the increasing concentration of added hydrogen resulting in higher NO\(_x\) conversions, the overall absorption is not significantly shifted to lower wavenumbers, and the original spectrum increases in intensity; only low intensity tail at low wavenumbers appeared. This development of the spectrum feature indicates that with increasing concentration of hydrogen small charged Ag\(_n^{\delta^+}\) clusters, likely of a similar dimension, are increased in concentration and larger metallic agglomerates are formed only at rather low extent.
Fig. 3-28. Effect of hydrogen on decane-SCR-NO over Ag/Al₂O₃-1.8 at 473 K. GHSV = 30,000 h⁻¹. Feed: 1,000 ppm NO, 300 ppm C₁₀H₂₂, 6% O₂, 12% H₂O and 0 – 4,000 ppm H₂.

a) *In-situ* diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 in flow of O₂ (-----) and under reaction conditions: without H₂ (-----) and with 1,000 ppm H₂ (-----), 2,000 ppm H₂ (-----) or 4,000 ppm H₂ (-----).

b) Difference spectrum between that under reaction conditions and the spectrum in flow of O₂.

c) and d) Catalytic activity as a function of hydrogen concentration. NO₄ or C₁₀H₂₂ conversion (■), N₂ or CO₂ yield (○) and N₂O or CO yield (▲).
At higher temperature (523 K) compared to the previous experiment, the effect of hydrogen on C_{10}H_{22}-SCR-NO over Ag/Al_{2}O_{3}-1.8 was more pronounced (Fig. 3-29). In-situ UV-Vis-NIR spectra of Ag/Al_{2}O_{3}-1.8 under reactant stream showed formation of Ag_{n}^{6+} clusters (broad band around 31,000 cm⁻¹) already at the SCR-NO_{x} reaction without hydrogen presence. At these conditions the conversion of NO_{x} was 25% and decane 18.5% (Fig. 3-29c and 3-29d). When hydrogen was added into the feed both the NO_{x} and decane conversions and the intensity of the broad band at 31,000 cm⁻¹ were substantially increased. With increased hydrogen concentration slightly higher yields of N_{2}O and CO were found. It is to be mentioned that the broad band around 31,000 cm⁻¹ exhibited similar shape at the C_{10}H_{22}-SCR-NO_{x} reaction and at that with 1,000 ppm of hydrogen added, while at 2,000 ppm of hydrogen the maximum of the absorbance was shifted to 30,000 cm⁻¹ with a tail ranging from 10,000 to 25,000 cm⁻¹. It is worthwhile to be noted that the NO_{x} and decane conversions did not substantially increase when the hydrogen concentration was increased from 1,000 to 2,000 ppm, compared to the higher relative increase in the intensity of the broad band ascribed to Ag_{n}^{6+} clusters.

As for the changes in the intensities of the bands at 41,600 and 46,600 cm⁻¹, it is to be noted that with a change of the reaction temperature from 473 to 523 K the intensity of the band at 46,600 cm⁻¹ was increased and the band position was shifted to 47,000 cm⁻¹. However, that could be induced by an increase of the broad band above 50,000 cm⁻¹ belonging to the spectrum of Ag^{+} ions. A substantial changes in the intensity of the broad band at 47,000 cm⁻¹ at the C_{10}H_{22}-SCR-NO_{x} reaction at 523 K (Fig. 3-29) and at H_{2}/C_{10}H_{22}-SCR-NO_{x} at 473 K (Fig. 3-28) might be a result of a balance of the effects of higher rate of oxidation of NO to NO_{2}, and thus formation of adsorbed NO_{x}⁻ species, and at the same time the increased rate of NO_{2} (adsorbed NO_{x}⁻) reduction by hydrocarbons. However, the changes in the intensities of the absorbance in the range 45,000 – 50,000 cm⁻¹ could not be analysed with respect to adsorbed species as several components might contribute to the absorbance in this region.
**Fig. 3-29.** Effect of hydrogen on decane-SCR-NO over Ag/Al\(_2\)O\(_3\)-1.8 at 523 K. GHSV = 30,000 h\(^{-1}\). Feed: 1,000 ppm NO, 400 ppm C\(_{10}\)H\(_{22}\), 6% O\(_2\), 12% H\(_2\)O and 0 – 4,000 ppm H\(_2\).

a) *In-situ* diffuse reflectance UV-Vis-NIR spectra of Ag/Al\(_2\)O\(_3\)-1.8 in flow of O\(_2\) (– – – – ) and under reaction conditions: without H\(_2\) (– – ), with 1,000 ppm H\(_2\) (– – – ) and with 2,000 ppm H\(_2\) (– – – – ).

b) Difference spectrum between that under reaction conditions and the spectrum in flow of O\(_2\).

c) and d) Catalytic activity as function of hydrogen concentration. NO\(_x\) or C\(_{10}\)H\(_{22}\) conversion (●), N\(_2\) or CO\(_2\) yield (○) and N\(_2\)O or CO yield (▲).
3.4.5.2 Effect of decane and oxygen concentration

As the results indicate that the amount of Ag$_n^{5+}$ clusters at the C$_{10}$H$_{22}$-SCR-NO$_x$ reaction (even without hydrogen co-assistance) depends on the reaction temperature and thus on NOx conversion, the effects of concentrations of decane and oxygen, both affecting NO$_x$ conversion, were also investigated. With increasing decane concentration, conversion of NO$_x$ increased especially between 300 and 600 ppm of decane (Fig. 3-30). Higher concentrations of decane only slightly increased NO$_x$ conversion. Yields of N$_2$O and CO were not affected by decane concentration. In-situ UV-Vis-NIR spectra of Ag/Al$_2$O$_3$ under the same conditions of increasing decane concentrations showed increasing intensity of the band around 31,000 cm$^{-1}$ and a decreasing intensity of the absorbance above 47,000 cm$^{-1}$. That indicates a substantial increase in the amount of Ag$_n^{5+}$ clusters and a decrease in the amount of adsorbed NO$_x^-$ with increasing decane concentration, due to enhanced NO to N$_2$ reaction.

Surprisingly, similar effect of the increasing amount of Ag$_n^{5+}$ clusters was found with the increasing concentration of oxygen (Fig. 3-31). Conversions of NO$_x$ and decane increased with increasing concentration of oxygen especially between 3% and 6% of oxygen and this effect was accompanied by an increase in intensity of the broad absorbance around 31,000 cm$^{-1}$ of Ag$_n^{5+}$ clusters, and by the very high intensity increase at 47,000 cm$^{-1}$, attributed to adsorbed NO$_x^-$ species.

It follows that the number of Ag$_n^{5+}$ clusters formed increases not only due to hydrogen presence, as reported in literature, but with increasing NOx conversion to N$_2$, regardless this is achieved by H$_2$, O$_2$ or decane. This finding is decisive for the SCR-NOx reaction over silver alumina and will be analysed in detail in the Discussion part.
Fig. 3-30. Effect of decane concentration on decane-SCR-NO at 523 K over Ag/Al₂O₃-1.8. GHSV = 30,000 h⁻¹. Feed: 1,000 ppm NO, 6% O₂, 12% H₂O and 300–1200 ppm C₁₀H₂₂.

a) In-situ diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 in flow of O₂ (——) and under reaction conditions: with 300 ppm decane (— — —), 600 ppm decane (— — —), 900 ppm decane (— — —) and with 1200 ppm decane (—— —).

b) Difference spectrum between that under reaction conditions and the spectrum in flow of O₂.

c) and d) Catalytic activity as function of decane concentration. NO₄ or C₁₀H₂₂ conversion (■), N₂ or CO₂ yield (●) and N₂O or CO yield (▲).
Fig. 3.31. Effect of oxygen concentration on decane-SCR-NO at 523 K over Ag/Al₂O₃-1.8. GHSV = 30,000 h⁻¹. Feed: 1,000 ppm NO, 300 ppm C₁₀H₂₂, 12% H₂O and 0–12% O₂.

a) In-situ diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 in flow of O₂ (-----) and under reaction conditions: without O₂ (-----) and with 3% O₂ (-----), 6% O₂ (-----), 9% O₂ (-----) and 12% O₂ (-----).

b) Difference spectrum between that under reaction conditions and the spectrum in flow of O₂.

c) and d) Catalytic activity as function of oxygen concentration. NO₅ or C₁₀H₂₂ conversion (■), N₂ or CO₂ yield (○) and N₂O or CO yield (▲).
Thus, in the C_{10}H_{22}-SCR-NO\textsubscript{x} reaction both the increasing concentrations of decane and oxygen resulted in an increase in the intensity of the broad band (around 31,000 cm\textsuperscript{-1}) roughly at the same wavenumbers, i.e. at ca 27,000, 38,000 cm\textsuperscript{-1} and 30,000 – 32,000 cm\textsuperscript{-1}. The above result indicate that there could be some correlations between the number of Ag\textsubscript{n}^{5+} clusters and conversion of NO\textsubscript{x} to N\textsubscript{2}. To confirm or disapprove that correlation the time-resolved experiments of hydrogen addition and removal into reactant stream were carried out.

3.4.6. Rate of growth and redispersion of Ag\textsubscript{n}^{5+} clusters at SCR-NO\textsubscript{x}

To estimate the rate of changes in NO\textsubscript{x} conversion and Ag\textsubscript{n}^{5+} clusters formation, the time-resolved experiments of hydrogen switching on/off at the C_{10}H_{22}-SCR-NO reaction at 523 K were performed (Fig. 3-32). The added hydrogen resulted in an immediate change in the gaseous product composition. A fast NO\textsubscript{x} consumption, including NO\textsubscript{x} conversion and NO\textsubscript{2} enhanced adsorption, was accompanied by a nearly similar rate of the increase in absorbance with maximum at ca 31,000 cm\textsuperscript{-1} (Fig. 3-15a). On the other hand, hydrogen switch off, also causing a fast drop of NO\textsubscript{x} conversion (Fig 3-15b), did not result in a similar relative rate of a decrease in the intensity of the broad band of Ag\textsubscript{n}^{5+} clusters, but the process of decreasing of the number of Ag\textsubscript{n}^{5+} clusters was clearly much slower. It implies that there is not a straightforward relationship between the rate of the change in NO\textsubscript{x} conversion and the amount of the charged Ag\textsubscript{n}^{5+} clusters present at the reaction conditions.
Fig. 3-32. Effect of hydrogen switching on and off in decane-SCR-NO over Ag/Al₂O₃-1.8 monitored by NO/NOx analyser and *in-situ* UV-Vis spectroscopy. Reactant stream: 1,000 ppm NO, 600 ppm decane, 6% O₂, 12% H₂O, and 0 or 2,000 ppm H₂; T = 523 K, GHSV = 60,000 h⁻¹.

a) Changes in NO₅ consumption and evolution of the intensity of *in-situ* diffuse reflectance UV-Vis spectra of Ag/Al₂O₃-1.8 at 31,000 cm⁻¹ after hydrogen switch on as function of time.

b) Changes in NO₅ consumption and evolution of the intensity of *in-situ* diffuse reflectance UV-Vis spectra of Ag/Al₂O₃-1.8 at 31,000 cm⁻¹ after hydrogen switch off as function of time.
3.4.7 Selective catalytic reduction of NOx by decane at CO vs. H2 presence

Fig. 3-33 shows the in-situ UV-Vis spectra of Ag/Al2O3 collected during the decane-SCR-NOx reaction under similar conditions to those in the catalytic tests as depicted in Fig. 3-21. The spectra revealed that even at 473 K, where negligible conversion of NO to N2 takes place, traces of Ag\textsubscript{n}^{5+} clusters are formed (low absorption intensity around 28,000 and 38,000 cm\textsuperscript{-1}). The presence of adsorbed nitrates was reflected in an increased absorbance intensity with a maximum around 47,000 cm\textsuperscript{-1}. The addition of CO to the reaction mixture caused an increase in the absorption intensities with maxima at ca 25,000, 34,000 and 38,000 cm\textsuperscript{-1}. These bands can be attributed to the formation of small Ag\textsubscript{n}^{5+} clusters. When H\textsubscript{2} was added into the feed instead of CO, the intensity of the broad band ranging from 20,000 to 40,000 increased substantially. This band showed similar features (intensity maxima at 24,000, 28,000, 34,000 and 38,000 cm\textsuperscript{-1}) to that obtained under a CO-containing feed, indicating that similar types of silver clusters are formed in each case. The increase of the spectrum intensity around 47,000 cm\textsuperscript{-1} after hydrogen or CO addition can be accounted for by the presence of some adsorbed species on Ag or Al ions, e.g., some nitrates as well as carboxylates.

Thus it was shown that although co-fed CO resulted in the higher number of Ag\textsubscript{n}^{5+} clusters (n≤8) in the Ag/Al2O3 catalyst at SCR-NO the conversion of NO to N2 was not enhanced.
Fig. 3-33a. *In-situ* diffuse reflectance UV-Vis-NIR spectra of Ag/Al₂O₃-1.8 during exposure to different reactant gas mixes. SCR feed: 720 ppm NO; 435 ppm n-C₁₀H₂₂; 4.3% O₂; 4.3% H₂O; (7,200 ppm CO or H₂).

Fig. 3-33b. Difference spectra to that of Ag/Al₂O₃ in flow of O₂.
3.5 Selective catalytic reduction of NOx enhanced by hydrogen peroxide over silver alumina catalyst

As the results of SCR-NOx and that co-assisted by hydrogen indicate that the reaction mechanism might involve radical reactions (see the Discussion) the effect of hydrogen peroxide, as a source of radical species, on SCR-NOx was investigated [78].

Conversion of NOx in the SCR reaction with decane over Ag/Al2O3-1.8 at 473 - 523 K without co-fed hydrogen peroxide or hydrogen was low (Fig. 3-34a). The NO conversion was increased considerably by addition of hydrogen peroxide and this effect was also accompanied by a higher conversion of decane (Fig. 3-34b). Simultaneously, the reaction co-assisted by hydrogen peroxide yielded high conversion of NO to NO2. The greatest enhancement of NOx conversion was achieved at low temperatures. When hydrogen was employed as an additive over Ag/Al2O3-1.8, the conversion of NOx was higher (Fig. 3-34 and Tab. 3-4) and the conversion of NO to NO2 was much lower compared to the reaction with co-fed hydrogen peroxide.

Thus, in comparison with hydrogen, in addition to the improvement of the reduction of NO to N2, hydrogen peroxide enhances much more oxidation of NO to NO2. This effect is more pronounced at low temperatures (Table 3-4), where the SCR-NOx reaction contributes less to the overall transformations.

Table 3-5 shows a comparison of C10H22-SCR-NOx co-assisted by hydrogen peroxide over Al2O3 and Ag/Al2O3-1.8 at 523 K. The activity of Al2O3 itself in SCR-NOx without hydrogen peroxide in the feed was negligible and the effect of the added hydrogen peroxide was remarkable in both N2 and NO2 formation. The NO conversion to nitrogen was significantly higher over Ag/Al2O3 in comparison with Al2O3 as well as in the reaction co-assisted by hydrogen peroxide. Contrary to alumina, with Ag/Al2O3-1.8 higher yield of molecular nitrogen than NO2 was obtained under co-assistance of H2O2 to decane.

The positive effect of hydrogen on CH-SCR-NOx has been observed only with silver on alumina or Ag-zeolite catalysts [48,49]. Analogously to hydrogen, with Cu-MFI and Fe-MFI catalysts the increase in NOx conversion under hydrogen peroxide presence was not observed [78].
Fig. 3.34a,b. Effect of hydrogen peroxide and hydrogen on conversion of NOx to N₂ (a) and C₁₀H₂₂ to COx (b) in C₁₀H₂₂-SCR-NO over Ag/Al₂O₃-1.8 depending on temperature. Feed: 1,000 ppm NO, 600 ppm C₁₀H₂₂, 6% O₂, 12% H₂O and 0 ppm H₂O₂ (■), 2,000 ppm H₂O₂ (●) or 2,000 ppm H₂ (●). GHSV = 60,000 cm⁻³.
Tab. 3-4 Comparison of the effect of hydrogen and hydrogen peroxide on the C_{10}H_{22}-SCR-NO reaction over Ag/Al_{2}O_{3}-1.8 at 473 K. GHSV = 60,000 cm⁻¹. Feed: 1,000 ppm NO, 600 ppm C_{10}H_{22}, 6% O_{2}, 12% H_{2}O, 0 or 2,000 ppm H_{2}O_{2} and 0 or 2,000 ppm H_{2}.

<table>
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<th>Decane + H_{2}O_{2}</th>
<th>Decane + H_{2}</th>
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<td>21.0</td>
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<tr>
<td>Yield of NO_{2}</td>
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<td>48.2</td>
<td>28.5</td>
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</table>

*conversion of NO to nitrogen and nitrogen dioxide

Tab. 3-5 Comparison of the activity of Al_{2}O_{3} and Ag/Al_{2}O_{3}-1.8 in the C_{10}H_{22}-SCR-NO reaction, co-assisted by hydrogen peroxide at 523 K. GHSV = 60,000 cm⁻¹. Feed: 1,000 ppm NO, 600 ppm C_{10}H_{22}, 6% O_{2}, 12% H_{2}O and 0 or 2,000 ppm H_{2}O_{2}.

<table>
<thead>
<tr>
<th></th>
<th>Al_{2}O_{3}</th>
<th>Ag/Al_{2}O_{3}</th>
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<td>0 ppm H_{2}O_{2}</td>
<td>2,000 ppm H_{2}O_{2}</td>
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<tr>
<td>xNO⁺</td>
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</tr>
<tr>
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<tr>
<td>Yield of NO_{2}</td>
<td>0.1</td>
<td>28</td>
</tr>
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</table>

*conversion of NO to nitrogen and nitrogen dioxide
4 Discussion

4.1 Structure of the silver catalyst

4.1.1 State of silver in alumina and MFI zeolite

The peculiar structure of the silver species on alumina has not been analysed so far in detail particularly at the conditions of the SCR-NOx reactions. It is known that impregnation of alumina supports with a silver salt solution leads to a wide distribution of silver species depending on loading and atmosphere over silver alumina. According to the literature [14,20,34,45,46,48], silver species in alumina, highly flexible in the valence state, have been suggested to adopt structure of Ag$^+$ ions atomically dispersed, small silver oxide or silver aluninate species, metallic charged Ag$_n^{6+}$ clusters of various nuclearity and charge, and larger metallic silver particles (see Chapters 1.4.5 and 1.4.6).

The electronic spectra of silver in solutions, inert gas-solid matrices and in zeolites show that Ag$^+$ ions and small Ag clusters exhibit characteristic absorption bands in the UV-Vis region. It is widely accepted that the components of the UV bands above 40,000 cm$^{-1}$ correspond to $4d^{10} \rightarrow 4d^95s^1$ electronic transitions of Ag$^+$ ions in various matrices [42] and the bands between 30,000 – 40,000 cm$^{-1}$ are ascribed to the $4d^{10}5s^1 \rightarrow 4d^95s^15p^1$ and $4d^{10}5s^1 \rightarrow 4d^95s^16p^1$ transitions in Ag$_n^{6+}$ clusters with $n \leq 8$ [43,79]. There is no doubt that the observed UV absorption bands at 41,600 and 46,600 cm$^{-1}$ in Ag/Al$_2$O$_3$ samples studied (Fig 3-1) correspond to the isolated Ag$^+$ ions. However, all the Ag$^+$ ions could not be quantitatively reflected in these bands. Beside the $4d^{10} \rightarrow 4d^95s^1$ Ag$^+$ transitions below 49,000 cm$^{-1}$ reported for various solids, the spectrum of Ag$^+$ ions can be also reflected in the region above 50,000 cm$^{-1}$, and moreover, the absorption in this region can be dominant [42]. This was observed for Ag$^+$ ion aqueous solutions [42] and recently also for some Ag$^+$ ions in Ag-MFI zeolite [31,80]. Thus some types of Ag$^+$ ions or a part of their spectrum can be "invisible" for UV-Vis spectroscopy recorded in a standard region of the UV-Vis spectrometers up to 50,000 cm$^{-1}$. The possibility of the presence of the spectral component above 50,000 cm$^{-1}$ in our Ag/Al$_2$O$_3$ samples is indicated in some experiments by an increase of the absorbance intensity around 50,000 cm$^{-1}$ (see, e.g., Fig. 3-1).

UV-Vis spectra of all oxidised Ag/Al$_2$O$_3$ catalysts in this study have similar pattern and show without any doubt that the silver is predominantly in a form of Ag$^+$ ions. A shoulder at 35,000 – 38,000 cm$^{-1}$ found with increasing metal content of the catalyst, indicating small silver clusters, have very low intensity and thus represents very small part of silver.

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The bands at 42,400 and 46,400 cm\(^{-1}\) observed in the spectra of oxidized Ag-MFI zeolites in H\(^+\) form show that silver is in a form of Ag\(^+\) ions. On the other hand, strong band with maximum at 37,500 cm\(^{-1}\) in the spectrum of AgNa-MFI zeolite revealed a presence of small silver Ag\(_n\)\(^{6+}\) (n≤8) clusters [31,65]. The difference between the state of Ag in AgNa- and AgH-MFI zeolite treated under the same conditions can be accounted for a lower tendency of AgH-zeolite to reduction due to presence of H\(^+\) ions and also higher mobility of Ag\(^+\) ions. The nature and size of the metal-type Ag\(_n\)\(^{6+}\) clusters, ascribed to bands below 40,000 cm\(^{-1}\) in the spectra of Ag/Al\(_2\)O\(_3\), is still under discussion (see Table 4-1). The EXAFS experiments enabled direct identification of cluster size in zeolites only up to four Ag atoms (see Refs. 49,65). The surrounding local field of silver in zeolites is different from that affecting Ag clusters on the alumina support. Moreover, in the case of zeolites, strong guest-host interaction between the Ag species and the framework can also be accompanied by spatial restrictions, as shown, e.g., in Ref. 79. Pestryakov and Davydov [43] attributed the bands found with Ag/Al\(_2\)O\(_3\) at 34,000 – 36,000 cm\(^{-1}\) and 25,000 – 27,000 cm\(^{-1}\) to small Ag\(_n\) clusters (n = 2-7) with s-s* and n-s* electron transitions, respectively. As they observed a strong donor-acceptor interaction between the Ag\(^+\) ions and the alumina carrier when using adsorbed CO, they suggested induction of an effective charge on silver clusters with formation of Ag\(_n\)\(^{6+}\) species.

It could be concluded that silver in oxidized Ag/Al\(_2\)O\(_3\) and Ag-MFI zeolites studied is in the form of Ag\(^+\) ions. However, in the Na-form of the zeolite also small Ag\(_n\)\(^{6+}\) (n≤8) clusters are formed. As the positions of absorption bands at UV-Vis spectra of the silver clusters of different nuclearity are not yet determined (Tab 4-1) and, moreover, might be different depending on the type of support, the assignment of the bands to the individual Ag\(_n\)\(^{6+}\) clusters is not clear.

4.1.2 Reducibility of silver catalysts

The shifts of the broad temperature maxima of H\(_2\) consumption and the deficit at hydrogen consumption at H\(_2\)-TPR with respect to complete reduction of Ag\(^+\) with increasing silver loading in Ag/Al\(_2\)O\(_3\) indicate various nature of the silver species (Fig 3-3). Bogdanchikova et al. [45] also suggested that the nature of the silver in Ag/Al\(_2\)O\(_3\) catalysts could markedly change with silver loading. They supposed that small oxide species and/or layer of silver oxide
are present in low loaded Ag/Al₂O₃, while a substantial part of silver aluminate beside silver oxide species is formed in highly loaded Ag/Al₂O₃.

This assumption is supported by the in-situ UV-Vis spectra of Ag/Al₂O₃-1.8 during its H₂-TPR (Fig. 3-23). The maxima of UV-Vis broad bands reflecting the formation of metallic charged Agₙ⁺ clusters are shifted to lower wavenumbers after temperature-programmed reduction performed up to 473 or 523 K. This indicates reduction of Ag⁺ ion species step by step with the increased temperature to charged metallic Ag clusters and further to larger Ag particles. Bulk silver oxides have strong broad absorption from NIR to UV region at UV-Vis-NIR spectra [81]. However, our spectra (Fig. 3-2) do not show presence of that absorption.

It could be concluded that in Ag/Al₂O₃ well dispersed Ag⁺ ions and small Ag oxide-like clusters are reduced to metallic Agₙ⁺ charged clusters and step by step to metallic silver particles. With difficulty are reduced Ag-aluminate species. Therefore it can be suggested that the oxidized Ag/Al₂O₃ contains predominantly atomically dispersed Ag⁺ ions and very small silver oxide clusters as well as a part of silver in the form of silver aluminate.

The hydrogen consumption at H₂-TPR clearly shows completely different character of Ag⁺ bonding in the zeolite compared to alumina. The three maxima of H₂-TPR profile of Ag-MFI-4.2 catalyst might indicate the presence of Ag⁺ ions of different reducibility bound to different lattice sites. On the other hand, the observed three peaks could be explained as Ag⁺ ions are reduced to charged metallic Agₙ⁺ clusters in the first and/or second peak and these Agₙ⁺ clusters are reduced to metal Ag particles in the second and/or third peak. Shibata et al. [65] supported this assumption by XRD patterns of Ag-MFI treated at various temperatures in H₂. They reported absence of diffraction lines of the metallic Ag crystallites after the H₂ treatment below 573 K. It seems that this result does not support the possibility that Ag⁺ ions are coordinated to different lattice sites, where they might exhibit different reducibility, but it is to be pointed out that XRD might detect only crystalline metallic silver. Thus, we suggest that Ag⁺ ions are reduced to charged silver clusters at the first and second peak and then the charged silver clusters are reduced to metallic silver. What is the most important is the fact that Ag⁺ ions in MFI zeolite, as ion exchanged and replacing bridging OH groups (see Fig. 3-4), are “ideally” atomically dispersed and reduced at much lower temperature compared to Ag species in alumina. This implies higher ionicity of bonding, and decreased charges on Ag⁺ ions in zeolites in comparison with Ag/Al₂O₃.
It can be summarized that well dispersed Ag cationic species in alumina (Ag⁺ ions, Ag₂O species and Ag-aluminate) are better stabilized with respect to their reduction to metallic Ag₅⁺ clusters compared to MFI containing exclusively Ag⁺ in charge balanced in cationic sites.

4.1.3 Interaction of silver with the supports

A decrease in intensities of bridging OH groups of the parent MFI zeolite and no changes in intensity of Si-OH groups clearly evidences that Ag⁺ ions in AgNH₄-MFI zeolite (see Fig 3-4) are at exchanged sites. A significant difference in intensity of the hydroxyl bands of parent Al₂O₃ and Ag/Al₂O₃-1.3 at 7,320 cm⁻¹ and 7,200 cm⁻¹ indicated that silver in alumina interacted predominantly with most basic and acidic OH groups (Fig. 3-5). However, a similar intensity of the hydroxyl bands for Ag/Al₂O₃ samples with higher Ag loading indicates that the interaction proceeds only to limited extent. This finding is not in contradiction with conclusions on Ag in alumina given in the literature [28].

The data of acetonitrile uptake (Fig 3-7 and Tab 3-2) indicate the heterogeneity of Lewis acid centers on the surface of alumina. There is clear evidence that silver interacts predominantly with strong acid Lewis sites and to less extent with weak Lewis sites (Fig.3-7 and Tab. 3-2). But it should be noted that also silver cations deposited on alumina could reflect themselves as weak Lewis sites with respect to acetonitrile and provide interaction with CN groups with the same characteristic vibration. Accordingly, the small decrease in the 2313 cm⁻¹ band intensity can be apparent. The IR spectra after adsorption of acetonitrile showed also bands of surface acetamide species formed by a hydrolytic process most probably with participation of basic OH groups [73] and formation of bands of OD and CD₂CN⁻ carbanion that could indicate presence of additional type of basic sites on alumina (O²⁻ anions). A substantial decrease of the number of basic OH groups after Ag⁺ ions introduction onto alumina is also shown in NIR spectra (Figs. 3-5). According to the obtained results the amount of the surface acetamide species is substantially higher on alumina than that on silver alumina catalyst. Due to possible migration of all these products the intensity of their bands can hardly be used for determination of the number of the basic sites. Nevertheless, it is seen that the number of the basic sites is higher on parent alumina than that on silver alumina catalysts.
It could be concluded that Ag\textsuperscript+ ions in alumina are stabilized by different interactions between them in contrary to these cations in the zeolite. Ag\textsuperscript+ ions in the MFI zeolite are exchanged and coordinated to bridging oxygen atoms, while in alumina they interact predominantly with strong acid Lewis sites and a part of them with basic and acidic OH groups.

4.1.4 Relationships among the Ag state, interaction with the support and reducibility of silver species

Silver in oxidized Ag/Al\textsubscript{2}O\textsubscript{3} and Ag-MFI zeolites studied exhibits various reducibility depending on the type of silver species and their interaction with the supports. Ag\textsuperscript+ ions in MFI zeolites are coordinated to framework bridging oxygen atoms and can be easily and completely reduced to Ag\textsubscript{0} clusters relatively highly stabilized by negative framework charge and metallic silver particles. The interaction of silver with alumina, occurs with the strong and weak acid Lewis sites and basic and acidic OH groups. We suggest formation of various Ag\textsuperscript+ species: atomically dispersed Ag\textsuperscript+ ions, very small silver oxide clusters and silver aluminate species, population of which depends on silver loading of Ag/Al\textsubscript{2}O\textsubscript{3}. The atomically dispersed Ag\textsuperscript+ and those in very small oxide clusters are reduced at relatively low temperatures, while silver aluminate species are reducible only at high temperatures.

4.2 Selective catalytic reduction of NOx by decane over silver catalysts

4.2.1 General features of the SCR-NOx reactions over silver alumina catalysts

Typical temperatures of diesel engine exhaust gases, determining operating temperature for selective catalytic reduction, are in the temperature window 470-720 K. However, the Ag/Al\textsubscript{2}O\textsubscript{3} catalysts generally exhibit sufficient activity in SCR of NO to N\textsubscript{2} only at temperatures above 620 K. Thus catalytic activity of Ag/Al\textsubscript{2}O\textsubscript{3} in the whole temperature range of 470-720 K should be considered as being of great importance.

The mechanism of SCR-NOx over silver catalysts is very complex and, although that numerous studies based on FTIR spectroscopy have been done, it has not been so far fully elucidated. Nevertheless, a general picture of the most significant steps of the reaction has been drawn [51, 52, 55]. It is assumed that the SCR-NOx reaction starts with formation of adsorbed
nitrates via oxidation of NO by $O_2$ and formation of acetate (formate) species by partial oxidation of a hydrocarbon with NOx and $O_2$. The acetates (formates), which can act as surface reductants, reduce nitrates via several steps to $N_2$. One of the most important steps is formation of $Ag^+\cdotCN$ species and their transformation into $-NCO$ via organo-nitrogen species [12,50]. It is supposed that $Ag^+\cdotNCO$ and $-CN$ adspecies react further with another N-containing compound to $-NH$ containing species and finally to $N_2$, [51,52,55]. Non-selective oxidation of hydrocarbon occurs in addition to SCR-NOx. Thus, in order to achieve effective $Ag/Al_2O_3$ catalyst it has to possess high selectivity in hydrocarbon utilization in the SCR-NOx reaction.

4.2.2 Activity of silver catalysts

The rate of $N_2$ formation at SCR-NO over $Ag/Al_2O_3$ is much higher than that over $Ag$-MFI catalyst in terms of NOx conversion per catalyst weight and TOF values per Ag atom. Moreover, the $Ag$-MFI catalyst suffers from deactivation by coking. We suppose that this coking originates from transformation of olefins formed by decane cracking, oligomerization and aromatization over strong acid sites of the zeolite.

The highest activity in the terms of conversion and TOF values exhibits medium loaded $Ag/Al_2O_3$-1.8 catalyst (Figs. 3-8a, 3-8b). These results correspond to those found in the literature Refs [14,18,28,29,31,32,47]. The $Ag/Al_2O_3$-1.8 catalyst proved also long-term stable performance with respect to NO-$N_2$ at the SCR-NOx process (Fig. 3-16). Values of TOF for $Ag/Al_2O_3$ show that ca 2 wt.% $Ag$ was an optimum $Ag$ loading for $C_{10}H_{22}$-SCR-NOx with maximum exploitation of single $Ag^+$ ions. The lower activity of silver alumina at higher silver loading could be connected with the state of silver. At higher loadings exceeding about 2 wt.% clustering of silver ions and their easier reduction have been indicated. It is known that metallic silver activates both molecular oxygen and hydrocarbons providing conditions for hydrocarbon oxidation. Thus decreasing SCR-NOx activity with silver loading over ca 2 wt.% has been attributed to formation of metallic Ag particles and high rates of $C_3H_6$ oxidation with $O_2$, at the expense of its reaction with NO in Refs. [14,45,46]. The formation of large metallic particles has been attributed to the detrimental effect of increasing of the particle size of silver oxide entities with increasing loading, yielding entities easily reducible to $Ag^0$ particles [14]. However, in Refs. [14,45,46] the activity of highly active $Ag/Al_2O_3$ (2 wt.%) was compared only with highly loaded
Ag/Al₂O₃ (ca 6 wt.% Ag) catalyst. On the other hand, the analysis of NOx and C₁₀H₂₂ conversions obtained in this study for Ag/Al₂O₃ catalysts containing 1.8 and 2.9 wt.% Ag shows that C₁₀H₂₂ conversion is lower for Ag/Al₂O₃-2.9. Hence, the decrease of activity in NOx reduction to N₂ cannot be only attributed to a substantial decrease in concentration of a hydrocarbon resulting from its higher non-selective combustion. Oxidation of hydrocarbons at SCR-NOx over Ag/Al₂O₃-1.8 is predominantly connected with activity at NOx reduction to N₂ (cf. C₁₀H₂₂ + O₂ and C₁₀H₂₂ + O₂ + NO). At Ag/Al₂O₃-2.9 is formed higher number of metallic silver then that at Ag/Al₂O₃-1.8 at SCR-NOx. However, the reason why the de-NOx activity decreases with higher silver loading could be more complex. It has been shown that small part of Ag⁺ ions interacts with support via hydroxyl group (Fig 3-5) and substantial part of Ag⁺ ions could interact by different route at least with acid Lewis or/and basic site on alumina surface (Fig 3-6). Bethke and Kung [14] supposed that the activity of the Ag/Al₂O₃ catalysts might not result solely from Ag, but Al₂O₃ itself may be involved in the reaction. They supposed that a similar mechanism as observed for Co/Al₂O₃ [82] and a mixture of Pt/SiO₂ with Al₂O₃ [83] occurred over Ag/Al₂O₃. The conversions of NO over the Pt/SiO₂-Al₂O₃ mixture were higher than the sum of the conversions over the individual components. It was suggested that this synergic effect resulted from a spillover or gas phase transfer of a short-lived intermediate, possibly a partially oxidized or activated hydrocarbon species. On the basis of these results, it could be expected a mechanism, where surface migration of a reaction intermediate from Ag species to surface of Al₂O₃ or vice versa occurs.

In conclusion the medium loaded Ag/Al₂O₃-1.8 catalyst exhibits the highest reduction activity at SCR-NOx by decane. It is suggested that a specific local structure of silver ion species localized in a surrounding Al₂O₃ is responsible for the high reduction activity of NOx. Nevertheless, the activity is low at low temperature region, which is essential for NOx abatement in diesel engine exhausts.

4.2.3 Effect of reactant composition on SCR-NOx over silver alumina

It was clearly shown (Tab. 3-3) that the conversion of NOx to N₂ in SCR-NOx over Ag/Al₂O₃-1.8 employing relatively high concentrations of NO₂ in NO/NO₂ inlet mixtures is lower compared to that if NO is used. It indicates some negative effect of NO₂ on the SCR-NOx
reaction. On the other hand, formation of ad-NOx (NO$_2$, NO$_3$) species on the surface sites is proposed to be the first reaction step. Nevertheless, the effect of NO$_2$ on the reduction of NOx to nitrogen over Ag/Al$_2$O$_3$ catalysts is reported controversially in the literature. Both a positive [14] as well as a negative effect [20,48] of NO$_2$ was found compared to NO. Bethke and Kung [14] have shown that enhancement of the conversion of propane-SCR-NOx by NO$_2$ also depends on the Ag loading on alumina. The different results are connected with the type of a hydrocarbon and reaction conditions used. The observed lower NOx conversions with NO$_2$ at low temperature might be explained by strong adsorption of nitrates and thus blocking of active sites [60].

Similarly to the case of NO, many authors have proposed formation of surface acetate and/or formate species by partial oxidation of hydrocarbons with O$_2$ as the first reaction step [16,50,51]. It is to be noted that NO$_2$ is a stronger oxidant compared to molecular oxygen. Accordingly, conversion of NO to N$_2$ at SCR-NOx over Ag/Al$_2$O$_3$-1.8 was enhanced by higher concentration of both decane and oxygen in the reaction stream (Figs 3-30 and 3-31). Molecular oxygen plays, besides NOx a key role as oxidant at the SCR-NOx process over Ag/Al$_2$O$_3$ due to its participation in the several steps of the complex process. Oxygen takes part in formation of intermediates like acetate (formate) and NCO surface species [12,16,50]. In addition, oxygen is essential for both keeping the catalyst in high oxidation state and cleaning the surface from carbonaceous deposit. The increasing O$_2$ concentration promotes not only the rate of total oxidation but also the rate of partial oxidation of hydrocarbon. If the oxidation activity is too low, the generation of the intermediates is slow and the rate of NOx-reduction becomes low.

Contrary, when CO was added to the reactant mixture beside decane (Fig. 3-21), to investigate whether another reductant could have a similar function to hydrocarbons, no promotion of the SCR-NOx over Ag/Al$_2$O$_3$-1.8 was observed. Thus Ag/Al$_2$O$_3$ cannot catalyse reduction of NOx in oxidizing conditions.

4.2.4 Decane-SCR-NOx enhanced by hydrogen assistance

Although the positive effect of hydrogen over Ag/Al$_2$O$_3$ for the CHx-SCR-NOx reactions was demonstrated for a spectrum of hydrocarbons, for methane, C2 and C3 paraffins and olefins, isobutane [20,48,58,67], octane [8,64], and ammonia [61], it is worthwhile to point out that with decane, as the main component of diesel engine exhausts, a similar hydrogen effect has been
observed. Among the Ag/Al₂O₃ catalysts studied, the Ag/Al₂O₃-1.8 catalyst exhibited the highest activity in NOx to N₂ reduction also in reduction of NOx by a mixture of decane and hydrogen. The conversion of NO to nitrogen was enhanced dramatically, at low temperature range (470-620 K) as well as at extremely high space velocities (shown up to 240,000 h⁻¹); (Figs. 3-10, 3-13, 3-15). Both these ranges of conditions are essential for NOx abatement in diesel engine exhausts. A slight decrease in NO conversion at high temperatures (>673 K) at lower space velocities (30,000 h⁻¹) is due to a lack of hydrocarbon in the reaction mixture (Fig. 3-13). This observation is quite typical for lean NOx reduction catalysts. During the H₂-assisted C₁₀H₂₂-SCR-NOx reaction, the presence of high excess of water vapor in the gas stream is beneficial with respect to the long-term catalyst operation as, without water vapor presence, a substantial decrease in the NOx conversion to nitrogen with time occurs (see Fig. 3-16). This is due to formation of deposits adsorbed on the catalyst surface. These deposits can be represented by olefin-type intermediates, as decane readily cracks with formation of olefins, which have tendency to oligomerize and further transform to high-molecular coke-like products.

Contrary to the highly beneficial effect of hydrogen on NO conversion, its presence slightly increases yields (up to 10%) of undesired N₂O and CO, especially at low temperatures (470-570 K); Fig. 3-10, 3-11. Generally, formation of N₂O is increased at conditions leading to increasing concentration of NO₂, i.e. at increasing hydrogen or oxygen concentration in the feed at SCR-NOx, while variation of decane concentration has no effect on the N₂O yield. This finding might indicate incomplete reduction of NOx to nitrogen.

However, without any doubt hydrogen enhances the rate of oxidation of NO to NO₂ at low temperatures (470-520 K) (Fig. 3-20, and ref. [48]) and thus leads to an increased concentration of NO₂ in the gas phase, and a pool of nitrates on the surface. But as the high concentration of NO₂ in the feed results in lower N₂ yields, the positive effect of hydrogen on the NOx conversion to nitrogen in the C₁₀H₂₂-SCR-NO₂ reaction (Table 3-3) could not generally be accounted for by enhancement of the reaction of oxidation of NO to NO₂. Thus, another function of hydrogen, reflected rather in hydrocarbon oxidation, could contribute to the enhanced SCR-NOx activity.

The mechanistic cause of enhancement of C₁₀H₂₂-SCR-NO activity by addition of H₂ over Ag/Al₂O₃ was also investigated with in-situ FT-IR spectroscopy in our laboratory [84,85]. It has been shown that formation of surface species during oxidation of NO or decane is greatly
affected by the presence of hydrogen. Surface monodentate nitrates are formed preferentially and are more reactive compared with the bidentate species. Oxidation of decane mostly yields surface acetates, and the presence of NOx favours the formation of formates (acrylates). The reaction steps most enhanced by the addition of hydrogen to the SCR-NOx reaction are the transformations of the intermediate –CN species into –NCO and oxidation of the hydrocarbon to formates (acrylates).

4.3 State of silver at the reaction conditions

4.3.1 Analysis of Ag species by UV-Vis spectra

Diffuse reflectance UV-Vis spectra monitoring during calcination and the decane-SCR-NOx reaction over Ag/Al₂O₃ catalyst and that reaction co-assisted by H₂ or CO (as well as during oxidation of NO and H₂ by molecular oxygen) at the identical parameters of the micro-reactor when the reaction kinetics was studied provided in-situ information on the catalyst structure at real conditions of the catalytic reactions. The studies and information obtained at such a level represent a dramatic step ahead for understanding of catalyst structure and its operation during catalytic reactions. Nevertheless, the application of UV-Vis spectroscopy for analysis of the state of Ag in Ag/Al₂O₃ brings about also some limitations. A surprising absence of a significant decrease in the spectrum intensity of Ag⁺ ions between 40,000 - 50,000 cm⁻¹ when Agₙ₆⁺ clusters are formed at oxidation of H₂ by molecular oxygen (Fig. 3-24 and 3-25) could be explained most probably by very high differences in extinction coefficients for Ag⁺ ions and Agₙ₆⁺ clusters, as follows from Fig. 3-23, but to some extent possibly also and by the occurrence of the Ag⁺ 4d → 5s transitions of some Ag⁺ species exclusively above 50,000 cm⁻¹. The high difference in the extinction coefficients of Ag⁺ ions and Agₙ₆⁺ clusters follows from a comparison of the intensity of the broad band of small Agₙ₆⁺ clusters when a quarter of Ag⁺ ions was reduced (Fig. 3-23) with that monitored during the SCR-NOx reaction. This shows that roughly only < 5% of the total amount of Ag⁺ ions was reduced. However, determination of extinction coefficients of Agₙ₆⁺ clusters could not be done, as a spectrum of clusters of various nuclearities are formed. This finding on the very low amount of Ag⁺ ions reduced might support speculation on the presence of silver in Ag/Al₂O₃ in the form of Ag₂O, as suggested in Ref. [20]. Low concentration of Ag₂O
could be hardly seen by a broad absorption, which is characteristic for bulk and thin layers of Ag₂O [81].

In conclusion, the UV-Vis spectra cannot provide complete quantitative picture on the behaviour of all the Ag⁺ ions in Ag/Al₂O₃ under the reaction conditions. Nevertheless, the results of UV-Vis spectroscopy with the H₂-TPR experiments suggest (i) assignment of the UV absorption bands at 41,600 and 46,600 cm⁻¹ to Ag⁺ ions in an oxygen ligand environment, vast amount of which does not undergo changes in the valence state at the conditions of the investigated SCR-NOx process, and (ii) semiquantitative analysis of formation of Ag₉⁺ clusters at real reaction conditions depending on the reaction mixture composition. Low number of silver clusters is suggested to be formed either from the Ag⁺ ions detected by absorption bands at 41,600 and 46,600 cm⁻¹ but it cannot be excluded that some of them originate from undetected Ag⁺ ions, such as represented by single Ag⁺ ions or very small Ag₂O species.

On contrary, the UV-Vis spectra of Ag/Al₂O₃ have provided some insight into the development of small Ag₉⁺ clusters depending on the reaction conditions, although assignment of the individual absorptions below 40,000 cm⁻¹ to Ag₉⁺ clusters of distinct nature and size is still under discussion (see Table 4-1).

The bands found with Ag/Al₂O₃ at 34,000 – 36,000 cm⁻¹ and 25,000 – 27,000 cm⁻¹ were attributed to small Agₙ clusters (n = 2-7) [43]. The absorption observed for the Ag/Al₂O₃ sample in the 30,000 – 32,000 cm⁻¹ region can be attributed to Ag₈⁺ clusters, as these were monitored by direct-mass spectrometric experiments, in aqueous solutions [42] and in the confined space of zeolites [48, 79]. The presence of Ag₈⁺ clusters is supported by the fact that Ag clusters exhibiting the same UV-Vis spectrum contain Ag atoms with three nearest neighbours in the first coordination sphere, i.e. represent Ag₄⁺ clusters with tetrahedral symmetry or Ag₈⁺ clusters with cubic symmetry. Presence of Ag₈⁺ clusters is more probable due to their significantly higher stability (magic clusters) compared to Ag₄⁺ clusters, which are extremely unstable [86].

However, the observations of silver clusters at conditions of SCR-NOx suffer due to presence of absorption bands of NOx species at the UV-Vis spectrum. In Ref [66] it was derived from the volumetric experiments that a substantial part of silver in Ag/Al₂O₃ is finally converted into silver nitrate at presence of NO₂ in the reaction stream. Therefore, the band at 33,400 cm⁻¹ in the in-situ diffuse reflectance UV-Vis spectrum during NO₂ adsorption experiment (Fig 3-27) is ascribed to silver nitrate. The assignment of the band at 26,600 cm⁻¹ is less evident [66]. It is
speculated that it is connected with the coordination of Ag⁺ with NO₂ preceding the formation of nitrate, which would explain its transient appearance. The intensities of the bands at 26,600 and 33,400 cm⁻¹ are low due to low extinction coefficients of the NOₓ species. The great difference between extinction of the bands of the absorbed NOₓ species in this region and silver clusters enables to observe the silver clusters on the silver alumina catalysts at the reactant stream containing nitrogen oxides. Contrary, the bands of NOₓ species above 40,000 cm⁻¹ have high intensity. An analysis of the individual NOₓ species and the bands of Ag⁺ ions cannot be made due to their overlap.

The assignment of the individual bands to silver species given in the literature and suggested in this study is summarized in Table 4-1.

4.3.2 Ag species under the reaction conditions of oxidation of H₂ and NO by molecular oxygen

At very mild reduction of silver in the Ag/Al₂O₃ sample under vacuum, as well as at low hydrogen pressure at RT, the bands monitored at 28,000 and 34,000 cm⁻¹ can be ascribed to the Agₙ⁺⁺ clusters. Under the conditions of the H₂ + O₂ reaction over Ag/Al₂O₃-1.8, these two characteristic bands were no longer resolved and the existence of a broad band ranging from 20,000 to 40,000 cm⁻¹ (Fig. 3-22) indicated the presence of several types of small Agₙ⁺⁺ clusters, which can hardly be defined with respect to their nucularity. Bearing in mind the relatively high stability of silver clusters with n = 8 [86], the observed local maximum of absorption around 31,000 cm⁻¹, can probably be ascribed to the presence Agₙ⁺⁺ clusters predominantly with n = 8. With the NO-NO₂ reaction using similar NO and H₂ concentrations as those in the C₁₅H₂₂-SCR-NOₓ reaction, only a very low intensity band of NOₓ species or/and insignificant concentration of Agₙ⁺⁺ clusters was formed, although the conversion of NO was increased dramatically (Figs. 3-26 and 3-20). We supposed that this extremely low number of Agₙ⁺⁺ clusters is not sufficient for enhancement of the NO-NO₂ reaction rate and the hydrogen function in the NO-NO₂ reaction is not connected with the function of these Agₙ⁺⁺ clusters. In Ref. [20], dissociation of oxygen on small Ag clusters was assumed, but without giving the experimental evidence. We speculate that the HO₂ radicals formed (see below par. 4.6) are responsible for NO to NO₂ oxidation at
hydrogen or hydrocarbon presence (cf. enhancement of NO-NO₂ oxidation by both hydrogen and decane, see Figs. 3-20 and 3-8c, resp.).

4.3.3 Ag species under the decane-SCR-NOₓ reaction and that co-assisted by hydrogen and carbon monoxide

The shape of the UV-Vis bands in the region from 20,000 to 40,000 cm⁻¹ of Agₙ⁺ clusters forming an envelope and observed during the C₁₀H₂₂-SCR-NOₓ reaction or that co-assisted by hydrogen at various reactant/product compositions is rather complex. Nevertheless, as the shape of this broad band is not significantly varied depending on reaction conditions and reactant compositions, it can be inferred that more or less similar Agₙ⁺ species are present. It should be pointed out that, under the reaction conditions investigated (with stable NOₓ conversions for many hours), we did not observe formation of large metallic Ag⁰ particles, which should be manifested in strong absorption in the Vis spectrum.

Based on the ex-situ UV-Vis spectra and EXAFS studies, analysing the state of silver in the Ag-MFI zeolite catalyst after the H₂/propane-SCR-NOₓ reaction [49,65], the authors suggested that the positive "hydrogen effect" is caused by formation of small Agₙ⁺ clusters with n = 2-4 and, therefore, these species represent active sites. Without co-assistance of hydrogen they did not report occurrence of Agₙ⁺ clusters. However, our results indicate that already during the decane-SCR-NOₓ reaction over Ag/Al₂O₃, the Agₙ⁺ clusters are definitively, and the most populated, besides clusters of other nuclearity, are probably Ag₅⁺ clusters.

It follows from a comparison of the UV-Vis spectra of Ag/Al₂O₃-1.8 in the H₂/C₁₀H₂₂-SCR-NOₓ reactions at various feed compositions (cf. Figs. 3-28, 3-29, 3-30) that in both the presence and absence of hydrogen as co-reactant, small Agₙ⁺ clusters are present in the catalyst. Their number clearly increases with increasing conversion of NO to nitrogen, regardless of whether this conversion increase is achieved by the increasing concentration of hydrogen or decane. This finding implies that there is some obvious relationship (although not quantitative) between the conversion of NO to N₂ and the number of small Agₙ⁺ clusters in the catalyst. Hence the conversion of NO to N₂ also depends on the catalyst activity in oxidation of NO and CHₓ by molecular oxygen, and CHₓ by NOₓ, the relationship between the Ag structure and SCR-NOₓ activity could be hardly established.
However, such apparent correlation between the NOx-N₂ conversion and amount of Agₙ⁺ clusters is not in agreement with the immediate responses of the system (completely reversibly) to hydrogen addition and removal followed by increased and decreased NO conversion, respectively. The responses in the changes in the number of small charged Agₙ⁺ clusters were substantially much slower (particularly at hydrogen removal from the reactant feed, see Fig. 3-32). It implies that the Agₙ⁺ clusters are not formed exclusively as a result of hydrogen addition, but that their number during the SCR-NOx reaction could be also controlled by the accumulation of surface organic intermediates. This conclusion is supported by the observation, obtained in our laboratory by IR spectra monitoring of surface species at in-situ conditions of the reaction, that enhancement of the NO-N₂ reaction by hydrogen is accompanied by a substantial increase of surface reaction intermediates [84].

To confirm the suggestion that Agₙ⁺ clusters are not a real active sites CO was added to the reactant mix to investigate whether another reductant could have a similar effect to hydrogen. Clearly, carbon monoxide does not promote the SCR-NOx reaction (Fig. 3-21). Although CO has no direct effect on the rate of NOx conversion, in-situ UV-Vis spectra show that it promotes, similarly to hydrogen, the formation of small Agₙ⁺ clusters during the CO/decane-SCR-NOx reactions as well as CO oxidation. The extent of Agₙ⁺ cluster formation when CO is added is less than that observed for hydrogen addition, but is nevertheless significant. Thus Agₙ⁺ cluster are not responsible for high activity of Ag/Al₂O₃ in SCR-NOx.

Consistently with those findings Breen et al. [63] reported just in 2005 that the enhanced activity found in the presence of hydrogen is thought to be due to a chemical effect and not the result of a change in the structure of the active site, as they concluded from the in-situ EXAFS study. Nevertheless, the EXAFS indicates that small silver clusters are formed to small extent during the SCR-NOx process particularly if H₂ or CO is co-fed.

Therefore, the number of small Agₙ⁺ clusters can be related to the reducing environment of reaction atmosphere present over the catalyst surface during the SCR-NOx reaction in both cases, i.e. in the presence and absence of hydrogen. Thus, the number of Agₙ⁺ clusters is predominantly a result of reducing effect of adsorbed surface intermediates.

It should be also mentioned that the enhancing effect of H₂ on the SCR-NOx reaction was reported only over Ag/Al₂O₃, much less over Ag-MFI (see Fig. 3-12), but not over other silver based catalysts. The NO-N₂ activity over Ag/TiO₂, Ag/ZrO₂, Ag/SiO₂, and Ag/Ga₂O₃ was
reported to be very low in both the presence and absence of H₂ [48], and thus no positive hydrogen-effect occurred. Although the process of SCR-NOx is very complex, it could be found some connection (not quantified) between the NO-N₂ conversion over Ag based catalysts and reducibility of Ag⁺ ions on these supports. It seems that the trend of the NO-N₂ activity of Ag on various supports Ag/Al₂O₃ < Ag-MFI < Ag/ZrO₂ < Ag/SiO₂ is reverse to that of Ag⁺ ions reducibility (see Refs. [14,47,65] and H₂-TPR results – Fig. 3-3). This implies that there is additional support for the conclusion that with the increasing stability of the Ag⁺ oxidation state increases NO-N₂ activity of the Ag based catalysts. Analogous trend is seen for the enhancement of the SCR-NOx reaction co-assisted by hydrogen.
Table 4-1  Band positions for various silver species in UV-Vis spectra

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Ag species</th>
<th>Comments</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>32,300</td>
<td>Ag(_2^+)</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>37,700</td>
<td>Ag(_4^{2+})</td>
<td>Mordenite</td>
<td>79</td>
</tr>
<tr>
<td>39,200; 32,800</td>
<td>Ag(_4^{2+})</td>
<td>ZSM-5</td>
<td>65</td>
</tr>
<tr>
<td>30,300</td>
<td>Ag(_5^0)</td>
<td>Mordenite</td>
<td>79</td>
</tr>
<tr>
<td>34,500</td>
<td>Ag(_7^{5+}) or Ag(_8^{6+})</td>
<td>Mordenite</td>
<td>79</td>
</tr>
<tr>
<td>30,800</td>
<td>Ag(_8^{6+})</td>
<td>Solution, magic cluster</td>
<td>86</td>
</tr>
<tr>
<td>31,300</td>
<td>Ag(_8^0)</td>
<td>Mordenite</td>
<td>79</td>
</tr>
<tr>
<td>28,200</td>
<td>(Ag(_4^{1}))^2</td>
<td>Mordenite</td>
<td>79</td>
</tr>
<tr>
<td>25,600-27,000</td>
<td>Ag(_n^{δ+}(n=2-7))</td>
<td>γ-Al(_2)O(_3), SiO(_2)</td>
<td>43</td>
</tr>
<tr>
<td>34,500-37,000</td>
<td>Ag(_n^{δ+}(n=2-7))</td>
<td>γ-Al(_2)O(_3), SiO(_2)</td>
<td>43</td>
</tr>
<tr>
<td>42,600; 47,600</td>
<td>Ag(_+)</td>
<td>ZSM-5</td>
<td>65</td>
</tr>
<tr>
<td>44,400; 47,600; 52,100</td>
<td>Ag(_+)</td>
<td>Ag(H(_2)O)(_4)</td>
<td>42</td>
</tr>
<tr>
<td>41,700</td>
<td>Ag(_+)</td>
<td>γ-Al(_2)O(_3), SiO(_2)</td>
<td>43</td>
</tr>
<tr>
<td>44,600; 47,200; 51,000</td>
<td>Ag(_+)</td>
<td>ZSM-5</td>
<td>31</td>
</tr>
<tr>
<td>52,600</td>
<td>Ag(_+)</td>
<td>ZSM-5</td>
<td>80</td>
</tr>
<tr>
<td>from NIR to UV region</td>
<td>Ag(_2)O</td>
<td>bulk</td>
<td>81</td>
</tr>
<tr>
<td>27,000; 28,000; 30,000; 31,000, 34,000; 38,000</td>
<td>Ag(_n^{δ+}(n ≤ 8))</td>
<td>γ-Al(_2)O(_3)</td>
<td>this study</td>
</tr>
<tr>
<td>ca &lt; 26,000</td>
<td>Ag agglomerates</td>
<td>γ-Al(_2)O(_3)</td>
<td>this study</td>
</tr>
</tbody>
</table>
4.6 Function of hydrogen at SCR-NO\textsubscript{x} over silver alumina catalyst

The number of small Ag\textsubscript{n}\textsuperscript{5+} clusters over Ag/Al\textsubscript{2}O\textsubscript{3} can be related to the reducing environment present on the catalyst surface formed by the SCR-NO\textsubscript{x} reaction in both cases, i.e. in the presence and absence of hydrogen. Also the increased activity in NO-NO\textsubscript{2} oxidation under presence of hydrogen is not accompanied with a significant increase of the number of Ag\textsubscript{n}\textsuperscript{5+} clusters. Accordingly, the presence of Ag\textsubscript{n}\textsuperscript{5+} clusters is likely not the reason for the enhanced NO-N\textsubscript{2} activity of Ag/Al\textsubscript{2}O\textsubscript{3}, but hydrogen itself has to take part in the reaction. In Refs. [87, 88] it was shown that hydrogen dissociates when adsorbs on Ag\textsuperscript{+} in zeolites and generates acidic protons and silver-hydride. Methane also dissociates on silver with formation of CH\textsubscript{4}\textsuperscript{+} and silver-hydride [87]. Similar processes of hydrogen dissociation as well as hydrogen atom abstraction from a hydrocarbon might occur at SCR-NO\textsubscript{x} over Ag/Al\textsubscript{2}O\textsubscript{3}. We speculate that silver-hydride at the SCR-NO\textsubscript{x} reaction mixture immediately reacts with oxygen to form hydroperoxy radicals (HO\textsubscript{2})

\[
\text{Ag} - \text{H} + \text{O}_2 \rightarrow \text{HO}_2 + \text{Ag}^0
\]

Hydroperoxy radical, which is highly active oxidant [89], readily react with NO to NO\textsubscript{2} and hydroxy radical [89,90] according to the following reaction

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}
\]

Both these radicals can react with hydrocarbons to their oxo/nitro derivates [89]. We suppose that hydrogen addition enhances formation of silver-hydride and thus support radical-type reactions. Such mechanism of hydrogen (and hydrocarbon) functioning is in accordance with the experimental observations obtained in this study that both hydrogen and decane enhances NO - NO\textsubscript{2} oxidation, hydrogen enhances all the SCR-NO\textsubscript{x} reaction steps, and that occurrence of gas phase radical-type transformations behind the catalyst bed was observed at octane-SCR-NO\textsubscript{x} (without hydrogen) over Ag/Al\textsubscript{2}O\textsubscript{3} catalyst [56].

The effect of hydrogen on SCR-NO\textsubscript{x} is likely very complex. The low activity of Ag/Al\textsubscript{2}O\textsubscript{3} at temperatures below 573 K was also ascribed to inhibition of active sites by strongly adsorbed nitrates [21]. It has been recently shown that addition of hydrogen into reactant stream enhances, but also limits decomposition, of stable nitrate species [60,66]. This limitation of amount of adsorbed nitrates could explain higher NO\textsubscript{x} to N\textsubscript{2} activity at H\textsubscript{2}/C\textsubscript{10}H\textsubscript{22}-SCR-NO\textsubscript{x} compared with H\textsubscript{2}O\textsubscript{2}/C\textsubscript{10}H\textsubscript{22}-SCR-NO\textsubscript{x}. 

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It was also speculated that silver is in the presence of hydrogen in SCR reactant stream reduced to atomic Ag\(^{0}\) and that they are the species responsible for high catalytic activity [20]. However, atomic Ag\(^{0}\) species were not observed in the Ag/Al\(_{2}\)O\(_{3}\) catalyst under reaction conditions and CO added to the reactant mix also promote Ag\(^{+}\) reduction but does not promote the SCR reaction [85].

4.7 Enhancement of SCR-NO\(_{x}\) over silver alumina catalyst by hydrogen peroxide

The observed enhanced rate of oxidation of NO to NO\(_{2}\) and NO\(_{x}\) reduction to N\(_{2}\) by addition of hydrogen peroxide to SCR-NO\(_{x}\) mixture supports the suggestion that the initial step in the mechanistic pathways of SCR-NO by hydrogen peroxide consists in generation of highly reactive hydroxy and hydroperoxy radical species. Hydrogen peroxide decomposition is a well-known process generating hydroxy and hydroperoxy radicals; however, competition between H\(_{2}\)O\(_{2}\) consumption in the oxidation reactions and its non-productive decomposition could be expected in the SCR-NO\(_{x}\) process. Simultaneous presence of nitrogen oxides, hydrocarbons and radicals results in high complexity of the reaction mechanism. Hydroxy alkyl radical and oxo/nitro radical species are formed [90,91]. Cyanide (-CN) and isocyanate (-NCO) species were found to be important intermediates in the formation of molecular nitrogen in the SCR-NO\(_{x}\) process over Ag/Al\(_{2}\)O\(_{3}\) [21]. Thus, the function of H\(_{2}\)O\(_{2}\) in the SCR-NO\(_{x}\) reaction is specifically based on the activation of relatively stable reactants as well as more reactive intermediates.

Therefore, the enhanced conversion of NO to NO\(_{2}\) and N\(_{2}\), accompanied by the increase in the decane oxidation, caused by the addition of hydrogen peroxide to the SCR-NO\(_{x}\) reactants, supports our previous suggestion that the initial step and the role of hydrogen in the mechanistic pathways of the H\(_{2}\)/CH-SCR-NO reaction might consist generation of the highly reactive hydroxy and hydroperoxy radical species. If hydrogen peroxide is used as a co-reactant with hydrocarbons, higher yields of NO\(_{2}\) are obtained compared to the reaction in which hydrogen is used. It should be mentioned that the increased formation of NO\(_{2}\) does not increase the degree of reduction of NO\(_{x}\) to nitrogen over Ag/Al\(_{2}\)O\(_{3}\), but that the opposite effect was found (see Tab. 3-3).
It can be suggested that the positive effect of hydrogen peroxide addition at the SCR-NOx process could be also utilized to boost the SCR-NOx process; this procedure might be especially important for applications to reduce emissions in the exhaust gases of mobile diesel engines.

4.8 Active site at SCR-NOx over silver alumina catalyst

The discovery of the promotion effect of hydrogen on SCR-NOx [58] opened a discussion about the role of small silver clusters in SCR-NOx over silver catalysts. The formation of small $\text{Ag}_n^{5+}$ clusters was related to the increased NOx to $\text{N}_2$ reduction activity and, therefore, the positive effect of added hydrogen on the SCR-NOx reaction was attributed exclusively to the formation of small charged metallic $\text{Ag}_n^{5+}$ clusters [48,49,58,65,67].

In this study, it was clearly shown by in-situ monitoring of the structure of $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst at real conditions of the SCR-NOx catalytic process in both steady-state and transition conditions (with respect to hydrogen concentration) that only a small part of very reactive $\text{Ag}^+$ (estimated to be $< 5\%$) is reduced to metallic charged $\text{Ag}_n^{6+}$ clusters ($n \leq 8$) during both the decane- and $\text{H}_2$/decane-SCR-NOx reactions. The number of $\text{Ag}_n^{6+}$ clusters formed depends mainly on the level of NO conversion to nitrogen, but it is to be stressed that regardless of whether the conversion level is attained by the addition of hydrogen or by an increased concentration of decane or oxygen in the feed. The time-resolved responses of NOx-$\text{N}_2$ conversion and of the number of $\text{Ag}_n^{6+}$ clusters to the addition/removal of hydrogen from the reactants indicate that the $\text{Ag}_n^{5+}$ clusters are mainly formed because of the reducing effect of adsorbed CHxO-containing reaction intermediates. A comparison of the function of added $\text{H}_2$ and CO into the feed also showed that although both carbon monoxide and hydrogen promoted formation of $\text{Ag}_n^{5+}$ clusters during the SCR-NOx reaction, but only hydrogen increased NOx-$\text{N}_2$ conversion, in contrast to carbon monoxide, which had not a significant effect on NO to $\text{N}_2$ reduction. This clearly demonstrates that the enhanced activity due to the addition of hydrogen to the NOx-SCR mixture cannot be attributed to the formation of $\text{Ag}_n^{5+}$ clusters. It was proposed that hydrogen itself participates directly in the reaction mechanism via its dissociation, formation of silver hydride and initiation radical reactions. The relationship between the activity of silver alumina catalysts and the state of silver clearly shows that the $\text{Ag}^+$ centre are the active sites participating in the SCR-NOx over silver alumina catalyst. Active $\text{Ag}^+$ ions are suggested to be
represented by a single $\text{Ag}^+$ ions and/or very small $\text{Ag}_2\text{O}$ species stabilized on alumina by strong mutual interaction.
5 Conclusions

Selective catalytic reduction of NOx to nitrogen with decane (decane-SCR-NOx), individual reaction steps (NO-NO₂, decane + O₂), and these reactions enhanced by co-fed hydrogen over silver alumina were investigated with the aim to bring an insight into behaviour of silver at these reactions and to contribute to application of the SCR-NOx process for abatement of NOx from exhaust gases of diesel engines. The main goal of the study has been a complex picture of the highly positive effect of hydrogen addition on SCR-NOx over Ag/Al₂O₃ catalyst. Multi-technique approach, consisting of UV-Vis-NIR, FTIR spectroscopy and H₂-TPR technique, was used for structural analysis. The structural analysis of the state of silver was attempted to provide information under the real reaction conditions in the steady-state and transient modes by in-situ UV-Vis spectroscopy.

Under simulated conditions of diesel engine exhaust composition, i.e. low concentration of NOx and high concentration of oxygen and water vapor, and using decane as main diesel fuel component, Ag/Al₂O₃ and Ag-MFI catalysts showed activity in C₁₀H₂₄-SCR-NOx. The activity of Ag/Al₂O₃ was superior to that of Ag-MFI. The optimum Ag/Al₂O₃ with 1.8 wt.% Ag exhibited the highest NO to N₂ reduction activity among the studied catalysts. The SCR-NOx over the Ag/Al₂O₃ catalyst is promoted by increasing concentration of oxygen and/or decane in the reactant stream [84], whereas is not affected by CO [85]. Nevertheless, at temperatures below 620 K the activity of Ag/Al₂O₃ is very low for its application at diesel engine exhausts.

Addition of hydrogen into reactant stream, like for SCR-NOx with low chain paraffins reported in the literature, dramatically increased the conversion of NO to N₂ with decane in the temperature region 470-720 K and at very high space velocities (60,000–240,000 h⁻¹), important for reduction of NOx at diesel engine exhausts. Also oxidation of NO or decane by oxygen over Ag/Al₂O₃ was greatly increased by the presence of hydrogen. As we have found that at low temperatures the increasing concentration of NO₂ in the reactant mixture had a negative effect on the SCR-NOx reaction due to strong adsorption of nitrates on surface catalyst, the positive effect of hydrogen on SCR-NOx is not based on the promotion of NO to NO₂ oxidation [84].

In calcined catalysts silver was in a form of Ag⁺ ions in both Ag/Al₂O₃ and Ag-MFI catalysts. All Ag⁺ ions were coordinated to bridging oxygen in Ag-MFI catalysts. Ag⁺ ions in Ag/Al₂O₃ catalyst were stabilised mainly on the account of the Lewis acid and basic sites and a
part of silver was exchanged with protons. Alumina support provided high dispersion and stabilization of single Ag⁺ ions and small Ag₂O species.

For the first time we monitored redox changes of silver occurring during the real SCR-NOx reaction performance [84]. Formation of small metallic charged Agₙ⁺⁺ clusters (with n ≤ 8) from Ag⁺ species during the decane-SCR-NOx reaction occurred in both cases of the absence and presence of hydrogen in a reactant stream. Moreover, it has been found that formation of Agₙ⁺⁺ clusters follows increasing conversion of NO to nitrogen, regardless of whether this conversion increase is achieved by an increase in the concentration of hydrogen or decane or even oxygen. The number of Agₙ⁺⁺ clusters formed under the SCR-NOx reaction has been estimated to be low, <5% of the total content of Ag in highly active Ag/Al₂O₃ catalyst. The time-resolved responses of NOx–N₂ conversion and the number of Agₙ⁺⁺ clusters to the addition/removal of hydrogen from the reactants feed clearly indicated that the number of Agₙ⁺⁺ clusters did not straightforwardly correlate with the NO to N₂ conversion [84]. Finally, it is to be mentioned that CO added into the reactants also increased the number of the Agₙ⁺⁺ clusters, but on contrary, did not increase NOx-N₂ conversion [85].

So far in the literature, the highly positive effect of hydrogen on SCR-NOx activity has been ascribed to formation of Agₙ⁺⁺ clusters and these have been suggested as highly active centers in the H₂/CHₓ-SCR-NOx process. However, we provided a completely different picture on the function of silver in Ag/Al₂O₃. On contrary, in this study we have evidenced that the active centers for the SCR-NOx reaction are Ag⁺ ions (either single cations or small Ag₂O species). In fact the presence of hydrogen (or increased concentration of decane or oxygen) is accompanied by the increased number of small Agₙ⁺⁺ clusters. Agₙ⁺⁺ clusters are suggested to be formed as a result of an increased formation of oxygenates from hydrocarbons strongly adsorbed and reducing the catalyst surface [84,85].

All this implies that the enhancement of SCR-NOx over Ag/Al₂O₃ by hydrogen is due to a chemical effect of hydrogen and not the result of a change in the structure of the Ag⁺ active site. The acceleration of the SCR-NOx reaction by hydrogen is suggested to originate mainly from the increased rate of oxidation of hydrocarbons and important intermediates. It is supposed that hydrogen itself participates in the SCR-NOx reaction by its dissociation on Ag⁺ ions with formation of Ag-hydride and proton sites. Ag-hydride is oxidized with NOx with formation of
hydroperoxy and hydroxy radical species. These radical species might dramatically enhance propagation of the SCR-NOx reaction [78,84,85].

This suggested pathway for a function of hydrogen is supported by application of H₂O₂ as ad-mixture at decane-SCR-NOx. Hydrogen peroxide as an additive over Ag/Al₂O₃ increased significantly conversion of NO-NO₂ and yield of N₂ [78]. These results, therefore, support the suggestion that the initial step in the mechanistic pathways of the activation of SCR-NOx by hydrogen might consist generation of highly reactive hydroxy and hydroperoxy radical species.

The thesis represents a substantial part of the European research project “Advanced nanostructured metal/metal-oxo/matrix catalysts for redox processes. Application for NOx reduction to nitrogen” coordinated through 2001-2004 years by the J. Heyrovský Institute of Physical Chemistry, Prague. On the basis of the knowledge obtained by this thesis further extended cooperation within the EU cooperative research is in progress.
References


[70] W. Hanke, K. Möller, *Zeolites* 4 1984 244
### Index to abbreviations and symbols

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A/F</td>
<td>air/fuel ration</td>
</tr>
<tr>
<td>$c_i$</td>
<td>concentration of the reactant $i$ after outlet of the reactor</td>
</tr>
<tr>
<td>$c_i^0$</td>
<td>concentration (ppm) of the reactant $i$ before inlet of the reactor</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{22}$-SCR-NOx</td>
<td>selective catalytic reduction of NOx by decane</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{22}$-SCR-NO</td>
<td>selective catalytic reduction of NO by decane</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{22}$-SCR-NO$_2$</td>
<td>selective catalytic reduction of NO$_2$ by decane</td>
</tr>
<tr>
<td>DTGS</td>
<td>deuterated triglycine sulfate</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESR</td>
<td>electron spin resonance</td>
</tr>
<tr>
<td>EURO</td>
<td>European emissions requirements</td>
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<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionisation detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform infrared</td>
</tr>
<tr>
<td>F($R_o$)</td>
<td>spectroscopic absorption defined by Kubelka and Munk</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>GHSV</td>
<td>gas hourly space velocity h$^{-1}$</td>
</tr>
<tr>
<td>HC</td>
<td>hydrocarbons</td>
</tr>
<tr>
<td>HC-SCR-NOx</td>
<td>selective catalytic reduction of NOx by hydrocarbons</td>
</tr>
<tr>
<td>HP</td>
<td>Hewlett Packard</td>
</tr>
<tr>
<td>H$_2$-TPR</td>
<td>temperature-programmed reduction by hydrogen</td>
</tr>
<tr>
<td>IIC</td>
<td>Institute of Inorganic Chemistry</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>$M_i$</td>
<td>cation of valency $n$</td>
</tr>
<tr>
<td>MAS NMR</td>
<td>magic angle spinning nuclear magnetic resonance</td>
</tr>
<tr>
<td>MFI</td>
<td>zeolite structure of ZSM-5 according to IUPAC</td>
</tr>
<tr>
<td>MOR</td>
<td>zeolite structure of mordenite according to IUPAC</td>
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<tr>
<td>MRP</td>
<td>member ring pore</td>
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<tr>
<td>NH$_3$-SCR-NOx</td>
<td>selective catalytic reduction of NOx by ammonia</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
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<tr>
<td>NOx</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>NSR</td>
<td>NOx storage-reduction technique</td>
</tr>
<tr>
<td>PM</td>
<td>particulate matter</td>
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<tr>
<td>QC</td>
<td>quartz cell</td>
</tr>
<tr>
<td>R_d</td>
<td>diffuse reflectance from a semi-infinite layer</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
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<tr>
<td>SCR</td>
<td>selective catalytic reduction</td>
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<tr>
<td>SCR-NOx</td>
<td>selective catalytic reduction of NOx</td>
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<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TOS</td>
<td>time on stream</td>
</tr>
<tr>
<td>TWC</td>
<td>three-way catalyst</td>
</tr>
<tr>
<td>urea-SCR-NOx</td>
<td>selective catalytic reduction of NOx by urea</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>y_j</td>
<td>number of j atoms in the corresponding molecule</td>
</tr>
<tr>
<td>Vis</td>
<td>visible</td>
</tr>
<tr>
<td>x_i</td>
<td>conversion of the reactants i</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>y_j</td>
<td>yield of component j</td>
</tr>
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List of publications

Publications in International Scientific Journals

1. P. Sazama, B. Wichterlová:
Selective catalytic reduction of NOx by hydrocarbons enhanced by hydrogen peroxide over silver/alumina catalyst.
Chemical Communications (2005) 4810 - 4811.

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6. G. Franková, E. Hynková, P. Sazama:
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7. G. Franková, E. Hynková, P. Sazama:
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