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NO_X REDUCTION BY HYDROCARBONS AND HYDROGEN ON METAL OXIDE AND ZEOLITE BASED CATALYSTS IN LEAN CONDITIONS

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ABSTRACT

The removal of nitrogen oxides (NO_x) from exhaust and flue gases is a demanding technical problem particularly in the presence of excess oxygen. The reduction of nitrogen oxides by hydrocarbons (HC-SCR) is a promising but also challenging method to utilize in applications, where fuels like diesel oil or natural gas might be used as a reductant. In this work new high activity HC-SCR catalysts were developed based on metal oxides (cobalt, indium, gallium) supported on sol-gel aluminum oxide or ZSM-5 zeolite. The interaction of indium and cobalt with aluminum oxide was studied by the catalysts prepared by impregnation, sol-gel, ion exchange and mechanical mixing methods. The active compounds were Co^{2+} on Co/Al_2O_3, In_2O_3 on In/Al_2O_3 and intrazeolitic InO^+ on In/ZSM-5.

A significant promotion in NO_x conversions was reached by mechanically mixing a small amount (5%) of Mn_3O_4 with In/Al_2O_3 or Ga/Al_2O_3 in propene-SCR and Mn_3O_4 or Pt/Al_2O_3 with In/ZSM-5 in methane-SCR. Gaseous or mobile surface intermediates are necessary to explain the observed promotion. Pt/alumina and Mn_3O_4 seemed themselves to catalyze the N_2 formation step in addition to promotion on HC and NO oxidation.

Surface intermediates were detected by in situ FTIR in the presence of flowing reaction gas mixtures. Before the reaction initiation the catalyst surface was usually covered with the inhibiting compounds (nitrates, carbonates), which disappeared at higher reaction temperatures (300-400°C) and the amount of surface reactants remained low in HC-SCR operation window (> 300°C). The derived reaction mechanisms for SCR by light hydrocarbons (C_1-C_3) included six potential surface reductants (H_2NCO, HNCO, NCO, NH_2, NH, N) for NO. The reductants with NH_i functional groups were found to be final reductants and the adsorbed NH_2 (amine) was the most probable in a single surface reaction.

The micro-kinetic modeling based on surface reactions was used parallel to other methods to evaluate the reaction routes and dynamics. The kinetic models for propene-SCR with Co/alumina and methane-SCR with In/ZSM-5 were based on the assumption that adsorbed H_2NCO (amide) acts as the reductant for NO. The improved model for methane-SCR on In/ZSM-5 was based on a mechanism where NO is reduced by NH_2. The binary catalyst combination (In/ZSM-5+Pt/Al_2O_3) was modeled using two different NO reduction mechanisms assuming NH_2 path on indium sites and NO decomposition to nitrogen on platinum sites. The models were able to quantitatively describe the concentrations of all observed gaseous reactants and products and as well as the defined surface coverages in propene- and methane-SCR. Finally, a generic reaction mechanism for HC-SCR was proposed.

The analysis of NO-H_2 reactions in transient conditions on Pt, Pt-Rh and Rh three-way catalysts was used as a tool to categorize the NO_x reduction mechanisms. The NO_x reduction studies resulted in four mechanisms to form nitrogen: 1) N route, 2) N_2O route, 3) ONNO route and 4) NH_i route. In fact, nitrogen formation on three-way and HC-SCR catalysts has similar final steps but requires different catalysts due to diverse conditions.

TIIVISTELMÄ

Typen oksidien poistaminen pako- ja savukaasuista on vaativa tekninen ongelma varsinkin, kun happea on läsnä ylimäärin. Typen oksidien selektiivinen katalyyttinen pelkistys hiilivedyillä (HC-SCR) on lupaava, mutta myös haastava menetelmä käyttökohteisiin, joissa käytetään pelkistimenä polttoaineita kuten dieselöljyä tai maakaasua. Tässä työssä on kehitetty uusia, erittäin aktiivisia HC-SCR-katalyyttejä, jotka pohjautuvat metallioksideihin (koboltti, indium, gallium) sooli-geelitekniikalla valmistetun alumiinioksidin tai ZSM-5-zeoliitin pinnalla. Indiumin ja koboltin vuorovaikutusta alumiinioksidiin tutkittiin katalyyteillä, jotka oli valmistettu imeyttämällä, ioninvaihtamalla tai mekaanisesti seostamalla. Aktiiviset yhdisteet olivat Co^{2+} Co/Al_2O_3:ssa, In_2O_3 In/Al_2O_3:ssa ja zeoliitin sisällä oleva InO^+ In/ZSM-5:ssä.

NO_x-konversioissa saatiin aikaan merkittävä parannus sekoittamalla mekaanisesti pieni määrä (5%) Mn_3O_4:a yhteen In/Al_2O_3:n tai Ga/Al_2O_3:n kanssa propeeni-SCR:ssä ja Mn_3O_4 tai Pt/Al_2O_3 yhteen In/ZSM-5:n kanssa metaani-SCR:ssä. Kaasumaiset tai liikkuvat pintayhdisteet ovat välttämättömiä selittämään havaitun parantuneen aktiivisuuden. Pt/Al_2O_3 ja Mn_3O_4 näyttivät katalysoivan typen muodostusvaihetta sen lisäksi, että ne edistivät hiilivetyjen ja NO:n hapetusta.

Pintavälituotteita analysoitiin käyttäen in situ FTIR:ää virtaavassa reaktiokaasussa. Ennen reaktion käynnistymistä katalyytin pinta oli täysin peittynyt inhiboivilla yhdisteillä (nitraatit, karbonaatit), jotka katosivat reaktiolämpötiloissa (300-400°C) ja pintareaktanttien määrä oli alhainen HC-SCR:n toimintaikkunassa (> 300°C). Kevyitä hiilivetyjä (C_1-C_3) pelkistimenä käyttävälle SCR:lle johdettiin reaktiomekanismit, jotka sisälsivät kuusi mahdollista pelkistävää pintayhdistettä (H_2NCO, HNCO, NCO, NH_2, NH, N) NO:lle. Funktionaalisen ryhmän NH_i sisältävät pelkistimet havaittiin olevan lopullisia pelkistimiä ja adsorboitunut NH_2 on todennäköisin yksittäisessä pintareaktiossa.

Reaktioreittejä ja –dynamiikkaa tutkittiin käyttämällä pintareaktioihin perustuvaa mikrokineettistä mallinnusta rinnakkain muiden tutkimusmenetelmien kanssa. Kineettinen malli propeeni-SCR:lle Co/Al_2O_3:lla ja metaani-SCR:lle In/ZSM-5:lla perustui oletukseen, että adsorboitunut H_2NCO on NO:n pelkistin. Parannettu malli metaani-SCR:lle In/ZSM:llä perustui mekanismiin, jossa adsorboitunut NH_2 pelkistää NO:n. Binäärinen katalyyttiyhdistelmä (In/ZSM-5+Pt/Al_2O_3) mallinnettiin kahdella NO:n pelkistysmekanismilla

olettaen NH_2-reitti indiumpaikoilla ja NO-hajotus typeksi platinapaikoilla. Kaikki havaitut kaasumaiset reaktantit ja tuotteet sekä määritellyt pintapeitot kyettiin selittämään mallien avulla kvantitatiivisesti propeeni- ja metaani-SCR:ssä. Lopuksi esitettiin HC-SCR:lle yleiset reaktiomekanismit.

NO-H_2-reaktioiden analyysiä transienteissa olosuhteissa Pt-, Pt-Rh- ja Rh-katalyyteillä käytettiin työkaluna NO_x-pelkistysmekanismien luokitteluun. NO_x-pelkistystutkimukset päätyivät neljään mekanismiin typen muodostamiseksi: 1) N-reitti, 2) N_2O-reitti, 3) ONNO-reitti ja 4) NH_i-reitti. Typen muodostuksessa kolmitoimi- ja HC-SCR-katalyyteissä on samanlaiset viimeiset reaktiovaiheet, mutta tarvitaan erilaisia katalyyttejä riippuen olosuhteista.

PREFACE

The research work of this thesis (II–VI) has been carried out mainly at the National Institute of Advanced Industrial Science and Technology (AIST) in the catalyst design laboratory located in Tsukuba Japan between November 1994 and December 1995. The Science and Technology Agency (STA) and AIST provided funding for that research visit, which is gratefully acknowledged. In addition, the first publication (I) in this thesis was based on the transient NO-H_2 experiments made in Kemira Metalkat (Ecocat) in 1993. Later those results have been analyzed, modeled and published during the period 1996-2006 as my personal free time concern to interpret deNO_x reactions.

The financial supports from the Antti and Jenny Wihuri foundation and Fortum foundation for finishing the research in Japan, preparing the thesis and finishing the thesis are also greatly appreciated.

I am most grateful to Professor Outi Krause and Dr. Hideaki Hamada for giving support, facilities and freedom to develop new ideas. I am grateful to Professor Emeritus Johan B-son Bredenberg for his support and advice on doctoral thesis studies. I am grateful to Juha Ahola for long-term co-operation with catalyst modeling and his important contribution to the articles.

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Oulunsalo, August 2007

Teuvo Maunula

LIST OF PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by the corresponding Roman numerals:

I. Maunula, T., Ahola, J., Salmi, T., Haario, H., Härkönen, M., Luoma, M. and Pohjola, V., Investigation of CO Oxidation and NO reduction on three-way catalysts with transient response techniques, Appl. Catal. B, 12 (1997) 287-308.

II. Maunula, T., Kintaichi, Y., Inaba, M., Haneda, M., Sato, K. and Hamada, H., Enhanced activity on In and Ga-supported sol-gel alumina catalysts for NO reduction by hydrocarbons in lean conditions. Appl. Catal. B, 15 (1998) 291-304.

III. Maunula, T., Kintaichi, Y., Haneda, M. and Hamada, H., Preparation and reaction mechanistic characterization of sol-gel indium/alumina catalysts developed for NO_x reduction by propene in lean conditions, Catal. Lett., 61 (1999) 121-130.

IV. Maunula, T., Ahola, J. and Hamada, H., Reaction mechanism and kinetics of NO_x reduction by propene on Co/Alumina catalysts in lean conditions, Appl. Catal. B, 26 (2000) 173-192.

V. Maunula, T., Ahola, J. and Hamada, H., Reaction mechanism and kinetics of NO_x reduction by CH_4 on In-ZSM-5 in lean conditions, Appl. Catal. B, 64 (2006) 13-24.

VI. Maunula, T., Ahola, J. and Hamada, H., Reaction mechanism and micro-kinetic model with the binary catalyst combination of In/ZSM-5 and Pt/Al_2O_3 for NO_x reduction by methane in lean conditions, Ind. Eng. Chem. Res., 46 (2007) 2715-2725 and correction note, Ind. Eng. Chem. Res., 46 (2007) 4726.

Contribution of the author to the publications:

I	The author designed and built the mass spectrometer equipment, contributed to the experimental plan, equipment modifications, experiments and the interpretation of the results, formulated the mechanisms for NO-H_2 reactions and wrote the majority of the manuscript.
II, III	The author defined the research plan, prepared the catalysts, carried out excepting XPS and plasma analysis the experiments and characterizations, interpreted the results and wrote the manuscript.
IV, V, VI	The author defined the research plan, prepared the catalysts, carried out excepting XPS and plasma analysis the experiments and characterizations, interpreted the experimental results, derived the reaction mechanisms, designed the catalyst simulations and wrote the manuscript excepting the kinetic models.

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NO_X REDUCTION BY HYDROCARBONS AND HYDROGEN ON METAL OXIDE AND ZEOLITE BASED CATALYSTS IN LEAN CONDITIONS

CONTENTS

APPENDICES: PUBLICATIONS I-VI

1 INTRODUCTION

Nitrogen oxides (NO_x) are one of the main pollutants emitted in combustion of gaseous, liquid or solid fuels which originate mainly from fossil energy sources. The other main harmful emissions are hydrocarbons (HC), carbon monoxide (CO), particulate matter (PM) and sulfur oxides (SO_x). The main nitrogen oxides formed in combustion are nitrogen monoxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O), which is a significant greenhouse gas. Usually NO is the main compound in exhaust gases but NO_2 is formed in lean combustion and N_2O is formed both under stoichiometric and lean conditions as the combustion conditions promote its formation. NO is an odorless gas that modifies the function of the lungs, irritates human's mucous membranes, oxidizes to NO_2 and forms nitric acid in the air. NO_2 has a sharp smell, red-brown color in higher concentrations, is more irritating than NO to the lungs and damages human tissue and mucous membranes (Schäfer and van Basshuysen 1993). Once produced, NO is oxidized by ozone, OH or HO_2 radical to form higher oxides of nitrogen (Fig. 1). In big cities like Tokyo and Los Angles of sunny climate (high UV radiation), nitrogen oxides have been observed to form photochemical smog in reactions with hydrocarbons. In the presence of NO_x, non-methane HCs and CO form ozone, which has a high oxidizing potential to form harmful oxygenates in the lower troposphere. Ozone is formed in the reaction between molecular and atomic oxygen, which is created under the sun's radiation from NO_2 ($NO_2 + h\nu \rightarrow NO + O$). The most important irritating nitrogen compound to the human body is peroxyacetyl nitrate (PAN). In addition to local effects, NO_x/SO_x emissions generate acid rain, when these oxides are carried for long distances in the atmosphere and then are deposited with rain as nitric (HNO_3) and sulfuric (H_2SO_4) acids. If nitrogen oxide emissions to the atmosphere are prevented, the further effects of NO_x pollution can be eliminated.

Stationary power plant and mobile vehicles are the main human originated NO_x emission sources. The first emission limitations were enacted at the beginning of 1970's for power plants and gasoline passenger cars in the United States and Japan, where the high NO_x emissions caused health problems to human beings. During the last 100 years, the use of fossil energy sources (oil, coal, natural gas) has increased very rapidly, which has caused concern for the sufficiency of fossil energy reserves (particularly oil), the fast increase of CO_2 release into atmosphere and the emission formation.

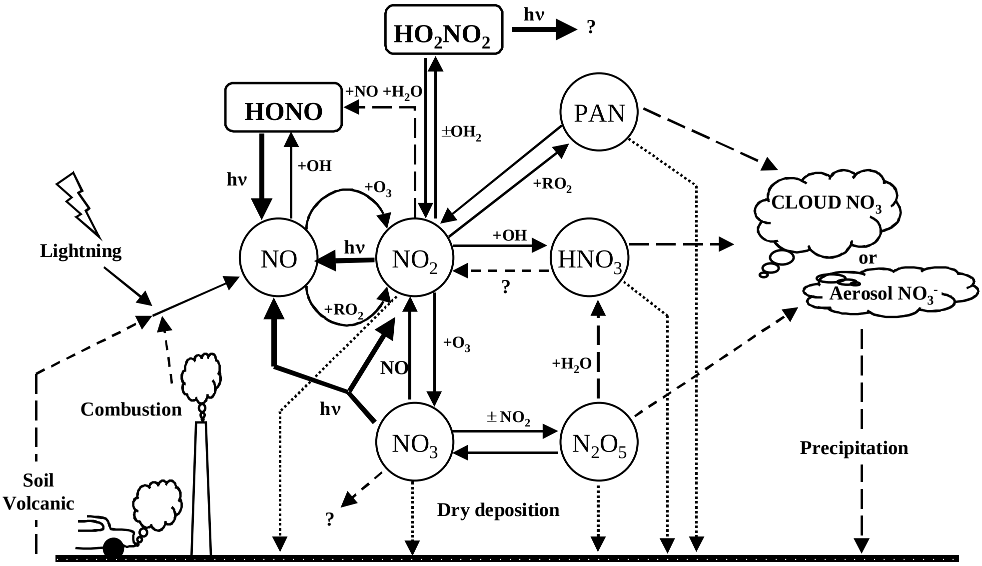


Figure 1. The upper atmospheric chemistry of nitrogen oxides (Armor 1992).

The first widely commercial aftertreatment method to reduce NO_x emissions in power plants was the selective catalytic reduction (SCR) of NO_x by ammonia in the early 1970's. The three-way catalysts (TWC) together with the closed-loop (λ) control have been also used to simultaneously reduce the CO, HC and NO_x emissions of gasoline engines since the 1970's.

The stricter NO_x emission limits in combustion applications have created a demand for other NO_x reduction methods (deNO_x) which might operate without ammonia in lean conditions. NO_x reduction by hydrocarbons (HC-SCR) is a promising but also challenging method for this purpose.

2 SCOPE OF THE WORK

The scope of this work was to evaluate the surface reaction mechanism on HC-SCR catalysts. HC-SCR catalysts were developed and investigated in this thesis based on profound experimental studies and widely published literature in this field. Propene and methane were mainly used as model light hydrocarbons to reduce NO_x on oxide and zeolite based catalysts. Transient NO-H_2 experiments in the absence of carbonaceous species enabled to understand NO reaction paths to nitrogen. This created knowledge was further utilized to development of more active catalysts, define active sites, propose mechanisms based on elementary reactions and create micro-kinetic models for HC-SCR reactions.

3 FORMATION OF NITROGEN OXIDES

NO_x can be formed by several reaction paths in combustion from molecular oxygen (O_2) and nitrogen (N_2) present in air and from nitrogen bound in fuel. If thermodynamic equilibrium is reached below 700°C, no detectable amount of NO_x, but mainly N_2, will be formed. In practice, the detected NO_x concentrations are usually between 100-2000 ppm in flue gases from boilers and engines. The reason is the slow decomposition of NO to N_2 and O_2.

The formation mechanisms to NO_x are divided to three categories (Flagan and Seinfeld 1988):

1. Thermal NO_x
2. Prompt NO_x
3. Fuel-NO_x

The thermal NO_x formation requires high temperatures to dissociate of stable molecular nitrogen by the Zeldovich mechanism

$$O + N_2 \Leftrightarrow NO + N \quad (1)$$

$$N + O_2 \Leftrightarrow NO + O \quad (2)$$

where the activation energy of the first step limits the reaction initiation. The amount of atomic oxygen is higher at higher temperatures. Thermal NO_x is significant when temperatures are above 1300°C in combustion. The hydroxyl radical can be an oxidant in fuel-rich flames:

$$N + OH \Leftrightarrow NO + H \quad (3)$$

The prompt NO_x is formed in radical rich flame zones, when molecular nitrogen reacts with hydrocarbon (HC) radicals. Sarofim and Pohl (1973) proposed that the prompt NO_x formation could be presented by the Zeldovich mechanism if the O, OH and H concentrations are not in equilibrium and HC will not have a role in reactions. No prompt NO_x was found in HC-lean conditions, i.e. in hydrogen or CO flames (Iverach et al. 1973). Prompt NO_x is formed from N_2:

$$N_2 + CH \Rightarrow HCN + N \quad (4)$$

$N_2 + C_2 \Rightarrow 2\ CN$ (5)

$N_2 + C \Rightarrow CN + N$ (6)

where one part of the cyanides is converted to NO and the other back to N_2 in a combustion chamber.

Fuel-N is present at high concentrations in heavier fuels such as coal and oils. However, the nitrogen content in wood is much lower than in crude oil or coal based fuels. The nitrogen concentrations in usual Finnish fuels (wt-%) are as follows (Hupa 1985, Alakangas 2000): 0.05% in natural gas, 0.01-0.03% in light oil, 0.3-0.8% in heavy oil, 0.8-1.2% in coal, 1-3% in peat and 0.1% in wood.

The main nitrogen containing species are amines and aromatic nitrogen species, but the type of N-species has a minor effect on the formation rate to NO_x (Pershing and Wendt 1977). The secondary nitrogen species are oxidized to NO_x or reduced to N_2 depending on local conditions in combustion (Fig. 2):

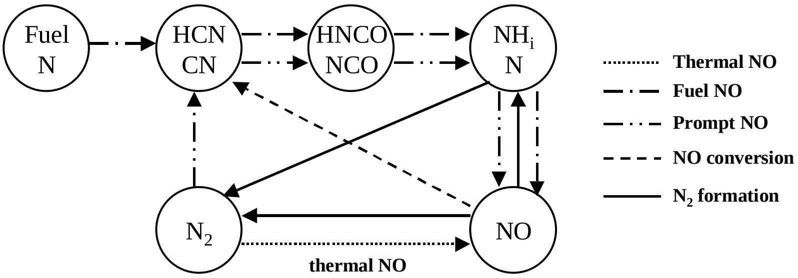


Figure 2. The formation routes from fuel-nitrogen to NO (Prasad et al. 1984).

Thermal NO_x is the main mechanism in engines and boilers with diesel, gasoline and gas fuels, but in coal power plants fuel NO_x is usually the major route for NO_x formation. Even if only 10-50% of coal-N is converted to NO, that amount corresponds to 200-800 ppm NO compared to about 50 ppm NO formed thermally (Pohl and Sarofim 1977).

The conditions in combustion have an essential effect on NO_x formation. The increasing temperature will mainly increase the amount of thermal NO_x but indirectly also the amount of fuel-NO_x (Fig. 3). The temperature dependence of thermal and prompt NO_x is the same with liquid or gaseous fuels. Coal-N is segregated into volatile and char fractions in thermolysis. Fuel-NO_x originates mainly (60-80%) from nitrogen in volatile fraction (Phong-anant et al. 1985). The local oxygen concentration in combustion has a crucial role in NO_x formation.

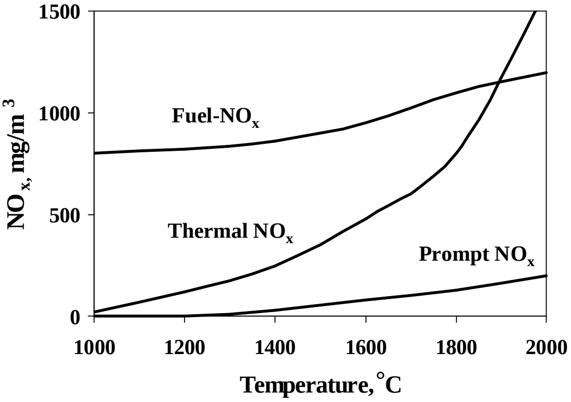


Figure 3. NO_x formation by different mechanisms in coal combustion (Schrod et al. 1985).

The specific NO_x emissions in diesel engines decrease as a function of λ value, but a wide range is used in the usual driving conditions (Fig. 4).

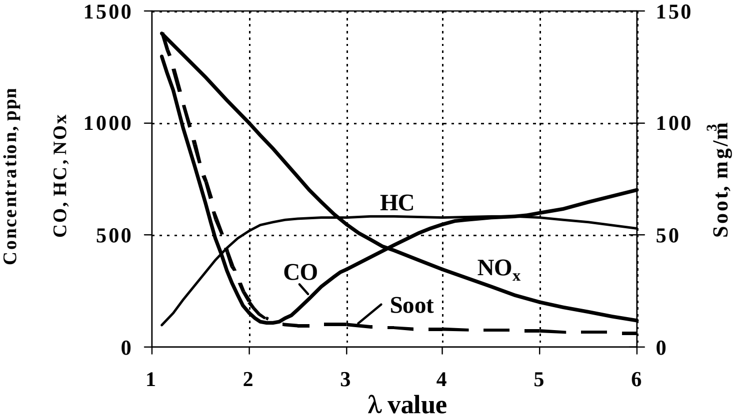


Figure 4. Raw emission concentrations in diesel engines as a function of λ value (Schäfer and van Basshuysen 1995).

4 EMISSION LIMITATIONS

4.1 Mobile applications

The driving forces to decrease emissions have been the concern about pollutants' health effects and the known, developed technologies for removing emissions. Sometimes, the new emission regulations have been enacted first, which have then been a driving force for the development in emission removal methods. The emissions from passenger cars are emitted mainly in cities, where the emissions are most harmful to human beings. The most demanding emission limitations have been traditionally in the USA (California), Japan and the EU, where general emission regulations have been phased into force. The other countries have mostly followed EU or US regulations almost directly, with a short delay. EU regulations have been divided into categories beginning from Euro 0. The current stage is Euro 4, since 2005, and the next stage, Euro 5, will be in power from 2009 onwards. The emission regulation system has been developed to cover as well the quality of fuel and the follow-up of aftertreatment systems. On-board diagnostics (OBD) are required for active aftertreatment systems to keep low emissions in use. The first OBD systems have been used since 1996 in the USA and since 2000 in Europe for passenger cars equipped with three-way catalysts (TWC). The share of diesel fueled passenger cars has increased recently up to 50% in many European countries because of the better fuel economy, drivability of modern diesel engines and tax benefits, but the share is very low (< 2%) in the USA and Japan. The emission limits for passenger cars in the EU area are based on the European driving cycle, which consists of urban (ECE-15) and extra-urban driving (EUDC) phases (Table 1).

Table 1. EU emission limitations for gasoline and diesel passenger cars (< 2500 kg) based on European driving cycle (EDC) emissions (Dieselnet 2006).

Standard	Year	CO g/km	HC g/km	**NO_x g/km**	HC+NO_x g/km	PM mg/km	Durability km/years	S in fuel max.ppm
Diesel								
Euro 1	1992	2.72	-	**-**	0.97	140	-	2000
Euro 2 DI	1996	1.00	-	**-**	0.90	100	-	500
Euro 2 IDI	1996	1.00	-	**-**	0.70	80	-	500
Euro 3	2000	0.64	-	**0.50**	0.56	50	80.000/5	350
Euro 4	2005	0.50	-	**0.25**	0.30	25	100.000/5	50*
Euro 5	2009	0.50	0.05	**0.20**	-	5	160.000	10
Gasoline								
Euro 1	1992	2.72	-	**-**	0.97	-	-	2000
Euro 2	1996	2.20	-	**-**	0.50	-	-	500
Euro 3	2000	2.30	0.20	**0.15**	-	-	80.000/5	150
Euro 4	2005	1.00	0.10	**0.08**	-	-	100.000/5	50*
Euro 5	2009	1.00	0.075	**0.06**	-	5	160.000	10

DI = direct injection; IDI = indirect injection; * S-free fuel (< 10 ppm) need to be available

The heavy-duty trucks are mainly driving on highways and therefore the test cycles simulate heavier driving than passenger car cycles. The latest driving cycles are the European Steady Cycle (ESC) and the European Transient Cycle (ETC), which are used to evaluate the aftertreatment systems beginning in Euro 4. OBD will be required also for heavy-duty aftertreatment systems at latest in Euro 5. US Transient has been used to evaluate the emissions from heavy-duty vehicles in the USA. HC and CO raw emissions are very low and easily removable by oxidation catalysts, but the critical emissions in heavy-duty vehicles are NO_x and particulates, which are also most difficult to remove and complicated aftertreatment systems are under development for future applications (Fig. 5).

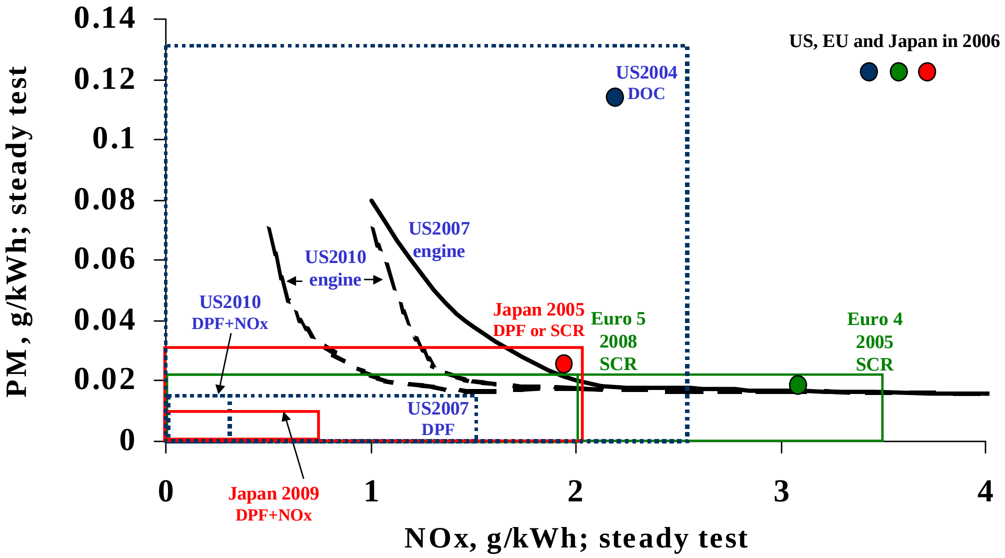


Figure 5. The exhaust gas raw emissions, engine modifications and aftertreatments with heavy-duty diesel vehicles in Europe, the USA and Japan to meet emission limits (Johnson 2006).

Fuel economy is more critical with heavy-duty than with light-duty vehicles and almost all heavy vehicles are equipped with diesel engines. The temperatures are lower in the US than in EU cycles meaning differences in raw emissions and potential aftertreatment systems (Fig. 6).

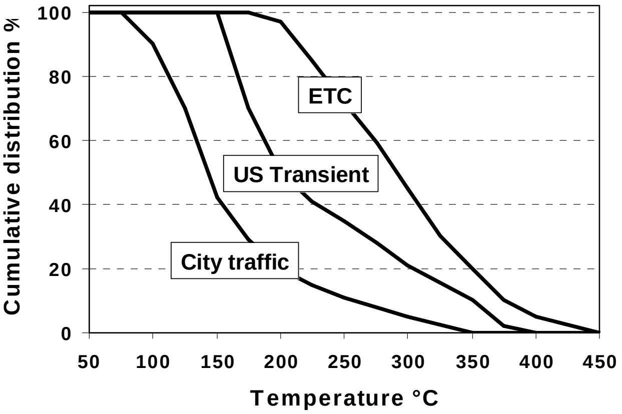


Figure 6. Cumulative temperature distribution after turbine of a heavy-duty diesel engine in European Transient Cycle, US Transient cycle and in city traffic (distribution vehicles) (Moser et al. 2001).

Separate driving cycles have been applied for busses and other distribution vehicles. Many city authorities have created voluntary aftertreatment programs to equip busses and distribution vehicles with aftertreatment systems like diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) to decrease their resident's exposure to pollutants. An example of a bus cycle is the Braunschweig cycle, where the exhaust gas temperature is barely 200°C on average.

4.2 Stationary power plant applications

The first emission regulations for power plant were ruled in Japan due to the documented NO_x emission problems in the 1970's. The first regulations in Europe came into force in Germany in 1985. Later other countries followed the same regulations and wide development was made to develop new types of burners for boilers. Because both NO_x and SO_x emissions originate from fuel in power plant applications, the SO_x and NO_x regulations have been developed jointly. Certain general total emission targets for emissions have been ruled on and e.g. the Finnish government has accepted a target to have 170.000 tons/year of NO_2 in 2010.

Separate regulations also exist for chemical plants such as nitric acid plants, which might emit NO_x. The emission regulations are usually daily average (mg/m^3) or total amounts of NO_2.

5 METHODS FOR NO_X REMOVAL

5.1 Primary methods

Primary methods are applied already in combustion. Combustion modifications have the same targets in boilers and engines but the exact methods are different because of space, mechanical design and timing reasons. NO_x formation is prevented by decreasing globally and locally the combustion temperature and oxygen concentration. The NO_x emissions can be decreased by 20-50% by using so called Low-NO_x burners. Other methods are the two-stage combustion, flue gas recirculation, the use of cooling surface, lowered air temperature and water injection (Rentz et al 1985). The limiting factors to applying the primary methods are incomplete combustion, decreased power and corrosion. Catalytic methods are possible already in combustion or in pressurized gasification.

NO_x formation from fuel-N can be reduced if gases are maintained fuel-rich long enough to form N_2 (Flagan and Seinfeld 1988). In-furnace NO_x reduction is a combustion system with three steps (main combustion, reduction and post-combustion zones) to decrease NO_x emissions (Fig. 7). In addition, it is possible to inject a secondary fuel like CO, CH_4 or NH_3 into the top layers of a boiler. The partially oxidized coal forms char, which is able to keep locally reducing conditions on its surface and catalyze NO reduction.

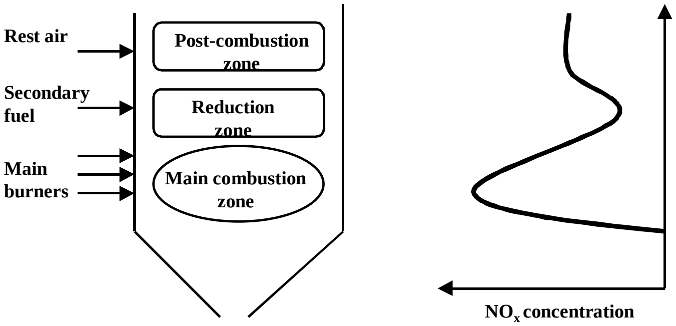


Figure 7. In-furnace NO_x reduction by three phases (Rentz et al. 1985).

The engine modifications are targeted to decrease the conditions in cylinder, where NO_x can be formed. Efficient combustion at high temperatures keeps PM, HC and CO emissions low, but oppositely NO_x emissions increase due to thermal NO_x formation. λ values (= $(A/F)/(A/F)_{stoichiometric}$) are usually about 1.25–3 in diesel engines meaning that a high excess of oxygen (4-18% O_2) exists in combustion and in exhaust gas. NO_x emissions are lower during slow speeds and high during high speeds and the temperature can vary in the range of 100-600°C, which makes the design of engine modifications and after treatment difficult. The freedom in engine modifications is very limited because the drivability and economy should not be adversely affected. The amount of air required in diesel engines is so high that turbocharged engines have replaced the older naturally aspirated engines. At the same time the specific power has increased and the fuel consumption decreased. In turbocharged engines, temperatures are higher and PM/HC emissions have decreased, but NO_x emissions increased. The cylinder design, injection timing, injection pressure, the type of the injectors and exhaust gas recycling (EGR) have been used to decrease NO_x emissions in diesel engines (Schäfer and van Basshuysen 1995). The more exhaust gas is recycled back to the engine, the lower the temperature and thermal NO_x formation. The improved quality of diesel fuel can be understood as a primary method in reducing particularly PM emissions.

5.2 Secondary methods to reduce NO_x emissions

5.2.1 NO_x removal methods

If the primary methods are not efficient enough or not in use, aftertreatment (deNO_x) methods are applied. The main methods are dry processes, and catalytic NO_x removal methods are more common than non-catalytic ones. Most efforts have been focused during the last 35 years on finding selective aftertreatments in the presence of excess oxygen, which will usually react first with reductants like hydrocarbons, hydrogen and CO. The NO_x removal method depends also on the NO_x concentration, temperature (outdoor–1000°C), flow rate and required conversion level. Traces of NO_x in gases or solutions can be purified best by adsorption methods. In the power plant applications, deNO_x and deSO_x methods have often been integrated and possibly the nitrogen and sulfur compounds can be even recycled and utilized as nitrate fertilizers or elementary sulfur. Energy economy in these processes has a key role and ordinarily it is not possible to cool or heat gas mixtures to the optimum operation temperature. The costs of deNO_x methods should be minimized and other possible byproducts (NH_3, N_2O, cyanides) are not allowed. Different NO_x removal methods have been categorized already 30 years ago (Fig.8).

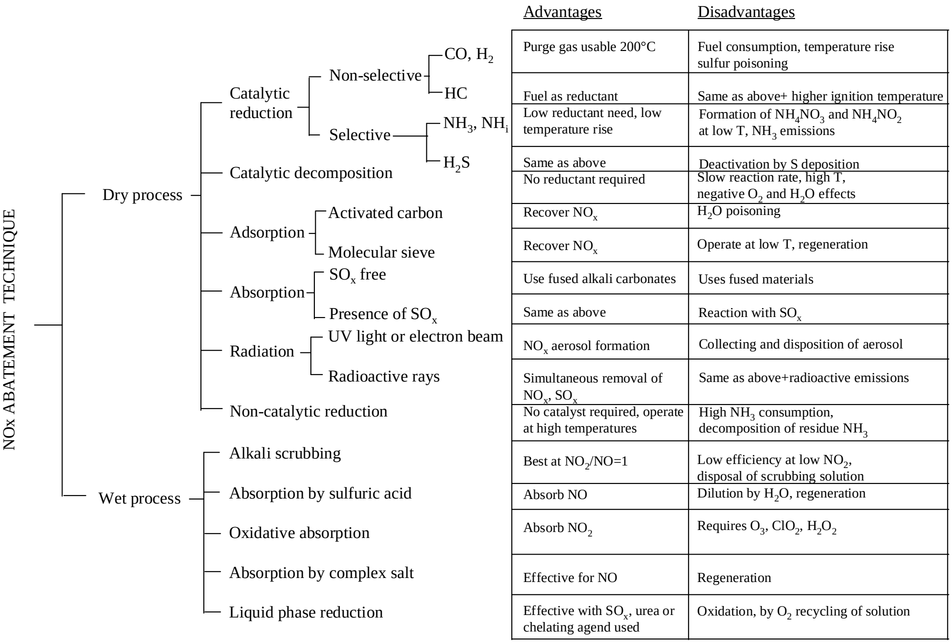


Figure 8. NO_x removal methods (Yamaguchi et al. 1976).

The reductions methods have been divided to catalytic and non-catalytic reductions:

- selective catalytic reduction (SCR) → usual NH_i-SCR systems
- non-selective catalytic reduction (NSCR) → O_2 consumed before NO_x reduction
- selective non-catalytic reduction (SNCR) → thermal deNO_x methods using NH_i
- non-selective non-catalytic reduction (NSNCR) → post combustion deNO_x

Non-selective methods have been used in the past in nitric acid plants with high NO_x concentrations (1000-3000 ppm), where NO_2 was converted to NO by hydrogen, methane or the fuel's hydrocarbons on noble metal based catalysts. This method means a very high reductant consumption and temperature increase as well as secondary emissions of the reductant. Traditionally, HC-SCR or H_2-SCR have been understood as non-selective in lean conditions, even if selectivity improvement has been attempted.

5.2.2 NO_x reduction in three-way catalysts

The commercial TWCs have platinum (Pt), rhodium (Rh) and palladium (Pd) as active metals on a porous support usually containing alumina, cerium oxide (CeO_2) and thermal stabilizers coated on ceramic or metallic honeycomb substrates.

In stoichiometric conditions, hydrogen and CO are the main actual reductants for NO_x. It has been found that reduction by H_2 is much faster than by CO (Niewenhuys et al. 1994). The N_2 formation in NO reduction by hydrogen and by NH_3 has the same temperature dependence suggesting that the same reaction steps are involved. Hydrocarbons in the exhaust gas are a source of CO and H_2. The desired reaction product is N_2 but also small amounts of N_2O and NH_3 in rich mixtures can be formed.

Main reactions of NO:

$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$ (7)

$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$ (8)

Side reactions of NO:

$2\ NO + H_2 \rightarrow N_2O + H_2O$ (9)

$2\ NO + CO \rightarrow N_2O + CO_2$ (10)

$2\ NO + 5\ H_2 \rightarrow 2\ NH_3 + 2\ H_2O$ (11)

If the stoichiometry of the exhaust gas is too lean, NO reduction by CO and H_2 is no longer selective and NO_x reduction drops sharply. In rich conditions, ammonia formation is a problem which can be controlled to a certain extent by the catalyst selection. The highest NO_x conversion to N_2 is reached in a narrow stoichiometric window. Pt has been known to be good in CO oxidation and NO reduction by H_2. Rh is known to be most active in NO reduction with CO and in N_2O decomposition. The synergic co-operation between Pt and Rh particularly in relation to NO reduction is widely utilized in three-way catalysis. Characterizations showed that NO is adsorbed preferentially on Rh and CO on Pt on Pt-Rh/Al_2O_3 (Granger et al. 1998). The high oxygen storage capacity (OSC) has a promoting effect on both oxidation and reduction reactions, because it keeps the conditions in an operation window preventing excessively rich or lean conditions. The main surface reaction path in NO_x reduction by H_2 or CO on noble metal (Pt, Rh, Pd) catalysts is widely proposed to occur by adsorbed N atoms formed by NO dissociation (* = active site) (Cobden et al. 1992):

$N^* + N^* \rightarrow N_2 + 2\ ^*$ (12)

$N^* + NO^* \rightarrow N_2O + 2\ ^*$ (13)

$N^* + 3\ H^* \rightarrow NH_3 + 4\ ^*$ (14)

The formation of adsorbed HNCO species was observed in NO-H_2-CO mixtures on Pt/SiO_2 but not on Pt/Al_2O_3 because HNCO was easily hydrolyzed on alumina surface (Dümpelmann et al. 1995). Therefore, the hydrolysis products of HNCO, like surface NH_i species, are evident in the presence of water on alumina based catalysts.

5.2.3 Selective catalytic reduction by ammonia

Among catalytic approaches, selective catalytic reduction (SCR) by NH_3 (or urea) has grown to become the best available technology in stationary and mobile applications. NH_3-SCR uses the catalysts to facilitate NO_x reduction in the presence of excess oxygen. The net reactions in standard SCR are as follows (Odenbrand et al. 1985):

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (15)$$

$$4\ NH_3 + 6\ NO \rightarrow 5\ N_2 + 6\ H_2O \qquad (16)$$

Iron, silicon or aluminum oxide based catalysts were first tried, but their poor durability resulted in the development of chemically durable TiO_2 based SCR catalysts. They are mainly extruded ones in power plant applications, but the coated ceramic and metallic catalysts are useful in mobile applications. V_2O_5-WO_3/TiO_2 based catalysts have over 90% NO_x conversions in power plant applications at 300-400°C (Fig. 9). The concentration of nitrous oxide as a byproduct is usually very low with these SCR catalysts, opposite to Pt based NH_3-SCR catalysts.

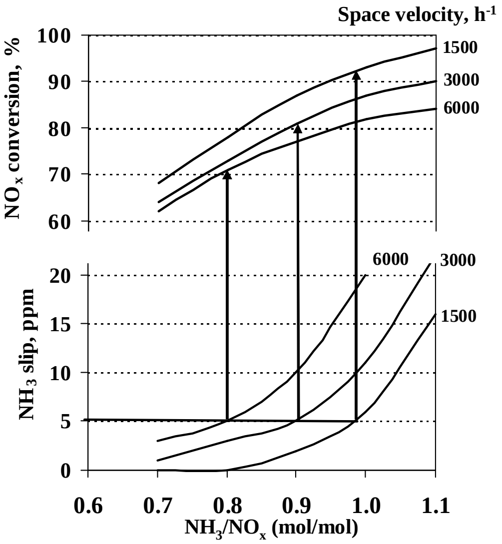


Figure 9. NO_x reduction efficiency by the NH_3 slip limit of 5 ppm on a V_2O_5-WO_3/TiO_2 based SCR catalyst (coal-SCR at 350°C) (Schrod et al. 1985).

At low temperatures, the limiting factors are the kinetically slow reactions but at high temperatures (> 400-500°C) NH_3 oxidation and decomposition prevents SCR on vanadia based catalysts (Ozkan et al. 1993). Ammonia decomposition to nitrogen is an unwanted reaction regarding reductant economy. N_2O formation proceeds partly by the reactions between two ammonia molecules (Vogt et al. 1988).

$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$ (17)

$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$ (18)

$2\ NH_3 + 2\ O_2 \rightarrow N_2O + 3\ H_2O$ (19)

The other path for N_2O formation is a partial reduction of nitric oxide in NH_3-SCR, which is promoted by the reduced and metallic active sites (Odenbrand et al. 1991). N_2O formation is related to the formation of dissociated N (both from NO and NH_3) which is low with vanadium and iron oxide based catalysts but particular high with platinum catalysts.

In mobile diesel engine applications, 32.5% urea-water solution is used as an on-road NO_x reductant. Urea produces ammonia for SCR reactions through thermolysis and hydrolysis

$(NH_2)_2CO \rightarrow NH_3 + HNCO$ > 200°C (20)

$HNCO + H_2O \rightarrow NH_3 + CO_2$ > 200°C (21)

These reactions proceed thermally at 200-300°C if the residence time is long and in a good mixing zone. NH_3 formation can be enhanced by the hydrolysis catalyst, which selectively catalyzes NH_3 formation instead of NO_x, HNCO or N_2 formation.

NO_2 enhances SCR on many titania and zeolite supported catalysts, which helps to keep the volume of a reactor small and to have SCR activity near 200°C, e.g. in mobile applications. The promotion effect of preformed NO_2 has been described as a "fast SCR" reaction (Kato et al. 1981, Tuenter et al. 1986, Jacob et al. 1998, Koebel et al. 2000):

$$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O \qquad (22)$$

which utilizes the equimolar mixture of NO and NO_2 formed in a Pt-based oxidation catalyst (Madia et al. 2002). Ammonia can also react according to the "NO_2 SCR" reaction (Kato et al. 1981, Matsuda and Kato 1983, Odenbrand et al. 1986)

$$4\ NH_3 + 3\ NO_2 \rightarrow 3.5\ N_2 + 6\ H_2O \qquad (23)$$

which is slower than other SCR reactions and is relevant when NO_2/NO is over 1. Therefore a moderate NO_2/NO_x ratio is preferred to have the highest promotion by NO_2.

In addition to conventional vanadia-tungsten/titania, many other types of catalysts (Al_2O_3, TiO_2, ZrO_2, MgO, SiO_2, zeolites) have been investigated for NH_3-SCR (Maunula et al. 1987, Lomma 2003). Iron supported on zeolites (Fe/ZSM-5 and Fe/Beta) have shown higher durability (Long and Yang 2002). The promotion by NO_2 on the activity on zeolite based SCR catalysts has been similar to the V-W/TiO_2 based catalysts (Rahkamaa et al. 2004). Long-term durability, particularly SO_x resistance, is a common problem with new candidates.

The reaction mechanism on V_2O_5/TiO_2-WO_3 catalysts has been widely investigated and the generally proposed reaction mechanism involves the catalysis based on mobile oxygen of vanadium oxides. Tungsten oxides promote and stabilize SCR reactions and decrease SO_2 oxidation to SO_3. Strong acid sites (Brönsted and Lewis) on high surface area TiO_2-WO_3 supports (> 50 m^2/g) have been found to enhance the formation of active vanadium particles (Ye et al. 2002). The oxides (V_2O_5, MoO_3, WO_3, Fe_2O_3, CoO, NiO, MnO_2, Cr_2O_3, CuO), which behave like n-type semiconductors, have been found as the most active catalysts in NO reduction by NH_3 (Matsuda and Kato 1983). P-type semiconductor oxides (CoO, NiO) show a particular activity in NO_2 reduction by NH_3. The reactions have been proposed to proceed both by the Langmuir-Hinshelwood and Eley-Ridel mechanisms, but the latter has been claimed to explain the observation with high NH_3 adsorption capacities (Inomata et al. 1980, 1982) (Fig. 10).

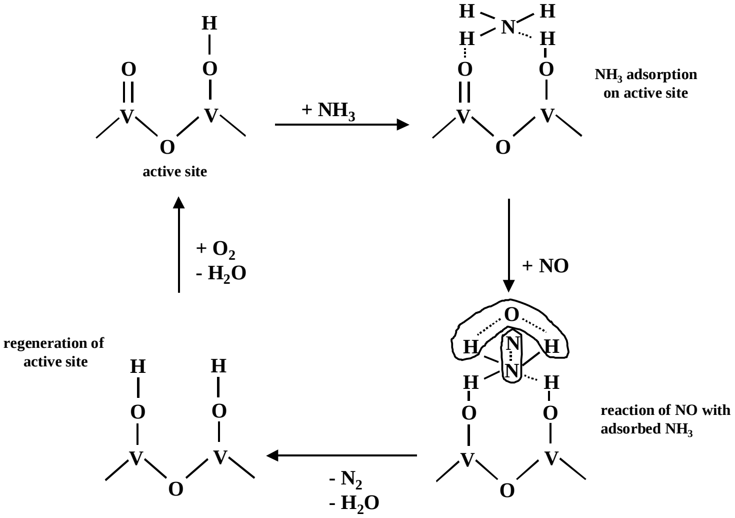


Figure 10. Eley-Rideal mechanism on NH_3-SCR on V/TiO_2 based catalysts (Inomata et al. 1980, 1982).

This reaction mechanism was later modified by the assumption that NH_3 is adsorbed on two oxidized V sites and forms adsorbed NH_2* linked to a vanadium atom (Janssen et al. 1987).

The Langmuir-Hinselwood mechanism has been proposed for a CuO/alumina catalyst by Otto and Shelef (1972) (* catalytic site; # lattice oxygen site).

$NO + * \rightarrow NO*$ (24)

$NH_3* + * \rightarrow NH_2* + H*$ (25)

$NH_2* + NO* \rightarrow N_2 + H_2O + 2\,*$ NO reduction (26)

$2\,H* + O\# \rightarrow H_2O + \#$ (27)

$O_2 + 2\,\# \rightarrow 2\,O\#$ (28)

The Langmuir-Hinselwood mechanism has been proposed for vanadia/titania catalysts even if the NO adsorption strength and coverages have been detected to be low in SCR conditions (Topsoe et al. 1995). The same mechanism has been postulated also for an iron containing catalyst (Kittrell and Eldridge 1985). Takagi et al. (1977) proposed that adsorbed NO_2 and NH_4 are the surface reactants with the interaction of lattice oxygen (TiO_2-WO_3)

$$NH_4^* + NO_2^* \rightarrow N_2 + 2\ H_2O + 2\ * \qquad (29)$$

Markvart and Pour (1967) presumed that oxygen would help the dissociative adsorption of NH_3 on catalyst surfaces. Thus, it can be assumed that the presence of oxygen and the reactive oxygen generator NO_2 would enhance the dissociation of ammonia to form the adsorbed surface reductant NH_2. Often it can be difficult to distinguish the hydrogen number in the intermediates in the presence of surface hydroxyl groups. Thus the different proposals for reaction mechanisms might vary by the type of adsorbed NH_i (i =2, 3 or 4). In the presence of OH groups a natural initiation reaction step can be proposed to be the formation and release of water leaving NH_2^* on surface.

The adsorption of both NH_3 as NH_4^+ and NO_2 on zeolitic sites on a Fe/ZSM-5 surface has resulted in the reaction mechanism, where a $NO_2(NH_4^+)_2$ complex reacts with NO to N_2 (Long and Yang 2002). In another study it was proposed that ammonium nitrite (NH_4NO_2) decomposes directly to N_2 (Sun et al. 2001). The role of iron is to catalyze NO_2 formation, which is a slow, rate-determining step in reaction sequences. In reaction conditions, the catalyst surface is nearly completely covered by adsorbed NH_4^+ and SCR reactions are first-order with respect to NO, zero-order with respect to NH_3 and nearly half-order with respect to oxygen (Huang et al. 2002). The formation of N_2O was negligible with Fe/zeolite catalysts in NH_3-SCR. Similar reaction mechanisms have been proposed also for Cu/zeolites, where the changes between Cu^{1+} and Cu^{2+} create the catalytic properties (Delahay et al. 2004). The final NO reduction step on zeolite based catalysts can be understood to be a Langmuir-Hinshelwood-type with two adsorbed species.

5.2.4 Selective catalytic reduction of NO_x by hydrocarbons

The general principle of catalytic NO_x reduction by hydrocarbons on zeolite based catalysts in lean conditions was introduced in the late 1980's (Held and Koenig 1987, Fujitani et al. 1988). NO_x reduction by hydrocarbons both on several zeolite and oxide based catalysts was described in more detail at the beginning of 1990's (Iwamoto et al. 1991, Shelef 1995, Hamada et al. 1991A). Cu/ZSM-5 and other zeolite catalysts showed a high efficiency in practical space velocities in the presence of water and sulfur oxides, but their hydrothermal durability has been reported to be a problem because of dealumination of zeolites and the sintering of copper sites (Hamada et al. 1993, Grindstedt et al. 1993, Keiski et al. 1996, Sasaki et al. 1992).

The chemical basis for NO reduction with hydrocarbons has been proposed already in the 1940’s and 1950’s, when NO reduction was observed by unsaturated hydrocarbons (isobutene), the promotion of oxygen/NO_2 and the intermediates like nitro hydrocarbons and the reaction chain with other N-containing intermediates to N_2 (Smits and Iwasawa 1995). Therefore, the reaction chains in HC-SCR have been familiar by reaction studies with nitrogen containing organic compounds. However, a boom of HC-SCR in the 1990’s was related to the findings in a practical aftertreatment application, which had a wide commercial and environmental need.

Alkanes have been found to be less active reductants than alkenes and NO_x reduction is limited to higher temperatures (Petuchi et al. 1993). Propene is the most common hydrocarbon representing hydrocarbons in HC-SCR experiments. Several simplified and detailed reaction mechanisms have been proposed for HC-SCR with different catalysts and hydrocarbons. Because the catalysts and operation windows are very different with methane and non-methane hydrocarbons, these concepts are treated separately in the next chapters. In addition, HC-SCR catalysts with Pt as an active metal are different by the reaction mechanism and operation window, which will have a particular role in our CH_4-SCR studies.

The HC-SCR conditions are also very different in so-called passive and active systems with lean engines. The distribution of hydrocarbons by carbon numbers is limited to small C-numbers below 7 in passive systems without post-injection of fuel. The higher C-numbers, matching fuel hydrocarbons, can be found in exhaust gases originating from fuel post-injection. Fuel hydrocarbons are usually more reactive in HC-SCR than hydrocarbons in engine-out emissions. (Akama and Matsushita 1999, Fig. 11)

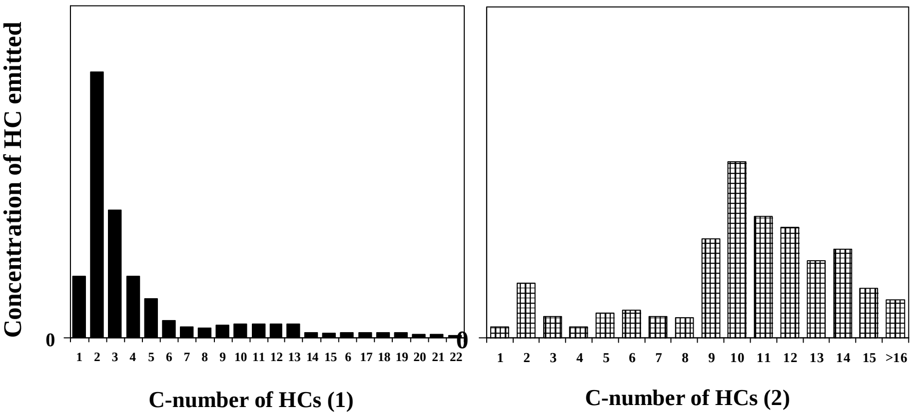


Figure 11. Distribution of hydrocarbons by carbon number in diesel engine exhaust.
1. Passive condition, 2. Active condition with post-injection by common rail (Akama and Matsushita 1999).

5.2.4.1 HC-SCR by non-methane hydrocarbons on zeolite based catalyst

Cu/ZSM-5:

The first, general reaction paths in NO_x reduction by hydrocarbons in lean conditions were proposed based on the studies with Cu/ZSM-5. It was proposed that NO is oxidized on the catalyst surface to NO_2, which is then converted to molecular nitrogen through nitrogen containing intermediates (Iwamoto and Hamada 1991). The total amount of acid sites in zeolite was observed to correlate with high activity and selectivity but to be independent of the strength of acid sites in a study of propene-SCR on several H-form and metal ion exchanged zeolites (Satsuma et al. 1995). The acid properties were detected by NH_3-TPD. It has been proposed that free radicals are formed in this reaction and the N-N bond is formed by the coupling of NO with adsorbed, nitrogen containing intermediates (Lukyanov et al. 1995). The H-abstraction on Cu/ZSM-5 has been reported to be related to the formation of NO_y complexes (nitrates ligated to Cu^{2+} ions), which are then reduced to N_2 (Beutel et al. 1995). The isotope labeled reactant and organic intermediate studies with FTIR and mass spectrometric gas analysis indicated the existence of nitrosopropane and its amine and amide type hydrolysis products as intermediates (Beutel et al. 1996) (Fig. 12). The isotope shift in FTIR spectra enables to detect usually overlapping compounds (Sadykov et al. 2003).

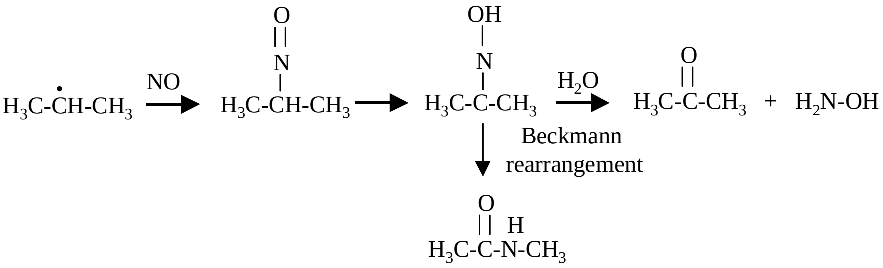


Figure 12. Propane reactions with NO_x (Beutel et al. 1996).

Nitropropane has been observed to be thermally stable up to 250-300ºC, is adsorbed more strongly on cobalt than copper cations (Cu/ZSM-5, Co/ZSM-5) and it reacts quickly in the presence of NO and oxygen at HC-SCR temperatures (Sadykov et al. 2003). Thus nitropropane has been proposed as an intermediate in HC-SCR and its formation as a rate-limiting step in nitrogen formation. Further, nitropropane reacts mainly to nitriles and/or isocyanates both on zeolite and on oxide based HC-SCR catalysts.

It was proposed that the residue on the catalyst surface has no essential catalytic function (Petunchi et al. 1993), but oppositely it has a deactivating effect. A surface intermediate with a C/N ratio close to 3 has also been found by a TPD study in NO reduction by propane in the presence or absence of oxygen (Rebrov et al. 1998). The excess of oxygen is necessary for the NO_x reduction activity because of NO_2 formation, hydrocarbon oxidation and regenerating the active sites from adsorbed species, which carbonaceous compounds might block active sites on Cu/ZSM-5 (Beutel et al. 1996).

The key path is the formation of surface N-species, which are able to react to N_2 in the presence of NO+O_2 or even O_2 only. The most reactive nitrogen species are species with a nitrogen oxidation state of –III (-CNO, -NCO, -NH_2), opposite to species with higher oxidation states (-$N^{+I}O$, - $N^{+III}O_2$, $N^{+V}O_3$). In the latest reaction mechanism proposals, the final step in HC-SCR on Cu/ZSM-5 was the NH_3-SCR reaction, where Cu/ZSM-5 is also a good catalyst (Liu et al. 2001). In the presence of nitroethane, the formation of methyl isocyanate (CH_3NCO) and HNCO was observed at reaction initiation temperatures. However, many of these intermediates in surface studies are observed in the gas phase in the absence of water, but they will usually disappear in the presence of water.

Surface studies by XANES showed that copper in ZSM-5 is reduced to Cu^+ in the presence of propene at elevated temperatures even in strongly oxidizing conditions (Liu and Robota

1994). This state transformation matched the NO_x reduction window. Propene has a very strong reducing effect, but methane has practically no ability to reduce Cu^{2+} to Cu^+ in lean conditions. Therefore, methane has a low activity in HC-SCR with Cu/ZSM-5. Cu^+ is the required copper state to have efficient NO decomposition or NO reduction by hydrocarbons. The Cu^+ sites are known for their ability to activate C-H bond in hydrocarbons by selective oxidation reactions (Sadykov et al. 2003). Propane and NO are competing for oxygen in Cu sites. The same copper state variation by conditions was detected also by a XPS study (Shpiro et al. 1994). Cu^{2+} and Cu^0 can be detected by UV-visible diffuse reflectance spectroscopy and Cu^+ by selective CO adsorption (Praliaud et al. 1998). Thus, the reaction mechanism is the same both in NO decomposition and reduction by hydrocarbons, but the activity is much higher with hydrocarbons, which are able to keep a higher amount of active copper on zeolite (Petuchi et al. 1993). In another study, isolated Cu^{2+} was found to be the key compound in active Cu/ZSM-5 to reduce NO_x with propane in lean conditions and a Cu^{2+} -O-N=O complex was a key intermediate in activating NO (Matyshak et al. 1997). The oxygen containing hydrocarbons like alcohols and aldehydes can be used as oxygen sources in HC-SCR in rich or stoichiometric conditions on Cu/ZSM-5 (Montreuil and Shelef 1992). A key property of Cu/ZSM-5 compared to Cu/Al_2O_3 is lower HC oxidation activity which keeps the HC concentration high enough to reduce NO. Gaseous isocyanic acid (HNCO) was detected at 240-390°C (Radtke et al. 1995) and gaseous HCN at 180-330°C (Radtke et al. 1994) in NO reduction with propene in dry conditions over Cu/ZSM-5. This was an indication about the formation of N-H compounds, which are able to act as reductants in NH_i-SCR reactions. It was claimed that hydrogen in HNCO was not originated from water, because in the presence of water and ammonia, no HNCO was formed. Oppositely, in the presence of water, ammonia was detected even in the gas phase. These observations proved that hydrocarbons are able to form in dry conditions HNCO, which reacts in hydrolysis to ammonia in the presence of water. The concentrations of HNCO, NH_3 and HCN were only a few percent of inlet NO_x concentration. However, these compounds might act as powerful reductants on catalytic surfaces. In the same study, it was concluded that zeolitic sites are able to form adsorbed NCO (isocyanic) from adsorbed CN (cyanic). The formation of adsorbed NO^+ on H^+ or Cu^+ sites was proposed by FTIR studies on Cu/H-ZSM-5 (Poignant et al. 2001). NO^+ reacts further to acrylonitrile and then to Cu^+CN or Cu^+NC, which have a reducing power to NO_x. The cyanic or isocyanic acids are harmful compounds but in the presence of water, like in all exhaust gases, these compounds disappear and form mainly ammonia or nitrogen.

NO dissociation on catalyst sites was proposed to be the reducing step in HC-SCR on Cu/ZSM-5 based on numerical simulations (Wilber and Boehman 1999). Cho (1995) proposed also the NO dissociation mechanism for Cu/ZSM-5 to simply modeling but mostly this mechanism has been applied for Pt catalysts (Burch et al. 1994), but not for Cu/ZSM-5 or other high temperature HC-SCR catalysts.

Co/zeolites:

The reactivities of different hydrocarbons were studied with Co/mordenite and Co/ZSM-5. In contrast to many other studies, it was claimed that the final NO reduction occurs on support acidic sites and NO_2 formation on Co sites (Miller et al. 1998). They proposed that N_2 formation occurs first by the protonation of the reducing agent by protons on zeolite and carbocations reacts with gas phase NO_2. A similar reaction sequence has been proposed for metal-free acidic zeolites (Shelef 1995). The ease of protonation (propene > propane > methane) correlates with the N_2 formation rate, which was used as a proof for this mechanism. The other proof was the observation that the weaker acid sites i.e. on SiO_2-Al_2O_3 are effective for NO_2 reduction by propene, but not by methane. They also proposed that either NO_2 formation or NO reduction could be the rate-limiting step in HC-SCR with these Co/zeolites. Spectroscopic characterizations combined with catalytic activity studies confirmed that highly dispersed cobalt is essential for NO_x reduction by propane on Co/beta (SiO_2/Al_2O_3 = 22) (Ohtsuka et al. 1998). Co_3O_4 was formed with a higher ion exchange ratio ($\geq$ 100%) and it promoted the low temperature but destroyed high temperature activity due to excessively fast propane oxidation. Co/beta(Si/Al_2 = 22) has shown a superior durability in propane-SCR compared to Co on ZSM-5, mordenite, ferrierite or Y zeolites in the presence of SO_2 (Tabata et al. 1998). The reason was claimed to be the micropore structure of beta zeolite, which is able to keep dispersed Co stable and prevent the Co_3O_4 formation in aging conditions.

Fe/zeolites:

The promising activities of Fe zeolites caused a second HC-SCR boom after Cu/ZSM-5 (Chen and Sachtler 1998). Fe/zeolites also have a high activity in N_2O decomposition. The first results have been reported by using solid ion exchanged iron (from $FeCl_3$) on ZSM-5 with the iron content up to 5%. In these catalysts, the active iron was located mainly out of ZSM-5 pores (Bitter et al. 2003). Later, a variety of results with iron zeolites has been published using different types of zeolites, SiO_2/Al_2O_3 ratios, preparation methods (solid and liquid ion exchange, impregnations) and iron contents. It was possible to prepare intra-zeolitic iron sites with a low iron concentration by a solid ion exchange method and to have a high HC-SCR activity by butane (Heinrich et al. 2001). Fe complexes located on zeolitic Brönsted acid sites have been proposed to be the active sites in solid ion exchanged Fe zeolites. In general, the flexible redox properties of iron in Fe/ZSM-5 are the key for the high activity, even if the Fe/zeolite catalysts are very sensitive to the preparation conditions (Heijboer et al. 2003). The main reaction mechanism schemes are similar to Cu/ZSM-5 and oxide based catalysts. Fe/ZSM-5 shows a particular high activity for NO oxidation. Reactive oxygen (superoxide or peroxide ions) is a reason for high NO_2 formation promoting HC-SCR (Lobree et al. 1999, Chen et al. 2000A). Isobutyronitriles formed HCN which was further able to form adsorbed NCO and NH_i compounds in isobutane-SCR (Liu and Cant 2003). The chemical and hydrothermal deactivation of Fe/ZSM-5 was seen to be a problem, which was attempted to be solved by changing the zeolite or the preparation method (Decyk et al. 2001).

Noble metals on zeolites:

Pt and Pd on zeolites differ from other catalysts by the operation window and reaction mechanism due to their high HC oxidation activities, which cause a narrow deNO$_x$ window. The maximum NO_x conversions coincides with the HC conversions of 60-80%. The highest NO_x conversions at low temperatures (150-300°C) are reached by using noble metal containing catalysts but N_2O formation is a problem (Shin et al. 1995). Platinum as an active metal has shown the best activity and durability in propene-SCR in the presence of water and SO_2. The NO_x reduction mechanism has been proposed to proceed by NO decomposition on Pt/ZSM-5 (Cho et al. 1995), which differs from the mechanism proposals for base metal (e.g. Cu, Co) exchanged zeolites. Pt/zeolite catalysts have a operation window matching light-duty vehicles driving conditions (150-300°C) and are quite durable up to 700°C. Pt/USY (Ultra Stable Y) showed better NO_x conversions than other Pt based catalysts in HC-SCR (Perez-Ramirez et al. 2001). Based on surface FTIR studies, NCO type intermediates have been seen to be the reactive species in propene-SCR on ZSM-5, beta, Y and ferrierite based Pt catalysts (Huuhtanen et al. 2005). However, these observations are related mostly to rich and dry conditions. Unsaturated hydrocarbons are found to be more efficient reductants compared to saturated hydrocarbons on Pt/zeolites (ZSM-5) (Rottländer et al. 1996). The coverage of carbon species was also higher on Pt/zeolites in the presence of propene.

Other zeolite based catalysts:

Other zeolite based HC-SCR active catalysts are e.g. Cu/mordenites (Torre-Abbreu et al. 1997), Ag/zeolites (ZSM-5, Na-beta, H-beta, H-ferrierite, K-ferrierite) (Furusawa et al. 2001, Seijger et al. 2003), Ce/zeolites (ZSM-5, beta, Y, mordenite, Y, ferrierite, Al-MCM-41) (Misono and Kondo 1991, van Kooten et al. 1999, Krishna et al. 2002, Long and Yang 1999) and Ni/zeolites (Mosqueda-Jimenez et al. 2003). When the Cu ion exchange ratio was lower on mordenite, copper on a sodium form showed higher activity than copper on a hydrogen form. It was claimed that the Brönsted acidity (H-form) did not promote NO reduction with propene. The active form on Ni/ZSM-5 was the isolated Ni^{2+}, but the formation of surface Ni^{2+} or Ni oxide clusters caused deactivation in HC-SCR (Mosqueda-Jimenez et al. 2003). Ag/ZSM-5 showed an unusual high selectivity to N_2 in NO reduction by propene. FTIR studies with acidic mordenites in the presence of NO_2 and propene resulted in a reaction scheme where NO and NO_2 react on acidic Brönsted sites to nitrosonium ions (NO^+), which is able to form acrylonitrile ($CH_2=CH-C\equiv N$) (Gerlach et al. 1999). The hydrolysis of acrylonitrile resulted in further adsorbed ammonium ions, which are efficient NO reductants. The studies with ethylene-SCR on H-ferrierite resulted in the reaction mechanism proposal, where nitroethylene or its nitrogen containing by-products like NH_3 reacts with NO_x to N_2 (Nanba et al. 2002). Clay type materials like saponite, smectites and TiO_2-pillared montmorillonites have also shown HC-SCR activity particularly with silver as an active metal (Sato et al. 1997). More rare zeolites like IM5 (Palomares et al. 2003), SUZ-4 (Subbiah et al. 2003) and AlTS-1 (Schay et al. 2002) have been reported to show a HC-SCR activity in the presence of cobalt or copper.

Metal silicates:

Metal silicates also had a good HC-SCR activity compared to ion exchanged Al-silicates in lean mixtures (Inui et al. 1995). In these metal silicates, active metals (e.g. copper) have replaced aluminum in zeolite structure (e.g. ZSM-5) and the additional ion exchange is not needed. The dispersion and hydrothermal stability are claimed to be better in these structures. The activity of Co-silicate was improved while the activity of Cu-silicate (both MFI type) was lost by high-temperature pretreatments (up to 1000°C) (Tapanee et al. 1999).

Bimetallic catalysts:

Co-cations (e.g. Co, Fe, Ni, Ca and Sr) in the same zeolite structure (usually ZSM-5) were attempted with the most active metals (e.g. Cu) on different zeolites (ZSM-5) (Teraoka et al. 1992, Keiski et al. 1996). The co-cations increased the maximum NO_x conversions, broadened the operation window and improved stability. The promotion in multicomponent catalysts is based on the increased number of total active sites in different reactions and temperature ranges. The thermal stability was improved with Cr as a cocation in Cu/ZSM-5

(Räisänen et al. 1997). The activity of Ce/ZSM-5 was improved by the addition of Sr (Ce-Sr/ZSM-5). A low amount (0.1%) of Pt in 1%Co/H-Y promoted NO reduction by propene (Furusawa et al. 2002). The drawback in the use of platinum is the higher N_2O formation as observed with Co-Pt supported on H-MFI and H-Y (Maisuls et al. 2003). In the same study, the final step in propene-SCR was claimed to be the reaction between adsorbed NCO and gaseous NO. The active form of Co was ion exchanged Co (Co^{2+}) with a low SiO_2/Al_2O_3 ratio and metallic platinum. Ce-Pd/H-mordenite showed good activity in NO_x reduction by dodecane (Cordoba et al. 2001) and Ag-Pd/H-mordenite by ethanol (Masuda et al. 1998). The optimal loadings were observed to be 3% Ag and 0.01% Pd. The addition of palladium amount decreased the activity due to the enhanced HC oxidation rate. Pd-Mo/H-ZSM-5 showed promising activity and good selectivity in ethanol-SCR (Salgado et al. 2003). A Cu-Rh/ZSM-5 catalyst showed combinatory NO_x efficiency compared to the ethylene-SCR activities of Cu/ZSM-5 and Rh/ZSM-5 (Sullivan and Cunningham 1998). If HC-SCR catalysts have similar HC oxidation activities or no mutual poisoning effects, these types of combination results are possible.

Two component catalysts:

Sn/ZSM-5 alone and mixed with Mn_2O_3 showed higher activity in the presence of water than in dry conditions for NO_x reduction by propene (Hirao et al. 1996). This observation was related to the particular property of Sn/ZSM-5 in wet conditions. The activity of Ce ion exchanged zeolites was improved by using the mechanical mixture of Ce/ZSM-5 with Mn_2O_3 or CeO_2 (Misono and Kondo 1991, Yokoyama and Misono 1994). The promotion has been explained by the bifunctional mechanism including the active sites both for NO oxidation to NO_2 and for NO reduction by hydrocarbons. The studied metal oxides were good catalysts for NO oxidation. The choice of oxidation catalyst was important because an excessively active HC oxidation catalyst ruined the HC-SCR activity (Fig. 13). Mn_2O_3 and CeO_2 promoted while CuO and Cr_2O_3 decreased the activity of Ce/ZSM-5 in propene-SCR.

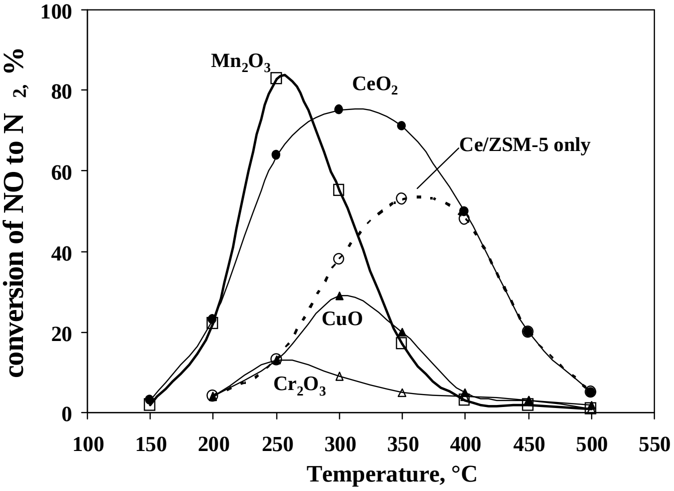


Figure 13. Effect of a few metal oxides on the conversion of NO to N_2 on Ce-ZSM-5 (mixing ratio 1:1 by weight) in NO-C_3H_6-O_2 reaction (Misono 1998).

Effect of oxygenated hydrocarbons:

The oxygenated hydrocarbons in feed are easily adsorbed zeolites or oxides without additional cations and promote HC-SCR (Hamada et al. 1992, Miro et al. 1999). NO_2 is more reactive in HC-SCR than NO particularly on these catalysts. Often their durability in reaction conditions is limited, because zeolitic H or Na sites are easily poisoned (Giles et al. 2000). The other problem is the limited NO_2 formation ability compared to the catalysts which contain an active metal for NO oxidation. The oxygenated hydrocarbons like methanol formed in partial oxidation reactions are able to convert NO to nitrogen even in gas phase reactions (Vassallo et al. 1995).

Promotion by plasma and NO_x adsorbents:

External energy like plasma has been applied to many reactions such as NH_3-SCR, HC-SCR and soot oxidation. The promotion in HC-SCR is based on the oxidation of hydrocarbons and NO (to NO_2) before HC-SCR catalysts (Kwak et al. 2003). Plasma enables higher NO_2 rates than with oxidation catalysts. Otherwise, reaction mechanisms are the same. NO_x adsorbing compounds such as barium in Y and ZSM-5 zeolites have showed a promotion in the presence of high concentrations of NO_2.

Although zeolite based catalysts have shown high activities, zeolite micropores might cause higher adsorption controlled diffusion with small HC molecules or geometry-limited diffusion limitations with large HC molecules (Shichi et al. 2001).

5.2.4.2 HC-SCR by non-methane hydrocarbons on oxide based catalyst

Alumina and Co/alumina:

Soon after the inventions with Cu/ZSM-5, various oxide based catalysts were found to be active as well in HC-SCR. Alumina, silica-alumina, titania and zirconia were first introduced as active oxide catalysts (Kintaichi et al. 1990). The acidity of these catalysts was proposed to be the key factor in activity. The durability of pure alumina or other supports like TiO_2 or SiO_2 was found to be poor and several metal oxides have been added as catalytically active compounds. Cu, Co, Ag, Au, Ga, In and Sn were found to be active for NO_x reduction on various oxide based supports like alumina. The addition of active metals on alumina enhanced the low temperature activity by catalyzing hydrocarbon and NO reactions. Alumina and zeolites are known to require low space velocities and moisture to reach practical NO_x conversions (Hamada et al. 1990 and 1992). The details in catalyst preparation methods (precursor salt, calcination temperature, metal loading) were seen to be critical in HC-SCR activity (Hamada et al. 1991A). In general, alumina based catalysts had higher activities with transition metals than silica based. Sulfate has been seen to have a kind of promotion on TiO_2, ZrO_2 and Fe_2O_3 but a deactivating effect on alumina in NO_x reduction by propane, even if the total conversions were at a relatively low level (Hamada et al. 1991B). It was concluded that the active form in Co/alumina was Co aluminate, which matched the observed color, XRD and XPS analysis. In the first publications, NO_x reduction was proposed to occur in the reaction between the partially oxidized hydrocarbons and NO_2 or NO. These assumptions were supported by the observations that NO_2 was reduced more easily than NO, and the hydrocarbons consisting of functional groups like alkenes (propene), alcohols (methanol, ethanol, propanol) were better reductants than alkanes (propane):

$$C_xH_yO_z + NO_2 \text{ --> } N_2 + CO_2 + H_2O \qquad (30)$$

It was also proposed that NO_2 was formed on dispersed Co species (CoO) and NO reduction to N_2 proceeded over alumina (Hamada et al. 1994). The role of alumina was to stabilize the metal oxides in certain oxidation states (e.g. Co^{2+}, Ag^{+}) and increase the surface area of active metal oxide (e.g. SnO_2) (Kung and Kung 2000).

Nitrogen containing organic compounds (R-CNO) were observed to react quickly to R-NCO and R-NH_2 or NH_3, which react to N_2 with NO_2 on alumina catalyst (Obuchi et al. 1998B). The final steps in this reaction mechanism proposal follow the conventional NH_3-SCR mechanism.

Ag/alumina:

Miyadera (1993) presented an Ag/alumina catalyst which showed a particular good activity in the presence of oxygenated hydrocarbons like ethanol and acetone. The deactivation effects of water and SO_2 on Ag/alumina were detected to be lower than on many other metal oxide catalysts, because Ag_2SO_4 sites are also active in lean HC-SCR (Abe et al. 1998). A key factor in the activity was a close interaction between Ag and alumina created by a high temperature calcination (Aoyama et al. 1997). The optimum Ag loading was about 2% Ag in alumina resulting Ag as the active oxidation state of +1 in reaction conditions. When the Ag loading was too high, silver was metallic (Ag^0) (Bethke and Kung 1997). Adsorbed organic nitro compounds like nitromethane and nitroethane were found by FTIR studies (Kameoka et al. 1998). Organic nitro compounds have been noticed by FTIR studies of ethanol-SCR to form adsorbed isocyanate (NCO), which reacts easily with NO to N_2 in lean and rich conditions (Chafik et al. 2000). Ag/alumina has been applied in diesel conditions because its activity was increased as the carbon number increased and it showed a high activity in the presence of octanes (Shimizu et al. 2000). The reaction mechanism paths were proposed to include several parallel paths, where the final reactants in N_2 formation were proposed to be adsorbed or gaseous NO_x, which reacted with adsorbed or gaseous NH_3, R-CN or R-NH_2 (Eränen et al. 2004). The presence of a low concentration of hydrogen has been detected to significantly enhance propane-SCR of NO_x on Ag/alumina at low temperatures (300-400°C) (Satokawa 2000). A reason might be the promotion related to saturated hydrocarbons and propane was operating similarly than propene as a reductant when hydrogen was present. Reactive hydrogen might initiate the formation of adsorbed species from propane and NO_x at lower temperatures.

Au/alumina:

Au/alumina was prepared by a method which kept Au in an active, finely dispersed form resulting in about 70% NO_x conversion in propene-SCR in the presence of water (Ueda et al. 1997). The optimal Au loading was 0.1-0.2 wt-%. The reaction mechanism is similar than for other alumina based catalysts by the promotion of NO_2 to form $C_nH_mN_xO_y$ surface species (Bamwenda et al. 2000).

Sn/alumina:

Sn/Alumina has shown a particular activity in HC-SCR in the presence of water (Tabata et al. 1994). Even pure SnO_2 had a HC-SCR activity and durability up to 800°C (Teraoka et al. 1993). Later studies confirmed that reducible, dispersed SnO_2 was the active form over a wide Sn concentration range. Al_2O_3 and ZrO_2 were better as supports than TiO_2, SiO_2 or MgO in C_2H_4-SCR (Auroux et al. 2000).

In/alumina and Ga/alumina:

We systematically measured the activity of alumina supported metal oxide catalysts (In, Co, Ag, Sn, Ga, Mn) (II, III). In and Ga on sol-gel prepared alumina showed high HC-SCR activities at 400-500°C even in wet conditions. Similar results with In and Ga on alumina were reported in another study (Miyadera and Yoshida 1993). Sol-gel prepared mixed oxides of In_2O_3-Al_2O_3 and Ga_2O_3-Al_2O_3 have shown promising results and durabilities (III, Haneda et al. 2001). The formation of various C,N,O-containing compounds was detected by GC-MS techniques for Ga_2O_3/Al_2O_3 and In_2O_3/Al_2O_3 in HC-SCR by propene (Haneda et al. 2001, 2002). Plasma enhanced the HC-SCR activity of these catalysts at lower temperatures (Tran et al. 2004).

Pt based catalysts:

Pt/alumina had HC-SCR activity in lean conditions (Sasaki et al. 1992). The reaction mechanism in HC-SCR with Pt containing alumina or silica based catalysts has been proposed be similar to Pt based zeolite catalysts (Burch et al. 1994 and 2002). It has been found that propene-SCR of NO_2 proceeds entirely on metallic sites and supports had no crical role with Pt and Rh on alumina or silica (Bamwenda et al. 1997). Oppositely, it can be generalized that oxide based catalysts (Ag, Co, In, Ga, Sn), which have a lower HC oxidation activity, utilize both support and supported compounds in HC-SCR catalysis. Organic nitro, nitrite and carbonyl species were detected to be reactive to form N_2 on Pt/SiO_2 in NO-C_3H_6-O_2 reaction (Tanaka et al. 1994). In another study, surface cyanide (-CN) species were detected on Pt/SiO_2 in propene-SCR conditions and were assumed to react with NO, NO_2 and O_2 to N_2 (Captain and Amiridis 2000). Particularly, in the presence of Pt as an active compound, the formation of nitropropane is evident which can be proposed to be due to high NO_2 formation. During the high activity in C_3H_6-NO-O_2, the surface was dominated by carbonaceous species, while in C_3H_8-NO-O_2 with a low deNO_x activity adsorbed oxygen was the main compound (Burch and Watling 1997A). In the later studies on octane-SCR, the reaction mechanism was clarified to be dependent on the HC/O_2 ratio and two different reduction schemes were taken into account for NO_x reduction.

In the case of a high HC/O_2, the earlier presented NO decomposition mechanism is prevailing but another reaction path via NO_x reduction by carbonaceous species was proposed in low HC/O_2 conditions (Burch et al. 1998). Thus, the second scheme is the principally same as that proposed for Pt-free HC-SCR catalysts. Later, other research groups proposed NO_x reduction by partially oxidized hydrocarbons to be the main route in HC-SCR with supported Pt catalysts (Captain et al. 2002). A lower Pt dispersion has been found to correlate to the higher HC-SCR, NO oxidation and HC oxidation activities (Denton et al. 2000). The optimum Pt dispersion on alumina or silica was observed to be as low as 2.6% in propene-SCR.

The active site on Pt/alumina has been proposed to be the partially oxidized or metallic Pt, whose state is cycling by HC and NO reactions (Schiesser et al. 2001). However, the original state of Pt had a minor effect on activity (Obuchi et al. 1993, Burch and Watling 1997B). NO_2 was not an essential intermediate in HC-SCR on Pt catalysts and the highest competition between hydrocarbon and NO on common Pt sites were observed during the highest NO_x conversions (Pitchon and Fritz 1999). In the same study, nitrogen containing hydrocarbon species were proposed to be the important intermediates.

In addition to alumina, many other oxide supports (TiO_2, SiO_2, ZnO, ZrO_2, La_2O_3) have been tested with Pt in HC-SCR reactions (Bamwenda et al. 1995, Burch and Sullivan 1999, Pitchon and Fritz 1999). Several additives (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti, Ag, Au, Pd, Pd) have been examined as promoters in Pt/alumina to find out a possible route for higher activities and selectivities in HC-SCR (Obuchi et al. 1993, Burch and Watling 1997). However, it was concluded that the reaction mechanism in HC-SCR remained as the same as with different Pt containing catalysts. When toluene was used as a reductant, N_2O formation can be prevented at low temperature, which showed that there exist possibilities to overcome the N_2O problem with Pt catalysts (Burch and Ottery 1996).

As a summary, the final reduction in HC-SCR proceeds on Pt catalysts by the following surface reactions (Amiridis et al. 2004):

$N^* + N^* \rightarrow N_2$	dissociation route	(31)
$CN^* + NO_x/O_2 \rightarrow N_2 + CO_2$	CN route	(32)
$NCO^* + NO_x/O_2 \rightarrow N_2 + CO_2$	NCO route	(33)
$NH_i^* + NO_x/O_2 \rightarrow N_2 + H_2O$	NH_i route	(34)

Rh and Ir catalysts:

Rh/alumina showed a medium temperature HC-SCR activity around 300°C but the maximum NO_x conversions were below 40% (Akama and Matsushita 1999). Ir on various supports had promising activities and durabilities with a low N_2O formation in HC-SCR compared to Pt catalysts (Nakatsuji 2000).

Other oxide based catalysts:

Most of the transition metals (Co, Cu, Fe, Ni, Mn, etc.) supported on alumina have shown a certain HC-SCR activity but the activity and durability are not usually good compared to the best known catalysts. Cu/alumina is very sensitive to the Cu loading and preparation method, and the stability of copper is a problem, even if alumina as a support is more stable than ZSM-5 zeolite (Chen et al. 1999B). Cu, Ni and Co have been proposed to be aluminates as active form on alumina (Shimizu et al. 1998). Vanadia/alumina, molybdena/alumina showed promising activities in NO_x reduction with methanol and dimethyl ether (DME) in lean conditions compared to alumina (Masters and Chadwick 1998 and 1999). Sulfated alumina remained active in methanol-SCR but sulfated molybdena/alumina upheld activity with both methanol and DME. Cu on sulfated zirconia has been examined in decane-SCR but the durability of these kinds of sulfated supports is limited (Figueras et al. 1998).

Coated alumina based catalysts:

The first studies were mainly conducted with powder samples, but in the practical conditions the catalysts should be coated on honeycomb structures. The effect of binders can be dramatic on HC-SCR activity. Coated sol-gel alumina based Co, In, Sn and Ag catalysts showed a higher efficiency in lean conditions (Fig. 14).

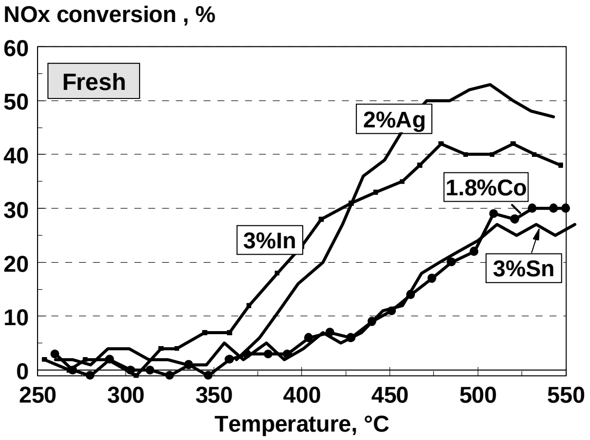


Figure 14. The activity of fresh sol-gel alumina based Co, Ag, In and Sn catalysts coated on a high-cell density metal substrate in a simulated lean exhaust gas (310 ppm NO, 900 ppm C_3H_6, 900 ppm CO, 8% O_2, 10% CO_2, 10% water, balance N_2; space velocity 50.000 h^{-1}, 130 cell per cm^2 (800 cpsi)) (Maunula 1997).

Bimetallic catalysts:

Sometimes more than one active compound has been added into the same support to promote HC-SCR reactions. Cu-Cs/alumina showed a higher NCO adsorption IR bands and a corresponding higher HC-SCR reactivity than Cu/alumina (Ukisu et al. 1992). The promotion was concluded to be related to the electron donation of Cs to Cu. In the presence of SO_2, 1% Co-5% Sn/alumina had a higher activity in decane-SCR than 1% Co/alumina (Cheung and Kung 1999). A high activity in propene-SCR was also reached by using a Co-rich combination: 6% Co-2% Sn/alumina (Chen et al. 2001A). The role of Sn was to stabilize Co^{2+} on alumina in aging conditions. Sol-gel prepared SnO_2- or In_2O_3-doped Ga_2O_3/alumina showed improved activity in the presence of water compared to sol-gel prepared Ga_2O_3/alumina (Haneda et al. 1998 and 1999). Co-In/alumina showed an improvement compared to Co/alumina in propene-SCR (Liu et al. 2004). Ga_2O_3-NiO/alumina had a higher activity in C_2H_4-SCR at low temperatures and Ga_2O_3-ZnO/alumina at higher temperatures (Zahir et al. 2003). Cu-Gd/alumina catalysts upheld activity in real diesel exhaust gases (Dziewiecka and Dziewiecki 1993). Mixed oxides of Zr and Cu, Ni and Co have also been used succesfully in C_3H_6-SCR (Bethke et al. 1994). A low concentration of Co on ZrO_2 kept Co well dispersed and reactive in propene-SCR (Pietrogiacomi et al. 2000). Cu and Cr on CeO_2 showed a good propene-SCR activity (Amin et al. 2003).

Perovskites (e.g. $La_{0.8}A_{0.2}MnO_3$ or $LaMn_{0.8}B_{0.2}O_3$; A=Sr, Ba, K, Cs and B= Ni, Zn, Cu) have shown in addition to a NO decomposition ability, promising activities for $deNO_x$ in the presence of hydrocarbons (Buciuman et al. 2001). The reaction mechanism has been proposed to be a conventional HC-SCR at 150-300°C and possibly a direct NO decomposition at 300-550°C. The inhibition by water, hydrocarbons and poisons is a serious problem of perovskite catalysts. In general, many published, promising HC-SCR results are related to dry and sulfur-free conditions with thermally fresh catalysts and these catalysts often have low activities in real exhaust gases.

If noble metals such as Pd, Pt or Rh are used as dopants with base metal catalysts, their concentration should be very low in order to not destroy the HC-SCR activity by a high HC oxidation rate. 0.005 wt-% Pd was optimum as a promoter with In/TiO_2-ZrO_2 in propene-SCR (Haneda et al. 1997). Similarly, a low amount (0.01%) of Pd promoted the performance of Ag/alumina in propene-SCR (Wang et al. 2004). In one study Rh-rich Rh-Ag/alumina had the highest propene-SCR activity, because Rh has a lower ability to oxidize HCs than other noble metals (Kotsifa et al. 2002).

Multicomponent and layered catalysts:

Mixtures of separate catalysts have been used to enhance HC-SCR usually by combining a good oxidation catalyst (NO --> NO_2) with a good HC-SCR catalyst. The promotion has been found e.g. with 30%Ga_2O_3/Al_2O_3+Mn_2O_3 (9:1) (Chen et al. 2000B), NiGa (1:3)O_x+ Mn_2O_3 (5-10:1) (Chen et al. 1999) and Au/alumina+Mn_2O_3 (Ueda and Haruta 1998), which mostly improved HC-SCR activity in the low temperature range (Obuchi et al. 1998A). Mn_2O_3 has been used as a promoter for Ni-Ga mixed oxide (Chen et al. 2001B). In our studies, the physical mixture of In/alumina or Ga/alumina together with Mn_3O_4 showed a significantly improved activity (III).

The layering of different catalyst compositions is a way to prevent negative interactions between separate phases and to maintain high activities in catalyst structures and washcoat layers (Obuchi et al. 1998C). H-ZSM-5 coated on the top of Pt/SiO_2 showed a superior catalytic activity in diesel exhaust gas conditions. The layered catalysts having highly dispersed Au/alumina or Pt/alumina on bottom and H-mordenite or Cu/mordenite on top improved low temperature activities compared to mordenite catalysts (Ahn and Lee 2003). Therefore, it has been beneficial to add a HC-SCR catalyst on the top layer to limit the diffusion resistance of hydrocarbons in washcoat layer.

In addition to multifunctionality in the same catalyst bed or particles, different catalytic HC-SCR properties have been utilized by assembling the catalyst beds into certain sequences by the flow direction. The operation window is the combination of low, medium and high temperature activities. The HC-SCR catalysts, which have very different HC oxidation abilities can not be mixed into the same bed, because the high HC oxidation activity of low temperature HC-SCR catalysts will practically consume hydrocarbons before they react on medium and high temperature catalysts (Vaccaro et al. 2002). The separate catalyst beds of In/alumina and Pt/alumina created a deNO$_x$ window at 200-550°C (Li et al. 2004). Similar results were reached with Ag/alumina, Cu/ZSM-5 and Pt catalysts in sequence by decreasing hydrocarbon oxidation activity (Fig. 15). The activity in transient conditions is a limitation of serial reactors.

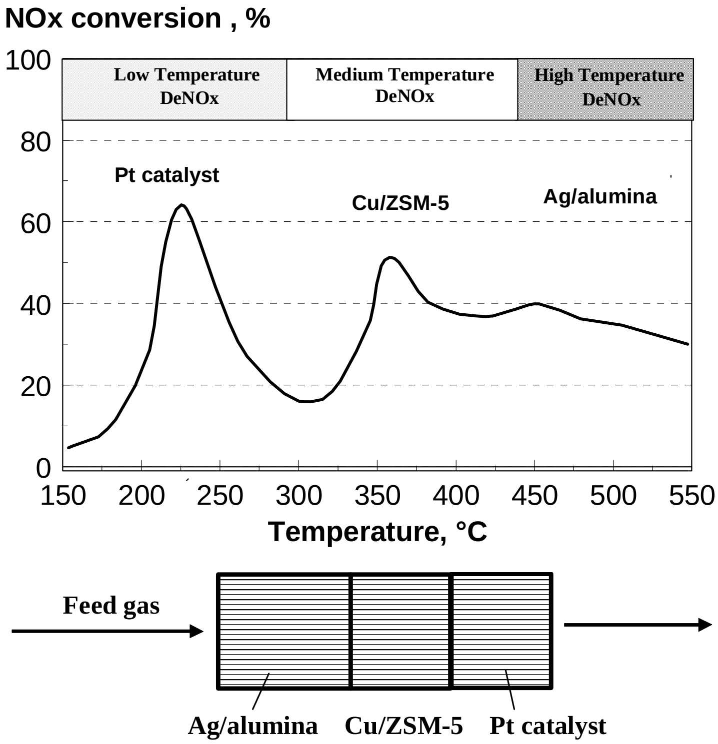


Figure 15. The HC-SCR window with a combination of three HC-SCR catalysts in a simulated exhaust gas without an additional fuel injection (Feed gas: 310 ppm NO, 900 ppm C_3H_6, 900 ppm CO, 300 ppm H_2, 8% O_2, 10 % CO_2, 10% H_2O, balance N_2; SV 50 000 h^{-1}, 130 cells per cm^2 (metallic substrate of 800 cpsi)) (Maunula 1997, Maunula and Nakatsuji 1997).

5.2.4.3 HC-SCR by methane on zeolite based catalyst

A lot of effort has been devoted in the last decade to the selective catalytic reduction of NO_x by methane (CH_4-SCR), because methane is used as a fuel in many stationary and mobile engines and as well in power plants. Methane differs particularly from unsaturated and oxygenated hydrocarbons by the reactivity and a high amount of energy it requires for cleavage of the first C-H bond in methane (the bond energy 436 kJ/mol and the ionization potential 12.98 eV) (Orlik 2001). Therefore the oxidation of methane is even catalytically difficult and the lowest light-off temperatures (T_{50}) are about 400-500°C in lean conditions. Ethane and propane are nearest by their properties to methane in catalytic reactions. The active catalysts in SCR of NO_x by non-methane hydrocarbons or complete methane oxidation are usually not active in CH_4-SCR. A rate-limiting step is the abstraction of a hydrogen atom from methane (Cowan et al. 1995). Therefore, new types of catalysts have been studied and introduced for CH_4-SCR, which is presented here as an separate SCR category.

<u>Co/ and Ga/zeolites:</u>

Co and Ga on zeolites (ZSM-5, ferrierite) were found as promising catalysts in CH_4-SCR in lean conditions (Li and Armor 1992, 1993A and 1994). The reaction mechanism was proposed to include on Co^{2+} the formation and adsorption of NO_2, which activated and broke CH_4 to CH_3NO_2, which further reacted to N_2. The formation of N-N bond was discussed to proceed by the reactions between CH_3NO_2 and NO or by N_2O_x ($x = 3$-5) complexes. In later FTIR studies, the role of CN surface species on Co/ZSM-5 was seen as essential in N_2 formation (Lobree et al. 1997). The location and distribution of Co ions in zeolite (ferrierite, ZSM-5, mordenite) framework had a significant effect on CH_4-SCR activity by vis spectroscopy data (Dedecek et al. 2002). The highest activity was found, when Co^{2+} ions are located in the main ferrierite channel and coordinated to four-framework oxygen (α-type Co ions). The β-type Co ions in the channel intersection of ZSM-5 showed a higher activity than α-type Co ions in the main channels of ZSM-5. Co/beta was more active than Co/ZSM-5 (Tabata et al. 1996). The simultaneous NO and N_2O reduction by methane was possible on Co/ZSM-5 (Li and Armor 1993B). The problem with Co zeolites was their low durability in the presence of water and SO_x. Empirical reaction kinetic equations depending on NO, CH_4 and H_2O concentrations were presented for NO-CH_4-O_2 reaction on Co/ferrierite (Li and Armor 1994B).

Pd/zeolites:

The high activity of Pd/H-ZSM-5 was connected to Pd^{2+} and protonic sites and the activity was clearly higher in CH_4-SCR than with Cu/ZSM-5 or Pd/alumina (Nishizaka and Misono 1993). Zeolitic protons and acidity are required to convert Pd oxide to Pd^{2+} (Adelman and Sachtler 1997). Bifunctional catalysis was needed to activate both NO and methane on Pd/H-ZSM-5 (Misono et al. 1997) and both NO_2 formation and the dissociation of a C-H bond can be rate determining by isotope (CH_4/CD_4) studies (Kato et al. 1997). NO_2 formation tends to be more rate controlling at low temperatures. PdO or metallic Pd were the main palladium phases resulting in a high methane oxidation ability on other supports or on ZSM-5 with high Pd loadings (Ali et al. 1998). Pd^{2+}/H-ZSM-5 has found to have a high ability to chemisorb NO strongly, which was related to the CH_4-SCR activity (Kikuchi and Ogura 2000). In situ IR spectra analysis on Pd/H-mordenite revealed that a Pd^{2+}-NO complex and NH_4^+ on zeolite acid sites are possible intermediates in CH_4-SCR (Shimizu et al. 2000B).

Ga/ and In/zeolites:

Ga and In on ZSM-5 were also found to be active in CH_4-SCR and In/ZSM-5 was fairly active even in the presence of 10% water (Kikuchi and Yogo 1994). The presence of NO_2 in feed had a remarkable effect on the activity and it was concluded that CH_4-SCR reactions proceed in two steps: (1) NO is oxidized to NO_2 on zeolitic sites and (2) NO_2 and CH_4 react on Ga or In sites. FTIR studies showed that the slow chemisorption of NO_2 on InO^+ is important (Ogura et al. 1998A). The presence of different indium species on H-ZSM-5 (Z) depended on preparation methods and In^+Z^-, InO^+Z^-, In_2O_3 crystals and highly dispersed noncrystalline InO_x were identified (Miro et al. 1999B).

Bimetallic catalysts:

Ir on In/H-ZSM-5 enhanced CH_4-SCR by accelerating NO_2 formation. In-Ce on ZSM-5 or on mordenite showed improved activity compared to In/ZSM-5 (Berndt et al. 2003). The role of Ce was to catalyze NO oxidation to NO_2, which was assumed to react with methane on Lewis-acidic and redox-active InO^+ species. The residual Brönsted acid sites on zeolite were also utilized in CH_4-SCR reactions. The addition of Fe on In/H-ZSM-5 resulted in an active In-Fe_2O_3/H-ZSM-5 catalyst (Wang et al. 2002). Other bimetallic catalysts presented for CH_4-SCR have been Co-Pd/zeolites (Pieterse et al. 2003), Pt-Co/ferrierite (Boix et al. 2000), Co-Pt/mordenite (Gutierrez et al. 2001), Pd-In/H-ZSM-5 (Heinisch et al. 1999), Pt-In/ferrierite (Gutierrez et al. 2001) and Pd-Co/zeolites (Ogura et al. 2002, Lee et al. 2003). In general, co-cations have been proposed to stabilize the primary cation, improve the hydrothermal durability or enhance particularly NO_2 formation, when the primary cation is acting as a NO reduction site.

The durability of 0.4% Pd/H-ZSM-5 was improved in the presence of water by using a second component like Rh, Ag, Ce and particularly 3.3% Co (Ogura et al. 2000). Bimetallic 0.6% Pd-2% Co on small-pore mordenite showed a good activity and durability (Hamon et al. 1998). Bimetallic Pd-Pt/mordenite had a higher activity and durability than Pd/mordenite in CH_4-SCR (de Correa et al. 2000). Ce-Ag/ZSM-5 was another bi-cation catalyst (Li and Flytzani-Stephanopoulos 1997). Ce ions were reported to supply NO_2 for Ag sites and to suppress complete methane oxidation. Ag sites are the active centers for NO_x reduction. A co-impregnated Zn-Co/H-ZSM-5 had a higher activity than Zn/Co/H-ZSM-5 prepared by successive impregnations (Ren et al. 2002).

Microwave promotion enhanced CH_4-SCR on In-Fe_2O_3/H-ZSM-5 (Wang et al. 2000). The reaction mechanism was not identified but Fe oxide was speculated to be a good NO_x adsorbent and a microwave absorbent.

Two component catalysts:

Physical mixtures have been also used in CH_4-SCR and a good oxidation catalyst (e.g. CeO_2, Mn_2O_3, Pt/Al_2O_3) for NO_2 formation has usually been mixed with HC-SCR catalysts (Ce/zeolites, Sn/zeolites). CeO_2 precipitate on the external surface of H-ZSM-5 catalyzed NO_2 formation but the results also supported the existence of short-lived intermediates like nitromethane or nitrosomethane which desorbed and reacted with NO on zeolitic Brönsted sites to N_2 (Liese et al. 2001). Similarly, a mixture of Co/Al_2O_3 and H-zeolites showed combinatory properties, which doubled the expected CH_4-SCR activities (Yan et al. 1998). A physical mixture of In/H-ZSM-5 and In_2O_3 catalyst contained two different kinds of In and showed a remarkable activity for CH_4-SCR compared to In/H-ZSM-5 (Ren et al. 2004). In an earlier study it was found that the physical mixture of H-ZSM-5 and In_2O_3 had a similar activity than In/H-ZSM-5 in CH_4-SCR (Ogura et al. 1998A).

Reaction mechanism in CH_4-SCR:

When methane is used as a reductant, the variety of possible surface complexes is lower than with heavier hydrocarbons but methane acts at low temperature (< 300ºC) like an inert gas and no surface intermediates are detected. Methane has been proposed to be activated by nitrite-nitrate complexes with nitrile intermediates (Aylor et al. 1997). The rate limiting step to nitrogen was explained to be the interaction between gas phase NO (NO_2)

with nitriles. However, these intermediates were detected only in the absence of oxygen at high temperatures and with high concentrations. The possible intermediates (nitromethane, HCN) were studied on Cu/ZSM-5 and Co/ZSM-5 in reaction conditions by FTIR (Sadykov et al. 2003). Similar to nitropropene, nitromethane reacted rapidly to isocyanates and certain polymerization products like melamine ($CN(NH_2)_3$) and cyanuric acid, which can block zeolite pores. However, in the presence of water and oxygen these intermediates were not formed or they were hydrolyzed on acid sites to NH_i type products like ammonia, which is an efficient reductant for adsorbed NO_x. The selectivity in HC-SCR is determined by formed C,N,O containing intermediates, whose formations depend on the catalyst type (Lombardo et al. 1998, Sadykov et al. 2003). Isotope labeled molecule studies with $^{15}NO_2$+CH_3NO_2 revealed that predominant N_2 had a N atom from NO_2 and another N atom from nitromethane. This observation supported the theory that nitromethane is an intermediate to form the reducing N species, which reacts with NO to N_2. In many surface studies the existence of various intermediates such as HCN, NCO, NH_3 as final reductant for NO has been postulated, but it can be concluded that N_2 formation is not fixed to a single reaction.

5.2.4.4 HC-SCR by methane on oxide based catalyst

The poor hydrothermal stability of zeolite based catalysts has motivated the studies of non-zeolitic catalysts. Many oxide based materials have good methane oxidation but usually low deNO_x properties in lean conditions. Therefore oxide based catalysts are usually orders of a magnitude less active in CH_4-SCR than the most active zeolite based catalysts.

Pd on acidic supports like on zirconia, sulfated zirconia and tungstated zirconia had promising activities in CH_4-SCR (Chin et al. 2000). Mn and Co on sulfated zirconia operated also in CH_4-SCR (Li et al. 2003 and 2004). Cu/ZrO_2 was active in the same reaction (Caballero et al. 2001). The addition of Ce or Gd improved the oxygen resistance of Pd/TiO_2 but the effect was lost in long-term aging in the presence of SO_2 (Mitome et al. 1999). Rare earth catalysts have shown a particular activity (Zhang et al. 1995). Nanocrystalline Sc, Y and La oxides also catalyzed NO_x reduction in lean conditions (Fokema and Ying 1998). The reaction mechanism on Y oxide catalysts was found to be similar to zeolite based catalysts. Nitrosomethane and nitromethane were proposed to react via HCN or NCO species to N_2 (Fokema and Ying 2000). 40% La_2O_3/alumina was studied in NO-CH_4-O_2 and rate equations based on the micro-kinetic reaction mechanism were derived (Toops et al. 2003). It was assumed that prior to NO NO_2 is the principal N-containing intermediate. The solid solution of Ga_2O_3-Al_2O_3 had maximum activity in CH_4-SCR with the Ga content of about 22% (Inoue et al. 2000). The addition of boron in the same catalyst (Ga:Al:B = 1:3:0.05) further improved the CH_4-SCR activity (Takahashi et al. 2002). Certain perovskites or mixed oxides like La-Sr-Ce-Fe-O are also active catalysts (Belessi et al. 2000). It was found that Pt enhanced NO_2 formation in Pt-Pd on sulfated zirconia (Ohtsuka and Tabata 2001). The addition of Fe further stabilized that catalyst and the NO_x conversion was maintained over 70% for 2400 hours (Ohtsuka 2003).

5.2.5 NO_x reduction by hydrogen in lean conditions

Hydrogen has usually been seen as a non-selective reductant for NO_x in lean conditions but in certain conditions there exist possibilities to have deNO_x activity (Frank et al. 1998). NO dissociation has been proposed to be the crucial step. Pt-Mo and Pt-Mo-Co on α-alumina had promising activities in lean NO-H_2-O_2 reaction. Oxygen showed a surprisingly promoting effect on NO_x reduction on these catalysts. Pt/TiO_2-ZrO_2 was found to be highly active in lean NO-H_2-O_2 mixtures at low temperatures (Machida et al. 2001). FTIR studies revealed mainly nitrates on catalyst surfaces and it was concluded that nitrates react with hydrogen to N_2. Pd/TiO_2 was another promising catalyst in NO-H_2-O_2 reaction (Ueda et al. 1998). The presence of SO_2 had a promoting effect on NO_x reduction with hydrogen on Ir/SiO_2 in lean conditions (Yoshinari et al. 2001). The presence of strong acid sites on zeolite (ZSM-5 and beta) based Pt catalysts resulted in the formation of adsorbed NH_4^+ species and a N_2O free path in H_2-SCR (Satsuma et al. 2003). The catalytic NO_x reduction by hydrogen was usually strongly poisoned by CO, which resulted in lower activities in practical exhaust gases (Macleon and Lambert 2002). N_2 formation was assumed to proceed on Pt/Al_2O_3 by the reactions between two adjacently adsorbed N. The required NO dissociation was faster at higher temperatures (> 200°C), where the selectivity to N_2 was higher than at low temperatures (50-150°C), where more N_2O was also formed. The promoting effects of Na and Mo on Pt/Al_2O_3 and Pt/SiO_2 were explained by the reduced intermediates, which are able to adsorb and reduce NO_x (Burch and Coleman 2002). As a summary, NO dissociation is a widely accepted mechanism for Pt catalysts in NO_x reduction by hydrogen in lean conditions.

5.2.6 Direct NO decomposition

Because thermodynamically molecular nitrogen (N_2) is favored after combustion in cooled exhaust gases, direct NO decomposition to N_2 has been studied as a potential deNO_x method since the 1970's (Shelef 1976). However, the same problems have always arisen against NO decomposition catalysts. The catalysts, which are able to dissociate NO are often poisoned by adsorbed oxygen, water or other compounds present in real gases. The selective catalysts should be able to dissociate NO but also move adsorbed oxygen away from the active sites (*)

$$2\ NO + 2\ ^* \rightarrow 2\ NO^* \quad (35)$$

$$2\ NO^* + 2\ ^* \rightarrow 2\ N^* + 2\ O^* \quad (36)$$

$$N^* + N^* \rightarrow N_2 + 2\ ^* \quad (37)$$

$$O^* + O^* \rightarrow O_2 + 2\ ^* \quad (38)$$

As net reaction

$$2\ NO \rightarrow N_2 + O_2 \quad (39)$$

Noble metals were studied naturally first in NO decomposition in relation to three-way catalysis. NO decomposition has been proposed as a plausible NO reduction mechanism in TWC conditions in the presence of reductants, which remove adsorbed oxygen. However, noble metals are deactivated by oxygen, water or poisons in lean conditions and N_2O formation is a drawback.

Cu on zeolites (Cu/Y zeolite) was first studied at the beginning of the 1980s (Iwamoto et al. 1981) and later a boom was created by the findings with Cu/ZSM-5 (Iwamoto et al. 1989). The reduced (*) and oxidized active site (O*) in the above reaction mechanism can be interpreted on Cu/ZSM-5 as transformations of copper state between Cu^{2+} and Cu^+, which is activated thermally at relatively low temperatures and is able to catalyze NO decomposition in the presence of excess oxygen. Most of the good NO decomposition results have been presented in conditions, where oxygen or water excess and space velocity were low. The prereduced catalysts are able to decompose NO with low space velocities for an extended period. After the catalyst surface is fully oxidized, NO decomposition will stop. These experiences in NO decomposition lead to the use of reducing hydrocarbons selective in lean conditions.

5.2.7 NO_x storage and reduction catalysts

Conventional three-way catalysts are not active in lean gasoline and diesel applications. New types of NO_x storage and reduction (= NSR) catalysts (NO_x traps) were introduced for lean applications in Japan in the 1990's (Miyoshi et al. 1995). Nitrogen oxides in exhaust gas were trapped during lean driving conditions ($\lambda >> 1$) even for several minutes and reduced during short enrichment peaks ($\lambda < 1$), which took at maximum a few seconds. Several NO_x storage compounds, mainly alkali and alkaline earth metals (e.g. Ba, Sr, La, Li, K, Na) are able to adsorb NO_x (Hepburn et al. 1996). The catalysts usually contain Pt or Rh, which are active metals in catalytically reducing NO to nitrogen during the enrichment phase.

NO is oxidized on Pt to NO_2, which is adsorbed as nitrates on metal oxides (M_xO) sites (Ketfi-Cherif et al. 2000):

$2\ NO + O_2 \rightarrow 2\ NO_2$ on Pt (40)
$2\ NO_2 + 0.5\ O_2 + M_xO \rightarrow M_x(NO_3)_2$ on NO adsorbent (41)

Stored nitrates are decomposed and reduced on active metal sites by reducing species. The NO_x removal efficiency can reach the levels of 60-90% even if the fuel economy requirements limit NO_x conversions in driving conditions (Maunula et al. 2001). Carbon monoxide and hydrogen are supposed to be the actual reductants but hydrocarbons are their source:

$M_x(NO_3)_2 \rightarrow 2\ NO + 1.5\ O_2 + M_xO$ decomposition/desorption (42)
$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$ on Pt and Rh (43)
$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$ on Pt and Rh (44)

The reaction mechanism in NO_x reduction by hydrogen and CO is the same as in three-way catalysts although the reduction during the few second enrichment peaks makes the conditions axially and radially transient. If the reduction peaks are too strong, NH_3, CO, hydrocarbons and hydrogen will be found after catalysts. SO_x poisoning originating from sulfur in fuel and lubrication oil is a practical problem concerning NSR catalysts. The use of NSR catalysts in diesel conditions has been limited by poor fuel economy and the difficulties in adjusting diesel engines to rich peaks.

Active carbon, silica gel, activated alumina and zeolites are appropriate adsorbents in actual NO_x adsorption methods, which require a regeneration step. It was possible to bind even 100 mg NO_2/g adsorbent (iron oxide) in the presence of 400-800 ppm NO_x and 3% O_2.

5.2.8 Non-catalytic reduction methods

Liquid fuel and other burning compounds (methane, CO, hydrogen, char) can be injected into partially cooled mixtures after a combustion chamber in postcombustion NO_x methods, which can utilize the shift in the equilibrium NO concentration associated with temperature decrease (Flagan and Seinfeld 1988). Efficient reduction requires that the excess of oxygen is consumed, which results in poor fuel economy. Usually a low NO_x reduction (10-40%) can be reached in these partially rich zones.

In addition to selective catalytic reduction methods, selective non-catalytic reduction (SNCR) with NH_i compounds has been used commercially. The same NO_x reactions, which proceed catalytically at lower temperatures (200-500°C), are actual thermally at 700-1000°C with selective reductants like ammonia, urea or any NH_i containing species (deNO_x > 70%). The operation window with ammonia is at 900-1000°C. H_2S is also a selective NO_x reductant but its use has been limited because of environmental drawbacks. A NH_2 radical acts as the actual reductant in this selective, thermal reduction. Although the reaction is called selective, the selectivity is not so good as in SCR and a high NH_3/NO_x ratio (1-4) is required to reach over 70% conversions due to the fast NH_3 oxidation rate. The single reaction paths with NO and NH_3 are numerous as shown by Salimian and Hanson (1980), but the net reaction routes are similar as in NH_3-SCR and SNCR is limited by the kinetically slow reaction of NO with NH_3 (< 900°C) and by the excessively fast NH_3 oxidation rate (> 1000°C).

Because the reactants in SNCR are molecules and dissociated radicals like OH or O with NO and NH_2 in the reaction zone, the addition of hydrogen (H_2) decreases the operation window due to enhanced OH formation at lower temperatures (< 800°C) (Salimian and Hanson 1980). Other reactants having the same effect are hydrogen peroxide (H_2O_2) and CO formed e.g. from urea (Fig. 16). The excess of urea ($NH_i/NO_x = 2$) was needed to reach over 80% NO_x conversions.

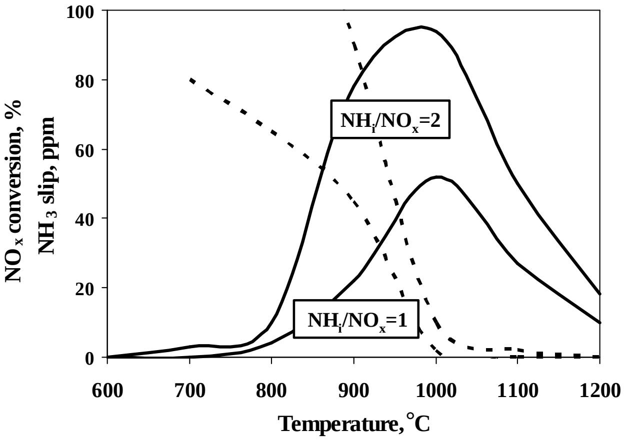


Figure 16. The influence of temperature on NO_x reduction (solid line) and NH_3 slip (dotted line) in urea based SNCR (Lin et al. 1995).

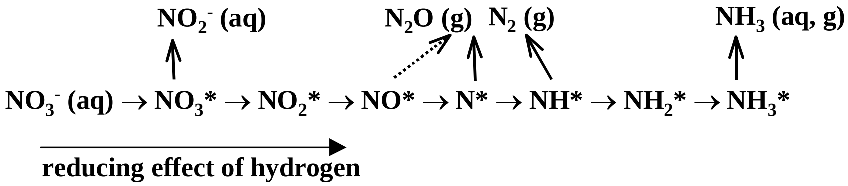
The reaction mechanism and radicals observed in known thermal deNO_x methods have been applied in this work to interpret catalytic SCR reactions with similar reactants as adsorbed.

5.2.9 Wet methods for NO_x removal

Absorption methods in the liquid phase are often simultaneous deNO_x/deSO_x methods, where the final nitrogen products are N_2 or nitrates. Because NO has a low solubility into water, the formation of NO_2 of NO complexes precludes NO_x absorption (Ando 1983, Schrod et al. 1985). In an absorption-reduction method, NO is bound with iron chelate (Fe(II) EDTA) and reduced to N_2 with sodium sulfite with over 90% deNO_x/DeSO_x. SO_2/NO_x molar ratio needs to be over 3 to reach NO_x conversions of 70%.

Ozone or ClO_2 have been used to form NO_2, which is absorbed in a sulfite containing water solution to form nitrogen. The Walther process uses alkaline ammonia containing solutions to form ammonium nitrate, which can be used as a fertilizer (Schrod et al. 1985).

The catalytic reduction of nitrates has been used to prepare drinking water from ground water. Hydrogen was used as a reductant but other reductants such as formic acid are also possible. The high selectivity to N_2 is a target, because traces of NH_3 or N_2O in water are not accepted. The reaction mechanism and selectivity in these liquid-gas reactions are similar to NO_x gas reactions on solid catalysts. NO_3^- is reduced by hydrogen in stages to adsorbed, soluble and gaseous compounds. We proposed the reaction paths from nitrate to N_2, N_2O or NH_3 to proceed in the following sequence (Wärnå et al. 1994 but N* and $N_2O(g)$ also included):



N_2O formation proceeds analogically to the gas phase and TWC reactions by the reaction between NO* and N* dissociated from NO* or NH*. Therefore, similar reaction pathways like in exhaust gas conditions also cover these reactions with NO_x-NH_i species, even if the kinetic and mass transfer parameters are quite different in gas-solid and gas-liquid-solid reactions.

6 EXPERIMENTAL

6.1 Catalyst preparation

6.1.1 Oxide based catalysts for HC-SCR

Four principally different types of aluminas (denoted as Al-sg, Al2, Al3 and Al-ref) were used as carriers for the catalysts where the metal and their precursors and concentrations as well as the calcination temperature were varied. Al-sg was prepared by the sol-gel method (Al-iso-propoxide in 2-methyl-2,4-pentanediol, Toyo Gosei) and consisted mainly of high surface area γ-Al_2O_3 after final calcination at 600°C (II-III). Al2 consisted mainly of δ-Al_2O_3 (Degussa, Alumina C) which had a lower surface area and bulk density. α-alumina (Al3) was used as a very stable, low surface area alumina. Commercial γ-Al_2O_3 (Al-ref) was a reference to Al-sg. Cadmium, cobalt, copper, gallium, indium, iron, manganese, nickel, palladium, platinum, silver and tin were impregnated by the pore filling method using $CdCl_2$,, $Co(NO_3)_2{\cdot}6H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(CH_3COO){\cdot}H_2O$, $Ga(NO_3)_3{\cdot}9H_2O$, $In(NO_3)_3{\cdot}3H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Pd(NH_3)_4(NO_3)_2$, $Pt(NH_3)_4Cl_2$, $AgNO_3$ and $SnCl_4{\cdot}5H_2O$ as precursor salts in aqueous solutions. Because of the different atomic weights of elements, the metal loadings were based on the same number of metal atoms in each catalyst (Table 2). The molar ratio of Al/M (M = impregnated metal) was varied between 20 and 650 (65 or 650 as standard). After the impregnation, the catalysts were dried at 110°C overnight, calcined at 600°C for 3 hours and screened to the particle size of < 250 µm to homogenize powder samples and to decrease mass transfer limitations in experiments. Some of catalyst powders were recalcined at 700, 800, 900 or 1000°C for 3 h. Commercial TiO_2 (Degussa P-25) and SiO_2 (Fuji Silysil Chemical) were also used as supports. The active metals and supports are usually oxides in test conditions but the catalysts were coded by the elements without specifying the oxidation state (e.g. Al = Al_2O_3, Ti = TiO_2, Si = SiO_2, In = InO_x, Co = CoO_x).

The InO_x sample (mainly In_2O_3) was prepared by precipitation with Na_2CO_3 solution (0.8 g/dm^3) from 0.06 M indium nitrate solution. The dried sample was calcined at 600°C. Commercial precipitated Co_3O_4 and Mn_3O_4 from Soekawa Chemicals were used as pure oxide samples.

Table 2. The oxide based powder catalysts used in HC-SCR studies.

Catalyst code	**Metal loading**		**BET area**	**Publication**	**Remarks**
	Al/M	**wt-%**	**m^2/g**		
Al-sg *	-	-	301	II, III, IV	γ-Al_2O_3
Al2	-	-	99	IV	δ-Al_2O_3
Al3	-	-	-	IV	α-Al_2O_3
Al-ref	-	-	162	II, IV	γ-Al_2O_3
Co/Al-sg(20,nitr)	20	5.46	180	IV	
Co/Al-sg(45,nitr)	45	2.50	198	IV	
Co/Al-sg(65,nitr) *	65	1.75	215	II, IV	
Co/Al-sg(130,nitr)	130	0.88	205	IV	
Co/Al-sg(650,nitr)	650	0.18	224	IV	
Co/Al-sg(65,acet)	65	1.75	223	IV	
Co/Al-sg(65,nitr,wet2)	65	1.75	204	IV	
Co/Al2(65,nitr)	65	1.75	84	IV	
Co/Al2(65,acet)	65	1.75	90	IV	
Co/Al-ref(65,nitr)	65	1.75	150	IV	
CoO_x	0	99.9	-	IV	Co_3O_4
In/Al-sg(20)	20	10.1	180	II, III	
In/Al-sg(45)	45	4.8	206	II,	
In/Al-sg(65) *	65	3.3	216	II, III, VI	
In/Al-sg(130)	130	1.7	214	II,	
In/Al-sg(300)	300	0.74	223	II,	
In/Al-sg(650)	650	0.34	223	II	
In/Al-sg(65,acet)	65	3.3	241	III,	
In/Al-sg(65,wet2)	65	3.3	261	III	
In/Al-ref(65)	65	3.3	145	II	
In-Al-sg1(65)	65	3.3	271	III	
In-Al-sg2(65)	65	3.3	199	III	
In/Al-sg(pe)	-	80**	85	III	
In/Ti	-	3.3	45	II	
In/Si	-	3.3	335	II	
InO_x	-	100	27	II, III	precipitated
Ag/Al-sg(65)	65	3.14	205	II	
Ag/Al-ref(65)	65	3.14	149		
Sn/Al-sg(65) *	65	3.52	195	II	
Ga/Al-sg(65)	65	2.07	231	II	
Mn_3O_4	-	99.9	1	II, VI, VI	
Cu/Al-sg(65,nitr)	65	1.87	211		
Cu/Al-sg(65,acet)	65	1.87	221		
Cu/Al-sg(650,nitr)	650	0.19	223		
Fe/Al-sg(65)	65	1.67	215		
Fe/Al-sg(650)	650	0.17	214		
Ni/Al-sg(65)	65	1.74	175		
Mn/Al-sg(65)	65	1.63	181	II	
Pt/Al-sg(65)	65	5.58	216	VI	
Pt/Al-sg(650)	650	0.59	222		
Pd/Al-sg(65)	65	3.04	222	VI	
Pd/Al-sg(650)	650	0.30	194	VI	calc. at 700 °C
Ir/Al-sg(65)	65	5.50	234	VI	
Cd/Al-sg(65)	65	3.34	240		
TiO_2	-	-	nd	II	Degussa
V/TiO_2	-	2.80	nd		calc 400 °C
SiO_2	-	-	260	II	CariACT

nd: not detected, Acet: from acetate precursor, other from nitrate;
* reductants studied using C_3H_6, C_3H_8, CH_4, ethanol, methanol and i-propanol (results in Publications); ** XRF

The V/TiO_2 catalyst was prepared by impregnating NH_4VO_4 into TiO_2 (Degussa P-25) in an oxalic acid solution, drying at 110°C overnight, grinding and calcining at 400°C for 2 hours. The composition represents a model ammonia-SCR catalyst.

6.1.2 Sol-gel prepared InAl oxides for HC-SCR

The sol-gel processed InAl samples were prepared using aluminum iso-propoxide $Al(OCH(CH_3)_2)_3$ based Al(OOH) sol and indium nitrate ethyl glycol solution (In-Al-sg1) or indium nitrate water solution (In-Al-sg2) (Table 2). The sol mixtures were gelated, dried, calcined and screened to ready samples (details in III). InAl-sg1 had nearly as high a surface area (271 m^2/g) as sol-gel processed pure alumina Al-sg (301 m^2/g) but the addition of In nitrate as water solution into Al sol (In-Al-sg2) resulted in a lower surface area (199 m^2/g). This result was clear evidence that when In and Al precursors were surrounded by organic hydrophobic ligands in aqueous media, the controlled gelation of Al and In compounds prevented the common negative effects of water. Another interpretation is the interaction between Al sol and ethyl glycol itself, and ethyl glycol was adsorbed on the Al precursor complex in sol, which prevented the hydrothermal collapse of the aluminum oxide surface during gelation and drying. The high initial surface area was a guarantee for a high surface area after calcination at 600-900°C.

The reactions occurring between aluminum and indium during sol-gel processing can be described in the following way. An evenly distributed, polymerized aluminum group in aluminum sol is indicated as Al-OR, where R describes an organic group. A small amount of indium solution is distributed evenly in the aluminum sol network. Al and In precursors were surrounded by several alkoxy and hydroxyl groups and ring type connections are formed in polymerization (Ji 1993). The hydrolyzed indium precursor reacts with aluminum precursors during the gelation, where the inorganic network is formed by hydrolysis and condensation reactions (Ji 1993, Miller and Ko 1997, Narendar and Messing 1997):

$$\text{Al-OR} + H_2O \rightarrow \text{Al-OH} + \text{ROH} \qquad (45)$$

$$\text{Al-OR} + \text{Al-OH} \rightarrow \text{Al-O-Al} + \text{ROH} \qquad (46)$$

$$\text{Al-OH} + \text{In-OH} \rightarrow \text{Al-O-In} + H_2O \qquad (47)$$

Therefore, the network contains Al and In atoms, which are 3-dimensionally joined by oxygen bridges. The characterization of sol-gel prepared samples showed that the type of solvent used for the indium salt added into Al sol has a significant effect for aluminum-indium oxide network formation during sol-gel process. Organic compounds with a lower surface tension and higher boiling point compared to water enlarge the possibilities to decrease capillary forces and modify pore dimensions and volumes in the post-gelation and drying processes. The organic solvents have a contribution in the formation of porous catalysts, whose pore size range can be controlled by the molecule diameter and ligands of the solvent.

6.1.3 Zeolite based catalysts for HC-SCR

Cu/ZSM5 was prepared by a conventional ion exchange method (Keiski et al. 1996) and it was used as a reference in HC-SCR to compare the differences in reaction mechanisms. The washed ZSM-5 zeolite (Tosoh SiO_2/Al_2O_3 = 23) was ion exchanged in 0.01 M $Cu(CH_3COO)_2$ for 24 hours at 25°C, dried and calcined at 500°C for 3 hours (Table 3). The ion exchange ratio of Cu^{2+} was calculated to be 91% by quantitative XRF analysis. The H-ZSM5 catalyst was prepared by ion exchanging in 1 M NH_4NO_3 solution at 80°C for 24 hours and calcined at 500°C for 3 hours to interpret the difference between sodium (original zeolite) and hydrogenated forms.

In/ZSM5 was prepared by the ion exchange method at elevated temperatures. Washed ZSM-5 zeolite (Tosoh Si/Al_2 = 23) was ion exchanged in 0.04 M $In(NO_3)_3 \cdot 3H_2O$ for 24 hours at 80-90°C, dried and calcined at 500°C for 3 h. The ion exchange ratio of In^{3+} in aluminum sites was about 140% (In/ZSM-5) and 55% (In/H-ZSM-5) by quantitative XRF analysis, which were also confirmed by plasma analysis. A small amount of Pt or Ir was impregnated on original ion exchanged In/ZSM-5 in Pt-In/ZSM-5 and Ir-In/ZSM-5 catalysts by a conventional pore filling method. The screening homologation ($< 250\ \mu m$) was also done for zeolite catalysts.

Table 3. Zeolite based powder catalysts used in HC-SCR studies.

Catalyst code	**Metal loading wt-%**	**BET area m^2/g**	**Publication**	**Remarks**
ZSM-5	-	219	II, V	untreated
H/ZSM-5	-	314	(V)	NH_4NO_3 treatment
Cu/ZSM-5 *	3.7	237	II	IER = 91%
In/ZSM-5	7.2	269	II, V, VI	IER = 140%
In/H-ZSM-5	2.7	303	V	IER = 55%
Pt-In/ZSM-5	Pt 0.28 + In 7.2	252	VI	Pt by pore filling
Ir-In/ZSM-5	Ir 0.27 + In 7.2	238		Ir by pore filling

IER: Ion Exchange Ratio, Paper: the publications, where used.

* in C_3H_6-SCR, other in CH_4-SCR studies

6.1.4 Three-way catalysts

The three-way catalysts used in transient studies (I) were 0.9% Pt/Al_2O_3, 0.2% Rh/Al_2O_3, 0.9% Pt/Al_2O_3-CeO_2, 0.2% Rh/Al_2O_3-CeO_2 and 0.9% Pt + 0.2% Rh/Al_2O_3-CeO_2 supported on a metal substrate formed from flat and corrugated foils (about 80 cells per cm^2 (500 cells per square inch), with foil thickness 44 μm, and coating amount about 40-43 g/m^2 (~160 g/dm^3).

6.2 Activity experiments

The steady-state HC-SCR activity was detected using simulated oxygen rich exhaust gas containing usually about 1000 ppm NO_x (NO or NO_2), 1000 ppm hydrocarbon (propene, propane, ethene, methane, ethanol, methanol or 2-propanol) and 10 or 0 % oxygen in helium in temperature range of 150-600°C. Instead of NO_x, about 500 ppm N_2O was also used to study the role of nitrous oxide in the reaction mechanism. The total flow rate of gas was 4 $dm^3\ h^{-1}$ and the amount of sample was 0.2 g meaning that F/W (Flow rate of gas /Weight of catalyst) was about 20 $dm^3\ h^{-1}g^{-1}$ (W/F = 0.05 g h dm^{-3}). The concentrations of N_2, N_2O, NO, NO_2, CO_2, CO, C_3H_6, C_2H_4, CH_4 in the gas phase were analyzed in parallel using two gas chromatographs (Shimadzu GC 8A with Porapak Q and Molecular sieve 5A columns) and chemiluminescence NO_x/NO analyzer (Shimadzu NOA-305A). The calibration gases and inlet concentrations were checked always when GC was switched on (II). The choice of NO and NO_x measurement was made manually by a 3-way valve (Flow through Mo converter (NO_x) and bypassing it (NO)). Both nitrogen oxides were measured during an experiment and it was possible to calculate total nitrogen balances, if no undetectable compounds were formed. The peaks for water and probably HCN and $(CN)_2$ were also detected in a few tests by GC, mostly with unloaded zeolite and alumina samples. (II-VI)

6.3 Characterizations

The surface area (BET) was detected by a standard nitrogen adsorption at -196°C (Micromeritics Flow Sorb II for powder catalysts and Sorptomatic 1900 for metal substrated three-way catalysts). X-ray diffraction (XRD) was detected by Shimadzu XD-D1. The compositions of catalysts were confirmed by XRF analysis (Seiko Instruments SEA2010). The indium main samples were also analyzed by plasma at Cosmo Oil R&D Center. XPS analysis of cobalt, indium and copper containing samples were performed by Rikagaku Denkikogyo XPS-7000 (5 kV,5mA, 25 W). The states of Co, In and Cu species were detected by the binding and kinetic energies of the peaks caused by these elements compared to pure metallic and oxide references. TG analysis was made for cobalt and indium samples to detect the changes in oxidation states of these metal oxides in static air by a Shimadzu DTG-50 analyzer. (I-VI)

Solid state ^{27}Al-MAS-NMR (Bruker MSL-400 in Cosmo Oil: rotation speed 3.5 kHz, resonance frequency 104.26 MHz, scan time 2 s, 800 cycles, 25°C) was applied to determine alumina phase.

The total acidity of alumina and zeolite based catalysts was measured by ammonia-TPD. Ammonia was adsorbed with the partial pressure of 132 mbar on a sample at 100°C for one hour and the reactor was heated with He flow (1.2 $dm^3 h^{-1}$) from 200 to 600°C by a heating rate of 10°C/min. The desorption rate of ammonia was measured by a thermal conductivity detector.

The noble metal dispersion degrees and mean particle sizes of three-way catalysts were analyzed by a volumetric CO chemisorption method at room temperature (I). The same volumetric method was used to measure the total acidity by NH_3 and the total basicity by CO_2 in pressures up to 1053 mbar (Sorptomatic 1900).

Thermodynamic equilibriums were calculated by a HSC program for gas and solid phases (Co, In, Cu, Mn compounds) to determine the stability of the compounds, the driving forces and limitations.

6.4 FTIR studies

The adsorption of single gases and in sequential steps was measured on the key catalysts between 50 and 450°C in the in situ FTIR chamber (Fig. 17). FTIR transmission spectra in the wavenumber range of 4000-1000 cm^{-1} were measured by a Shimadzu FTIR-8600PC equipped with a liquid nitrogen cooled detector using a resolution of 4 cm^{-1} both in static (preadsorption) and dynamic (flowing gas) conditions. The powder samples (0.1 g) were pressed to thin, infrared light transparency discs, which were installed at right angles to beam in the middle of a quartz reactor equipped with NaCl windows and thermocouple in a pocket inside the chamber. Before adsorption or dynamic experiments, the sample was outgased at 480°C for 30 min to remove moisture and contamination, cooled to set-point temperature (50, 150, 250, 350 and 450°C), where a background was measured under vacuum ($< 2.6 \cdot 10^{-3}$ mbar). Pure gases (NO, C_3H_6, CH_4 and oxygen) were introduced separately in different sequences in static or simultaneously as a gas mixture into the chamber in dynamic experiments (III-VI). The adsorption spectra of single gases (NO, N_2O, N_2, C_3H_6, CH_4, CO and CO_2) on catalysts were recorded with certain partial pressures to create a spectrum database exactly with the FTIR equipment and our catalysts (temperature range of 50-350°C). The database gave the possibility to detect the origin of the peaks. The main focus was to study the reactions at 300-440°C in contrast to many published results, where adsorptions have been studied at room temperature, where the catalyst surface is covered by adsorbed species, which will be desorbed before HC-SCR initiation. FTIR studies at 50°C could be used as surface characterization method.

The inlet composition and flow rate in dynamic NO-C_3H_6-O_2-He and NO-CH_4-O_2-He experiments were the same as in the activity experiments. FTIR spectra were measured in flowing mixture at 200-450°C by the interval of 40-80°C using the heating rate 10°C/min. Because the background spectrum was measured in the starting conditions on the purified sample in He flow at 200°C, the increasing temperature caused changes on spectra even in He flow. The temperature effects (distortion and desorptions) were eliminated by subtracting this He spectrum from NO-HC-O_2-He and HC-O_2-He spectra. In addition, the adsorption on the active metal and support can be distinguished by comparing the spectrum on support only and metal loaded support. The main compounds in the product gas were monitored with a mass spectrometer (Anelva AQA-200) by atomic mass units (amu): 4 (He), 16 (CH_4 or O), 18 (H_2O), 28 (N_2 or CO), 30 (NO), 42 (C_3H_6), 44 (CO_2 or N_2O)

and 46 (NO_2). The concentrations of by-products (N_2O, NO_2) were under the detection limits of MS in these conditions. (III-VI)

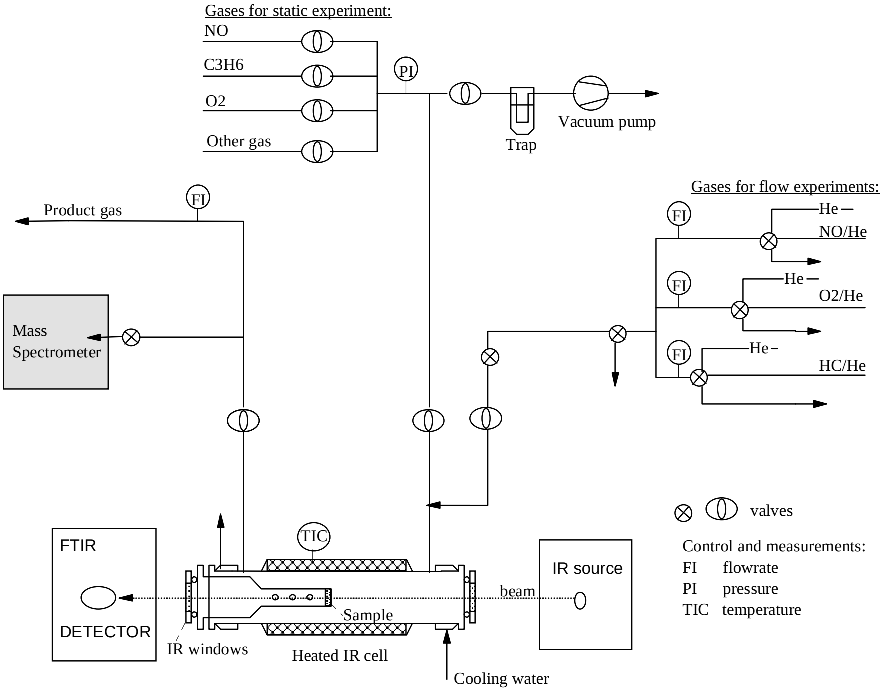


Figure 17. In situ transmission FTIR equipment.

6.5 Transient step exchange studies for NO-H_2 reaction

The purpose of step exchange experiments was to study the three-way catalysts in a usual operation window, where the conditions are near to stoichiometric but usually oscillating with a certain amplitude and frequency. The inlet gas composition and catalyst surface can change from lean to rich mixture or in the opposite direction in driving conditions. This type of drifting might cause inhibition both in lean and rich side. The properties and selectivities of platinum and rhodium and as well the effect of ceria were studied. The transient responses from a small quartz reactor were analyzed by a fast mass spectrometer (Balzers GAM 420). The following step exchange experiments were related to NO-H_2 reactions (inert = N_2 or/and He): (I)

He --> H_2/inert	H_2 adsorption on pure catalyst surface
He --> NO/inert	NO adsorption on pure catalyst surface
NO/inert ⇔ H_2/inert	Reactant switch on catalyst surface
H_2/inert ⇔ H_2/inert + NO/inert	Switch from H_2 to NO+H_2 and back
NO/inert ⇔ H_2/inert + NO/inert	Switch from NO to NO+H_2 and back

7 RESULTS AND DISCUSSIONS

7.1 NO_x reduction by hydrogen in stoichiometric and rich conditions

The reduction of NO by hydrogen was studied on model three-way catalysts with transient experiments near to stoichiometric conditions (I). A fast mass spectrometer (MS) analysis for reactants and products in gas phase enabled the studying of the effect of catalyst composition and reaction conditions in NO-H_2 reaction. The activities and selectivities with Pt, Rh and Pt-Rh catalysts supported on Al_2O_3 and Al_2O_3-CeO_2 varied by the conditions but the reactions followed certain general trends. NO reacted in catalytic reactions to N_2, N_2O or NH_3, which are favored in rich conditions, but not by higher degree to NO_2, which is formed in clearly lean conditions. Ceria promoted the formation of N_2 mainly due to the decreased light-off temperatures. It was observed that preadsorbed NO had an inhibiting effect on NO-H_2 reaction at low temperatures.

The step exchange experiments with Pt/Al_2O_3 at higher temperatures were analyzed in more detail to better understand the observations with Pt/alumina in HC-SCR. The formation of nitrous oxide was analyzed in step exchange experiment, where a reactant in flow was changed to another (1% NO → 1% H_2, 1% H_2 → 1% NO) or a reactant flow was switched to the stoichiometric mixture (1% NO → 1%NO+1% H_2, 1% H_2 → 1%NO+1% H_2) (Ahola 1993, Maunula et al. 1994). A peak of N_2O formation was detected immediately when NO was switched to H_2 or NO/H_2 and surface had a high coverage of NO (Fig. 18). These switches generated the conditions where NO was preadsorbed on catalyst and fed NO/H_2 and H_2 promoted NO dissociation when NO coverage was still high. The N_2O response in the switch from NO to H_2 was lower, because the total amount of reactants (NO) during an intermediate NO coverage range was lower. The switch from the rich mixture (H_2) to the stoichiometric mixture completely prevented N_2O formation. The steady state N_2O formation rate was very low at 350°C in the mixture, but in pure NO flow dissociation stayed remarkable for a longer time. Similar responses were detected both for Pt, Rh and Pt-Rh supported on alumina or alumina-ceria.

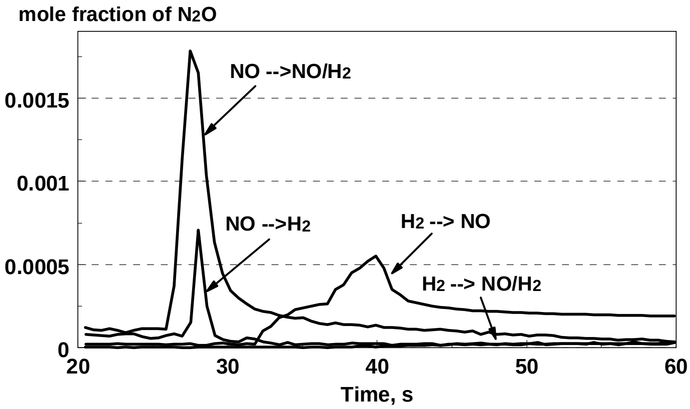


Figure 18. The formation of N_2O in step exchange experiments on metal substrated 0.9% Pt/alumina at 350°C.

The surface coverages were evaluated by these transient experiments (Fig. 19). Based on these observations, the N_2O formation conditions were clarified.

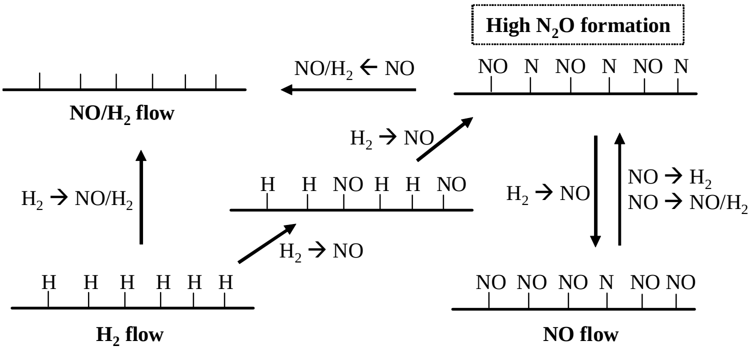


Figure 19. Schematic presentation of catalyst surface during NO-H_2 experiments.

The NO_x reduction paths to N_2 based on the transient and other three-way catalyst studies have been summarized in four NO reduction mechanisms: 1) N route, 2) N_2O route, 3) ONNO route and 4) NH_i route (Fig. 20). The NO reaction paths were categorized by the order of the N-O bond breakage and N-N bonding (I). In addition, the N-N bond breakage and N-O bond formation are possible, when the conditions are favorable to N_2 or NO oxidation. It was assumed that the N-N bond breakage of formed, adsorbed or gaseous N_2 and N_2O is possible solely by known thermal NO formation reactions at high temperatures (> 1000°C). In principle, the same reaction paths in respect to nitrogen species can be proposed for NO-CO reactions near to stoichiometric conditions but in addition NO can be reduced by NCO type compounds. The observed reaction rates are valid for precious metal catalysts (Pt, Rh, Pd), but in the case of other type of catalysts (e.g. base metals), the reactions proceed by the presented routes but the reaction select ivies are very different. This knowledge of the NO-H_2 reaction mechanism might explain H_2 promoted HC-SCR reactions (Satokawa 2000).

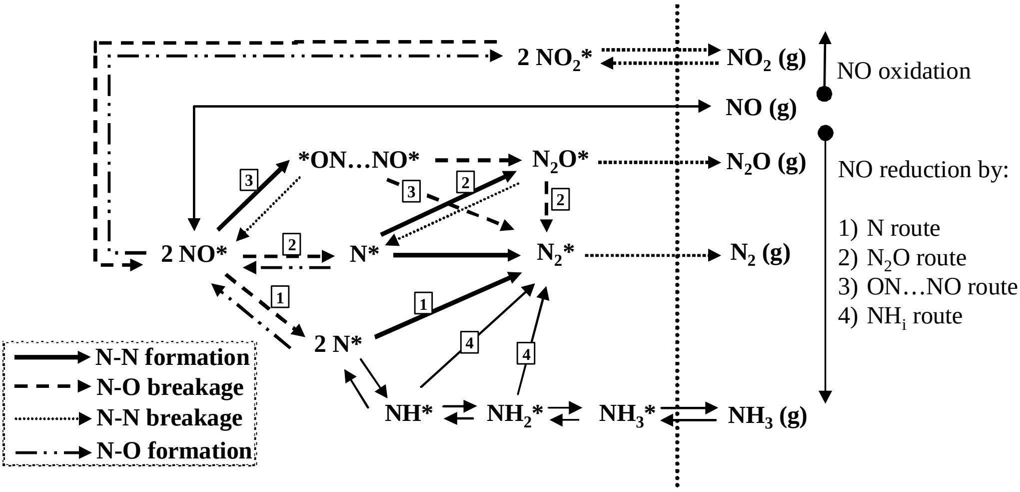


Figure 20. The proposed reaction pathways for NO reduction on three-way catalysts (I).

The NO-H_2 reaction is the simplest catalytic reduction reaction of NO and this reaction can be used as a model reaction to understand NO_x reduction paths, mechanism and dynamics. The basics in the reaction are related to the studies of three-way catalysts published widely 20-30 years ago, but a systematic bond breakage and formation analysis together with a N_2O formation analysis has been missing. In fact, the final reactions in TWC and HC-SCR are similar, but depending on the conditions, different types of catalysts are most active to form N_2.

7.2 NO_x reduction by hydrocarbons on oxide based catalysts in lean conditions

7.2.1 Screening experiments

Active metals supported on sol-gel alumina (Al-sg) with the fixed molar Al/M ratio (65) were screened to find the most promising catalysts to remove NO or NO_2 in lean and dry conditions (Table 4). In general, the elements from the periodic table groups 11, 13 and 14 have been active in HC-SCR. Two calcination temperatures (600 and 800°C) were used. In addition, the most interesting samples (Co, In) were also calcined at 700 and 900°C. The samples, which showed an excessively high HC oxidation activity, were also studied by the lower molar ratio of 650. The quartz reactor was inert in the presence of NO and NO_2 in blank experiments.

Table 4. The reduction of NO to nitrogen with propene on Al-sg supported (**Al/M = 65**) and other catalysts in dry mixture (Feed: 1000 ppm NO, 1000 ppm C_3H_6, 10% O_2, balance helium. F/W = 20 $dm^3\ g^{-1}\ h^{-1}$) (calcined at 600/800°C).

Sample	N_2 formation (%) at reaction temperature, °C								CO_2
	200	250	300	350	400	450	500	550	$T_{50}(CO_2)$, °C
Al-sg	8/8	13/10	20 /11	28/13	35/22	48/38	77/67	33/39	365/455
Co/Al-sg	8/10	14/13	10/9	22/17	53/70	51/74	35/51	14/17	370/390
Co/Al-sg(acet)	***12/-***	***17/16***	***17/12***	***21/15***	***39/32***	***53/49***	***45/48***	***27/32***	355/-
Cu/Al-sg	10/12	17/16	40/33	53/49	49/48	39/39	26/26	19/18	290/300
Cu/Al-sg(acet)	4/-	14/-	39/-	48/-	44/-	35/-	22/-	10/-	285/-
Fe/Al-sg	15/12	22/19	34/27	24/38	13/28	12/23	11/19	9/12	315/350
Ni/Al-sg	9/8	4/10	5/11	10/13	15/18	24/32	29/59	15/40	355/365
Mn/Al-sg	9/17	13/21	18/23	10/14	9/13	8/11	8/10	6/7	280/275
Ag/Al-sg	4/3	5/4	7/10	10/32	12/63	19/72	22/59	19/29	295/355
In/Al-sg	12/10	18/12	30/20	73/52	96/90	88/83	79/71	58/55	340/350
Sn/Al-sg	9/-	23/-	30/26	47/52	65/72	63/67	47/47	26/23	355/355
Ga/Al-sg	9/-	5/-	12/7	14/14	26/28	54/66	99/85	60/54	450/435
Cd/Al-sg	-	-	8/-	8/-	14/-	31/-	44/-	34/-	470/-
Pd/Al-sg	8/4	13/8	7/3	6/2	6/2	7/3	8/5	8/4	215/210
Pt/Al-sg	20/22	10/11	6/8	5/7	5/6	6/5	8/5	9/5	155/185
TiO_2	-	3/-	3/-	3/-	3/-	3/-	3/-	-	430/-
V/TiO_2	5/-	6/-	7/-	5/-	4/-	4/-	3/-	-	360/-
Cu/ZSM-5 ref.	12/-	27/-	52/-	58/-	48/-	44/-	39/-	-	250/-
Blank	2	2	2	3	3	3	3	-	> 550

The most promising results (> 60% to N_2 in dry mixture) were reached with Al-sg supported Co, Ag, In, Sn, Ga catalysts with Al/M = 65 and with Al-sg only. Ag/Al-sg showed very poor activity when calcined at 600°C, but the maximum activity was generated (max N_2: 22 → 72%) by the calcination at 800°C (Ag/Al-sg screened in the range of 600-900°C) mainly due to the reduction of the propene oxidation activity (T_{50} (CO_2) shift from 295 to 355°C) (see the discussion in II). Pt and Pd catalysts had too a high propene oxidation activity to have any HC-SCR activity above 300°C. Every time when the propene oxidation activity to CO_x initiated at temperatures below 300°C, the NO_x reduction rate was low. When the propene light-off temperature was above 300°C, maximum N_2 formation (NO_x conversion) on alumina based catalysts coincided with the propene conversion of about 70-80%. This looked to be a kind of general rule in HC-SCR based on the reaction dynamics. A rather high HC oxidation rate kept the surface reduced, which promoted the formation of reducing intermediates. The conventional NH_3-SCR catalyst, V/TiO_2, had no activity in propene-SCR, when ammonia was not present in feed.

The other group IV metals (Mn, Fe, Cu and Ni) impregnated on Al-sg showed activities with the maximum N_2 formation between 23 and 59%. Fe showed a particular high activity at 250-350°C but the activity decreased at higher temperatures. The propene oxidation on Mn/Al-sg was excessively fast, which destroyed HC-SCR activity. The activity of the Ni catalyst was clearly improved by the calcination at 800°C.

The reaction mechanism on Cu/ZSM-5 should differ from alumina based catalysts because it had a very low T_{50} value to CO_2 formation, but N_2 formation was still quite high up to 500°C. The ZSM-5 zeolite has a high adsorption capacity for hydrocarbons, acidity and hydrofobicity compared to alumina, which caused the detected differences. Slow surface reactions probably resulted in a broad operation window without any peaks. However, Cu/ZSM-5 used as a reference is known to be deactivated hydrothermally and chemically in real applications (Grindsted et al. 1993).

Ga/Al-sg was a promising catalyst found in screening. Ga/alumina had a particular high activity at high temperatures (maximum > 95% to N_2 in dry and > 60% in wet conditions at 500-550°C). The highest N_2 formation was reached with the catalyst calcined at 600°C but the operation window was the same with the calcination temperature of 800°C, which proved also its thermal stability up to 800°C.

The optimal calcination temperature for Sn/Al-sg was 700°C, when the maximum N_2 formation was 77%. Sn/Al-sg also showed a similar activity in dry and slightly lower activity in wet conditions than In/Al-sg in the presence of methanol and ethanol (II, table 2 and 3).

When the molar ratio was 650, metal oxides were highly dispersed on alumina and N_2 formation was shifted to higher temperatures compared to the results with Al/M = 65 (Table 5).

Table 5. The reduction of NO to nitrogen by propene on Al-sg supported (**Al/M = 650,** calcined at 600°C) catalysts in a dry mixture (Feed: 1000 ppm NO, 1000 ppm C_3H_6, 10% O_2, balance He. F/W = 20 $dm^3 g^{-1} h^{-1}$).

Sample	N_2 formation (%) at reaction temperature, °C								CO_2
	200	250	300	350	400	450	500	550	$T_{50}(CO_2)$, °C
Co/Al-sg	10	13	12	13	6	6	8	12	320
Cu/Al-sg	9	21	45	40	37	32	22	-	350
Fe/Al-sg	12	15	21	30	15	14	15	12	335
In/Al-sg	8	11	13	27	73	95	87	50	385
Pt/Al-sg	8	22	11	4	4	3	3	3	220
Al-sg	8	13	20	28	35	48	77	33	365

When NO_2 was used instead of NO in feed, the activity at low temperatures was improved (Table 6). The activity of Al-sg at 300°C reached such high conversions as 80% but the good activity at higher temperatures, detected with NO, disappeared. NO oxidation to NO_2 has been reported to be a limiting factor especially on unloaded alumina catalysts. Metal oxide loaded samples showed the same better activity by NO_2 than by alumina-only catalysts at lower temperatures, which was evidence that the NO reduction step might happen totally or partly on the Al_2O_3 surface on these catalysts. In the presence of NO_2, less N_2O was formed than with NO, which showed that NO_2 does not react directly with N formed by dissociation from NO: $N + NO \rightarrow N_2O$. The highest formation of CO coincided with the highest acceleration of HC oxidation.

Table 6. The reduction of NO_2 to nitrogen by propene on different Al-sg supported catalysts (Al/M = 65, calcined at 600°C) and Cu/ZSM-5 in a dry mixture (Feed: 1000 ppm NO_2, 1000 ppm C_3H_6, 10% O_2, balance He. F/W = 20 $dm^3 g^{-1} h^{-1}$).

Sample	N_2 formation (%) at reaction temperature, °C								CO_2
	200	250	300	350	400	450	500	550	$T_{50}(CO_2)$, °C
Al-sg	4	26	80	40	23	30	43	41	360
Co/Al-sg	7	15	38	21	46	43	32	19	375
Cu/Al-sg	14	23	39	41	38	28	21	19	280
Fe/Al-sg	14	43	49	19	8	9	8	7	260
Mn/Al-sg	8	14	13	9	8	8	8	7	275
In/Al-sg	8	12	48	84	90	83	77	62	330
Sn/Al-sg	9	28	58	68	65	51	32	17	380
Ga/Al-sg	5	26	66	84	95	99	98	83	350
Pd/Al-sg	8	11	4	3	3	4	5	7	225
Pt/Al-sg	11	8	4	3	3	5	6	6	170
Cu/ZSM-5 ref.	19	25	48	51	42	38	32	-	250
Blank	4	2	2	2	2	2	2	-	> 500

In the presence of NO_2, the activity of Al-sg supported catalysts with Al/M = 650, except of Pt/Al-sg(650), were enhanced to higher NO conversions to N_2 more clearly than with Al/M = 65. The lower active metal content lead NO_2 to react mainly on alumina sites. The presence of NO_2 slightly improved the propene oxidation on Fe/Al-sg and Cu/Al-sg catalysts.

CO, N_2O and C_2H_4 were detected as small quantities as side products in propene-SCR experiments. N_2O appeared in reactor outlet when HC-SCR initiated at low temperatures (< 300°C) due to an active oxidation catalyst (Pt, Mn) or reactive hydrocarbon (methanol) (II). Pt is known for its particular ability to dissociate NO at low temperatures where also N_2O formation is thermodynamically most probable (150-250°C). When the maximum N_2O formation was with other catalysts about 4-6%, it was with Pt/Al-sg(65) about 42-43% at 200°C both with NO or NO_2 in feed. The decrease in the Pt loading (5.6 → 0.6%) decreased the maximum N_2O formation to 23%. CO partially oxidized from hydrocarbons was detected with the poorest oxidation catalysts like alumina-only or In/Al-sg. CO and CO_2 have been treated as reactants which are not able to reduce NO_x or react back to reducing compounds. Thus, CO_x compounds are grouped in our HC-SCR publications (II-VI) to separate reactive and unreactive species present in gas and surface phases. V/TiO_2 was very selective to form CO from propene at low temperatures and the maximum CO formation was about 65% at 300°C.

The reaction mechanism on different catalysts was also studied by feeding NO and propene in the absence of oxygen and N_2O in the presence of oxygen with or without propene. NO reduction and decomposition in rich conditions were compared with the results in lean conditions and the role of oxygen and oxide species was analyzed in propene-SCR. The experiments in rich conditions showed that only Pd, Pt and Cu catalysts had complete NO reduction to N_2 below 550°C. Therefore, the other HC-SCR catalysts require the presence of oxygen to have a NO reduction activity.

The decomposition and reduction of nitrous oxide over Al-sg based catalysts (Al/M = 65) and Cu/ZSM5 as possible intermediate reactions in HC-SCR were investigated using 500 ppm N_2O and 0/1000 ppm C_3H_6 in the presence of 10% oxygen. Cu/ZSM5 was much more active to convert N_2O than any of the alumina supported catalysts and it also had an activity in N_2O reduction by hydrocarbons. This can be a reason for the reported high activity of Cu/ZSM-5. In addition, our propene-SCR experiments showed that N_2O formation was negligible on Cu/ZSM5. Pd, Cu and Pt on Al-sg had a slight activity to decompose nitrous oxide (Table 7).

Table 7. N_2O decomposition (T_{50}, °C) and reduction by propene on Al-sg supported catalysts calcined at 600°C.

	Co	In	Cu	Mn	Pt	Pd	Al-sg only	Cu/ZSM-5
$T_{50}(N_2O)$	> 600	> 600	495	> 600	525	465	> 600	410
$T_{50}(CO_x)$	405	350	270	240	< 150	< 200	380	225

500 ppm N_2O, 1000 ppm C_3H_6, 10% O_2, no water, He balance, F/W = 20 $dm^3\ g^{-1}h^{-1}$.

These results showed that N_2O was mainly decomposed to N_2 but not reduced by propene on investigated alumina based catalysts because the propene oxidation by oxygen initiated at much lower temperatures when the reaction of N_2O to N_2 was detectable. Because the N_2O decomposition temperatures were rather high, it was difficult to remove the formed N_2O in HC-SCR catalysts and N_2O was not a key reaction intermediate in NO_x reduction to N_2 with these alumina based catalysts but an embarrassing byproduct.

The activities of the best catalysts were confirmed also in the presence of 10% water and the highest activities (> 50% to N_2) were found with In/Al-sg and Sn/Al-sg (II) at lower temperatures (350-500°C) and with Co/Al-sg and Ga/Al-sg at higher temperatures (> 500°C) (II, IV). The activity of Ag/Al-sg (65) was also clearly improved (max. N_2 formation of 41% at 500°C) in the wet conditions when the catalyst was calcined at 800°C, whose high temperature was also found in another study to be necessary to create an active Ag/alumina catalyst for HC-SCR (Aoyama et al. 1997). Therefore, improved preparation conditions were found for Ag/alumina, which has been known also as a durable HC-SCR catalyst in the presence of water and particularly oxygenated hydrocarbons as reductants (Miyadera 1993). The high oxidation activity of the studied Ag/alumina catalyst was a limiting property and it was due to used high Ag loading and sol-gel alumina, which might promote the formation of excessively reactive Ag species (e.g. metallic Ag). Bethke and Kung (1997) found 2% Ag on alumina support to be the optimum. The importance of alumina type was seen in an experiment with Ag/Al-ref, which resulted in N_2 formation of 64% after calcinations at 600°C. In spite of interesting results with Ag/alumina, our more profound studies were focused on In, Ga and Co catalysts.

7.2.2 NO_x reduction by propene on all alumina catalysts

The different types of aluminas without active metals were studied and characterized in more detail in propene-SCR because the support has an essential role in HC-SCR activity and alumina based catalysts were studied with various active metals. The maximum N_2

formation varied by the calcination temperature of 600-800°C, but calcination at 900°C deactivated all these alumina catalysts (Fig. 21). Al-2 and Al-ref required a higher temperature calcination to decrease the propene oxidation activity and let propene react with NO instead of oxygen (IV). Thus, γ- and δ-alumina showed a HC-SCR activity both in dry and wet conditions. α-alumina (Al-3) had a negligible activity in propene-SCR.

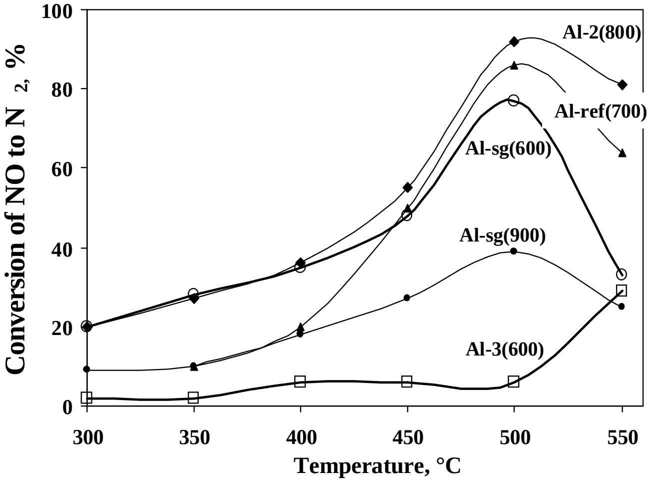


Figure 21. The highest N_2 formation with the optimal calcinations temperatures (shown in parenthesis) on each alumina catalysts in propene-SCR (IV, table 2).

The acidic and basic properties of two different aluminas (γ-Al-sg and δ-Al-2) were characterized by using NH_3 desorption and CO_2 adsorption methods (Table 8). However, the total acidity and basicity did not correlate to the propene-SCR activity but to total surface area. XRD analysis showed that Al-sg was shifted from γ- and δ-form clearly to the direction of θ-alumina, but no α-alumina was found after calcinations at 900°C.

Table 8. The acidity and basicity evaluation by ammonia-TPD and CO_2 adsorption measurements on Al-sg and Al-2 (Maunula et al. 1998).

Sample	Calcination temperature, °C	NH_3 by TPD Ncm^3/g	CO_2 chem Ncm^3/g	CO_2 ads at 1bar Ncm^3/g
Al-sg	600	11.5	2.4	20.2
	700	-	1.7	15.7
	800	9.7	1.6	15.1
Al-2	600	4.3	0.4	7.0
	700	-	0.7	8.6
	800	6.1	-	-

Chem: chemisorption, physical adsorption eliminated by the dual adsorption and back extrapolation methods; Ads: adsorption.

^{27}Al MAS-NMR analysis was conducted for Al-sg and Al-2 samples to trace possible structural differences (Fig. 22). The detected peaks were signified by the coordination of aluminum. The values of about 8 ppm, 42 ppm and 80 ppm meant six coordinated (octahedral), five coordinated (amorphic) and four coordinated aluminum, respectively. The thermal treatment at 800°C did not change the state of Al-2, which had a higher share of five coordinated aluminum than Al-sg, which had a higher share of four coordinated aluminum. The main peak in all samples was octahedral aluminum.

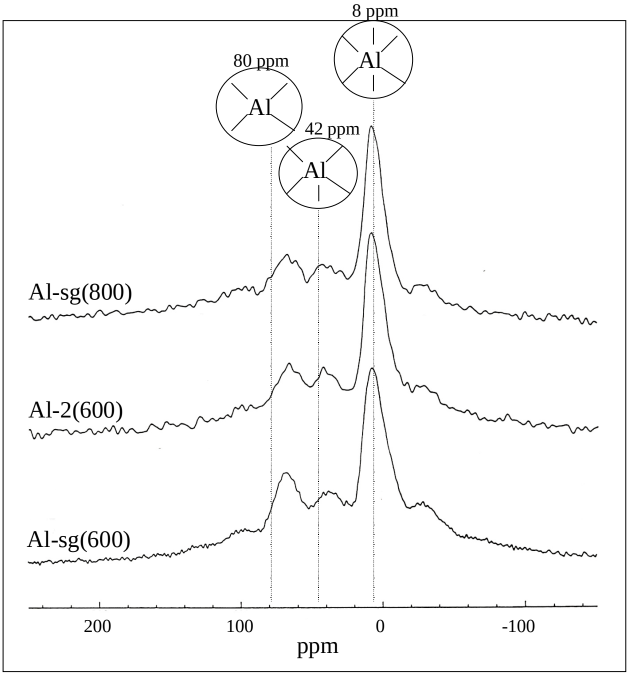


Figure 22. Results by ^{27}Al MAS-NMR with two aluminas (Maunula et al. 1998).

The difference FTIR spectra on Al-sg calcined at 700°C were analyzed between flowing reaction gas and helium gas conditions (Fig. 23). Adsorptions were strong at 200-280°C, where propene-SCR reactions were not yet initiated. The absorbance peaks on alumina were signified to formates (1600 cm^{-1}), nitrates (1227, 1600 cm^{-1}) and carbonates (1454 cm^{-1}) and the intensity of these inhibiting compounds decreased and very low surface coverages were observed in HC-SCR conditions (> 400°C) (see detailed identifications in publications III and IV). These peaks can be compared to the spectra with Co and In loaded Al-sg and to separate adsorptions on alumina support and active metals in reaction conditions. The changes in the range of alumina hydroxyl groups were observed rather similarly in He, C_3H_6-O_2-He and NO-C_3H_6-O_2-He flows (data not shown here). Thus, these changes were caused by collision assisted thermal desorptions in the presence of gas flow.

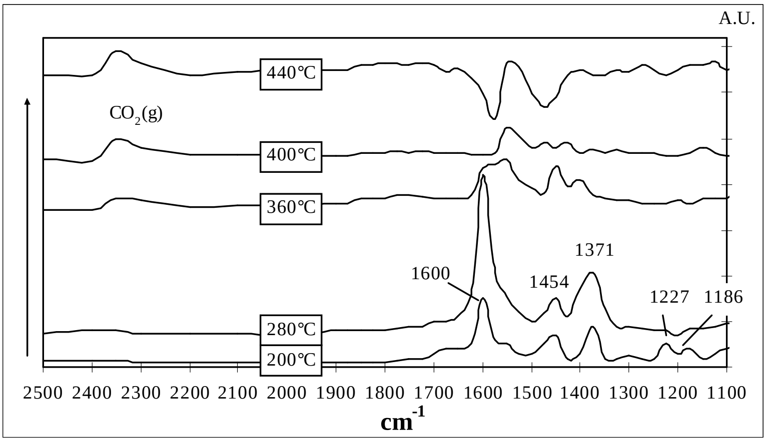


Figure 23. Difference FTIR absorbance spectra of NO-C_3H_6-O_2-He minus He in flowing gas and temperature ramp at 200-440°C on sol-gel alumina (Al-sg(700)).

It is concluded that the propene oxidation activity correlated best with the propene-SCR activity on all alumina catalysts.

7.2.3 NO_x reduction by hydrocarbons on In/alumina

In/alumina catalysts showed promising NO_x conversions in screening experiments in dry and wet lean conditions and thus the catalyst properties and reaction mechanism were investigated in more detail (II, III). It was attempted to improve the activity and clarify the reaction mechanism by varying the In loading (0.34–10.1 wt-%, Al/In = 20–650 mol/mol), support material (sol-gel γ-Al_2O_3, conventional γ-Al_2O_3, TiO_2, ZSM-5 zeolite, SiO_2, none = pure InO_x), In precursor (nitrate, acetate), In addition method (impregnations, sol-gel) and hydrocarbons (propene, propane, ethene, methane, methanol, ethanol and 2-propanol). The widest and highest operation window in HC-SCR was reached with In supported on sol-gel prepared γ-alumina (Al-sg), calcined at 600-700°C with the In concentration of 3.3 wt-% in dry and 1.7 wt-% in wet gas mixture. The best high temperature (450-550°C) activity was reached by using lower In loadings: 0.3-0.7% In in dry and 0.7% In in wet conditions. In/Al-sg(65,600) showed a higher HC-SCR activity (deNO_x 28–96%) in the presence of all studied hydrocarbons except methane (8%), although the exact comparison was not possible because of different C_1/NO_x ratios in the experiments (II, table 2 and 3).

The activity also depended on the In addition method and the wet1 method gave a higher activity than the wet2 method, where less In solution was used in preparation. The wet1 solution contained twice the amount of solution required to fill pores. That excess of solution was selected as a standard to guarantee free access of In on support sites in all conditions. Indium nitrate resulted in a higher activity than indium acetate as a precursor and thus indium nitrate was used in following experiments.

The role of In and Al cooperation was studied, in addition to conventional impregnations, by developed phase-equilibrium (pe) and sol-gel preparation methods and the mechanical mixtures of pure oxides (II, III). In the pe method, alumina and In nitrate was allowed to find during 12 hours at 80-90°C equilibrium solid phase, whose deposit was filtered to have an In rich composition (82% In oxide). Therefore, a part of alumina was dissolved into solution in this method. In/Al-sg(pe) showed the highest propene oxidation activity (T_{50} = 280°C) and the highest N_2 formation (37%) at 300°C, but due to the high HC oxidation activity, the HC-SCR activity at higher temperatures was poor. A reason for the high oxidation activity might be the higher surface area with such high In loading (Al/In = 0.67). The propene light-off (T_{50}) of In/Al-sg with high In loadings or pure InO_x was at lowest about 340°C. The sol-gel InAl oxides showed a higher maximum N_2 formation (80-85%) than In/Al-ref (max. 70%) but lower than active In/Al-sg. The reactions observed on indium/alumina were also partly created by using the mechanical mixture of Al-sg and InO_x with the Al/In ratio of 65. The activity of the mechanical mixture was about the same as with In/Al-ref and higher than the conversions predicted by the activity of InO_x and alumina, but clearly lower than with In/Al-sg. The presence of alumina and InO_x even as a macroscale mixture created a HC-SCR activity, which supported the possibility of short-lived gaseous intermediates and surface migration of adsorbed species. It can be concluded that a very high dispersion of indium is not necessary for this reaction. Therefore, the developed preparation methods, sol-gel alumina with the optimized In loadings resulted in the high active In/Al-sg catalyst, which had a high HC-SCR activity also in wet conditions.

NO_2 had a slight promoting effect on NO_x reduction by propene to N_2 and propene oxidation at low temperatures (III, Fig. 5). NO_2 was able to initiate HC-SCR and HC oxidation reactions but not to enhance these reactions at higher temperatures after the reaction initiation. FTIR studies revealed various strongly adsorbed species at lower temperature before the reaction initiation and the surface coverages of actual reactants to N_2 formation were proposed to be low.

7.2.4 Properties of In-Al oxides

7.2.4.1 In/alumina prepared by impregnation and ion exchange methods

It was generalized that the same principal interactions and phase formations occur when preparing the catalysts by impregnation, precipitation or sol-gel methods (III). Concerning final oxide framework structure, the conditions in solutions, sols, gels, drying and calcination have crucial importance. In the presence of water, the complicated solution chemistry, solubility and the adsorption strength of reactants dictate the crystal structure and the coordination of catalyst compounds. The surface of alumina can depend on pH and have a positive or negative charge in water solution:

$\text{Al-OH (s)} + H^+ \Leftrightarrow \text{Al-OH}_2^+ \text{ (s)}$ Acidic (48)

$\text{Al-OH (s)} \Leftrightarrow \text{Al-O}^- \text{ (s)} + H^+$ Basic (49)

Adsorbed species were condensed on solid surface (s) and other species were dissolved. In our study, it was used acidic, In nitrate water solution, where negatively charged anionic indium species (L = ligand attached to cation) were adsorbed on alumina surface:

$\text{Al-OH}_2^+ + \text{In-L}_x^- \Leftrightarrow [\text{Al-OH}_2]^+ [\text{In-L}_x]^-$ (50)

The ligand exchange is a way to build oxide framework precursors in impregnation and proceeding steps:

$\text{Al-OH (s)} + \text{In-L}_x^- \Leftrightarrow \text{Al-O-} [\text{In-L}_{x-1}]^- \text{ (s)} + \text{HL}$ (51)

During gelation, drying and calcination the ligands were decomposed and water was removed from the structure resulting in oxide structure, which contained Al and In connected by oxygen bridges (Al-O-In, Al-O-Al and In-O-In). When an organic solute like ethylene glycol was used in indium solution, the amount of moisture near precursors was lower during drying and calcination. Therefore, the ordinary hydrothermal collapse of aluminum oxide structure was partly prevented resulting in a sample with very high surface area. In that case indium was capsulated into the aluminum oxide framework during sol-gel processing. This caused a reduced HC oxidation activity and the increased stability in high temperature calcinations, which correlates to the improved stability of In sites in thermal aging conditions. The catalysts where indium was finely dispersed in Al_2O_3 structure by the sol-gel method, had the HC oxidation ability changed to the direction of pure alumina. The molecular diameter of propene and its adsorbed derivates are so large that they will interact with surrounding alumina matrix in the neighborhood of indium atoms. In later studies, similar reasons for the high activity of sol-gel prepared InAl catalysts also have been observed. Li et al. (2005) concluded that the high surface area, low average pore diameter and strong interaction between indium and aluminum in sol-gel prepared In_2O_3/Al_2O_3 are crucial for high HC-SCR activity.

The properties of In/Al-sg(pe) prepared by the so called phase equilibrium method showed that aluminum oxide was dissolved in that ion exchange process by In nitrate solution:

$$\text{Al-OH}_2^+ \text{ (s)} + \text{In-L}_x^- \Leftrightarrow \text{In-OH}_2^+ \text{ (s)} + \text{Al-L}_x^- \qquad (52)$$

The product prepared by the phase equilibrium method was in solid phase and was separated by usual gravimetric and filtration methods from solution or sol. As a comparison in coprecipitation methods all the compounds are originally dissolved in solution. The described reaction steps were the homogeneous and heterogeneous reactions to form bonding between indium and aluminum compounds. Compounds in equation 52 are attached to the wider adjacent solid framework (e.g. -O-Al-O-In-O-). Hydrolysis of aluminum on alumina and indium nitrate during the preparation may occur. Of course, the final composition of solid products by sol-gel processing and the phase equilibrium method depends on pH, temperature, solubilities and concentrations. The parameter optimizations in catalyst preparation processes by the described principles have offered a wide field for detailed studies.

The catalyst and surface characterizations resulted in the conclusion that In_2O_3 acts as an active site in addition to alumina sites for HC-SCR on In/alumina (II, III). It was found in other studies that the amount of crystalline In_2O_3 increases as a function of the In loading on In_2O_3/alumina (Park et al. 2002).

7.2.4.2 InAl oxides prepared by sol-gel methods

The addition of indium nitrate as an ethyl glycol solution into Al sol caused the formation of finely dispersed indium oxide in the Al_2O_3 structure. Indium oxide in InAl-sg1 was described as amorphous with a particle size less than about 10 nm by XRD (III). Alumina detected by XRD in InAl-sg1 resembles fresh Al-sg (γ-alumina) although the detection of various Al_2O_3 phases (γ, δ, κ, β, χ, θ, α) present in the samples, was not possible quantitatively by XRD spectra. However, the direction of transformations was seen qualitatively. Because few alumina phases are unstable intermediates, only the main phase shifts were evaluated.

The observations in activity experiments with InAl-sg1 and InAl-sg2 can be explained by earlier investigations which showed that metal atoms incorporated by the sol-gel method into the carrier framework are not easily accessible to reactants because the particle size of metal oxides is so small (Castillo et al. 1998, Cauqui and Rodriguez-Izquierdo 1992, Azomoza et al. 1992). An active metal capsulated in the carrier has new properties that stabilize and improve the high temperature activity of the catalyst. Oppositely, the lower temperature activity was generated by larger isolated active phase particles, which might be formed by high active compound loadings (In-Al-sg(pe)) and precipitation.

7.2.5 NO_x reduction by hydrocarbons on Co/alumina

The Co/Al-sg catalyst was investigated in respect to the optimal preparation method, catalyst properties (active sites), reaction mechanism and quantitative kinetic parameters in propene-SCR in detail (IV). CoO_x/alumina (Co/Al-sg(65, 700)) was used as a model catalyst for the base metal oxide containing alumina supported HC-SCR catalysts. Because the activity of CoO_x/alumina correlated with the combination of metal loading and calcination temperature, a test matrix in the range of 0.2–5.5 wt-% by the Co loading and in the range of 600–1000°C by the calcination temperature was conducted for propene-SCR reactions in dry and wet conditions. The results were fitted by the activity (N_2 formation) on two-dimensional (Al/Co and calcination temperature) contour graphs (IV, Fig. 2 and 3), where the optimum range at each test condition can be seen. The particular properties of sol-gel prepared Al-sg resulted in the high HC-SCR activity level of Co/Al-sg and the optimum was found with the Co loading of about 0.8–1.8 wt-% and with the calcinations temperature of 700°C. The preparation method was not only sensitive to the calcination temperature and alumina type but also for the Co precursor (→ nitrate) and the impregnation method used (→ wet1 with an excess of solution). The presence of Co on alumina (Al-sg and Al-2) clearly shifted the operation window of alumina to lower temperatures by about 100°C. Co/Al-sg(65,700) showed a particular high activity (73–91% in dry conditions) and a water resistance at higher temperatures (450-550°C) in the presence of propene, propane and ethene, but the activity in the presence of alcohols was lower (N_2 formation about 23-31% when 1000 ppm NO was reduced by 1000 ppm of each alcohol). It is usual that the hydrocarbons containing functional groups like double or triple bonding, -OH or =O groups are considered reactive in HC-SCR and light saturated hydrocarbons are more difficult to be activated (Hamada et al. 1991B). Therefore, the observed activity of propane on the developed Co/Al-sg in HC-SCR was seen as a promising result.

It was assumed by the catalyst characterizations (XPS, TGA, XRD) and other published studies that Co^{2+} was the main active Co phase in HC-SCR. The close interaction with alumina support was necessary to create highly dispersed Co species with high active surface area and it was not possible to reach the same activity by a mechanical mixture of Al-sg and precipitated CoO_x (Al/Co = 65). It has been found in a recent study that the morphology of Co/Al_2O_3 was changed as a function of calcination temperature and the surface layer of $CoAl_2O_4$ on γ-Al_2O_3 catalyzes the oxidation of NO to NO_2 but not the hydrocarbon oxidation (Okazaki et al. 2002). The presence of excessive Co_3O_4 efficiently catalyzes hydrocarbon oxidation and results in a lower HC-SCR activity. According to NMR and UV-vis studies, the coordination of Co species has a crucial effect on activity.

The dynamic FTIR spectra showed gaseous and adsorbed surface species in the temperature range of 200-440°C in flowing reaction gas mixtures. The same experiments made with reaction gases were also repeated with a He gas flow to eliminate the thermal effects in the presence of an inert gas at 1 bar. The comparison between dynamic FTIR spectra with Al-sg(700) and Co/Al-sg(65,700) showed that surface compounds are mostly on alumina support (Fig. 23 and 24). Nitrates on alumina (1230 cm^{-1}) disappeared between 200–280°C. Based on the static FTIR experiments, it was concluded that NO compounds cover the surface at lower ($\leq$ 250°C) but hydrocarbon species at higher temperatures (> 250°C) (IV, Fig. 6), which match to the observations in dynamic experiments, too. In the static FTIR measurements, the reactants were fed in sequences into chamber and IR spectrum was measured in the absence of gaseous compounds after evacuation. Gaseous NO and adsorbed NO_x species on Co compounds might be present as low amounts in the range of 1800-1900 cm^{-1}.

Nitrate, carbonates, hydrogen carbonates, formates and acetates are the main species in the range of 1370-1600 cm^{-1}. The intensities of the peaks connected to HCO_3 (1450 cm^{-1}) and HCO_2 (1590-1600 cm^{-1}) were very strong below 300°C, but the peaks disappeared or even turned negative at HC-SCR reaction temperatures. The negative peaks meant that the IR absorbance was lower than in the background spectrum in He flow at 200°C. The reason was the adsorption/collision assisted desorption of HCO_x and other species. The presence of gas flow at higher temperatures enhanced desorption compared to the evacuation at 480°C (pretreatment before background measurement). The presence of acetate species has been assigned to the wavelength of 1460 and 1570 cm^{-1} (Haneda et al. 2001A), whose compounds might also be present on the observed spectra but these peaks also exactly match the negative peaks caused by desorptions above 400°C. The oxygenated C_1 and C_2 compounds on alumina surface are very probable intermediates in the presence of C_3H_6 and oxygen but certain limit temperatures are required to activate propene by breaking C-C bonds. The peaks around 1550 cm^{-1} observed in the absence of propene have been assigned to monodentate nitrate on alumina (Haneda et al. 2001A, Eränen et al. 2004). The peak of the adsorbed formate (1375 cm^{-1}) on alumina decreased as a function of temperature and disappeared above 400°C. The formation of CN and NCO species (2100-2300 cm^{-1}) was undetectable under these conditions on Co/alumina.

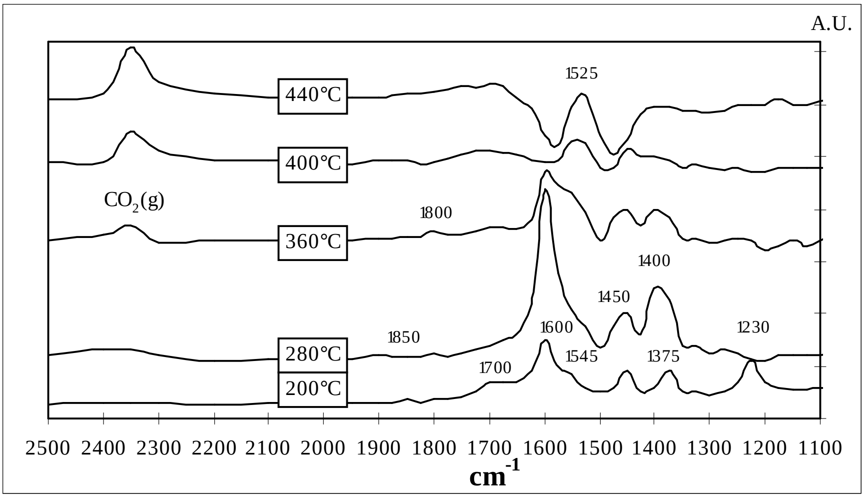


Figure 24. Difference FTIR absorbance spectra of NO-C_3H_6-O_2-He minus He at 200-440°C in flowing gas and temperature ramp on Co/Al-sg(65,700).

7.2.6 Enhanced activity by mixing Mn_3O_4 mechanically with In/alumina and Ga/alumina

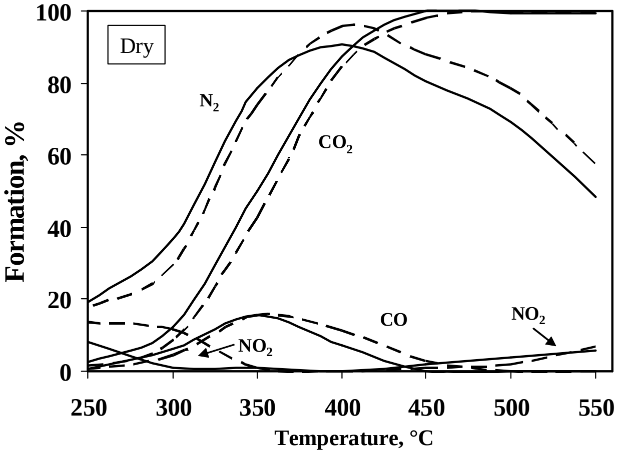
Because NO oxidation to NO_2 was seen to be a limiting step in HC-SCR, a small amount of a potential second catalyst was mixed together with the main HC-SCR catalyst. Mn_2O_3 has been used successfully earlier in many studies (Misono and Kondo 1991, Chen et al. 2000B, Ueda and Haruta 1998) but our thermodynamic calculations confirmed us to try more stable Mn_3O_4 in the catalyst mixtures. The improvement in the propene-SCR activity with In/Al-sg and Ga/Al-sg was significant both in dry and wet conditions (II, Fig 7). The N_2 formation rates increased with the addition of Mn_3O_4 and slightly more by using NO_2 in feed. The promotion with In/alumina on N_2 and CO_x formation was observed more clearly in wet conditions, but in dry conditions In/Al-sg showed already a rather wide operation window.

On Ga/alumina the promotion was also related to the improved propene oxidation activity both in dry and wet mixtures which shifted the operation window clearly to lower temperatures but also cut slightly down the high temperature activity to form N_2 (≥ 500°C). If the high temperature activity should be reserved and the low temperature HC-SCR activity slightly improved, the amount of Mn_3O_4 should be decreased. The observed difference in propene oxidation below 330°C can be assumed to be related to propene oxidation by NO_2 on alumina surface (III, Fig. 5).

Similar improvements in HC-SCR have been described in earlier publications (see chapter 5.2.4.2), but a part of the earlier experiments has been made e.g. by mixing metal oxides with a support only (alumina, zeolite or silica) having a low initial activity. In our study we managed to increase the propene-SCR activity of originally very active sol-gel alumina based In and Ga catalysts. Because the reaction mechanisms and operation window on alumina supported Co, In, Ga, Sn, Ag catalysts are similar (II-IV), it can be assumed that the promotion effects by the addition of Mn_3O_4 on them are the same.

The oxidation activity was controlled by the use of low surface area Mn_3O_4 (1 m^2/g) instead of high surface area oxides and by the amount of Mn_3O_4. The total amount of HC-SCR active catalysts was kept constant and the amount of secondary catalyst designed to enhance NO_2 formation kept at a minimum. It was proposed that a higher selectivity to NO_2 oxidation compared to HC oxidation could be reached by using a lower active metal surface area on oxidation catalysts (Maunula et al. 2003). The use of Mn_3O_4 also matched this principle. The high thermal stability and low surface area of Mn_3O_4 guarantees better stability in use conditions.

The detailed analysis of side products in the experiments with In and Ga on alumina gave us new observations related to the reaction mechanism (Fig. 25 and 26). Due to the lower promotion of Mn_3O_4 on In/Al-sg in dry conditions, the differences were also low by byproduct formations. In fact, the detected NO_2 concentration at low temperatures was higher in the absence of Mn_3O_4. NO_2 reacted better on In/Alumina in the presence of Mn_3O_4. A small part of detected NO_2 in gas phase might have formed thermally in the reactor and lines. NO_2 was not detectable by the chemiluminescence analyzer in wet conditions. N_2O formation was slightly increased in the presence of Mn_3O_4, but the formation rate was negligible (< 1% of NO_x).



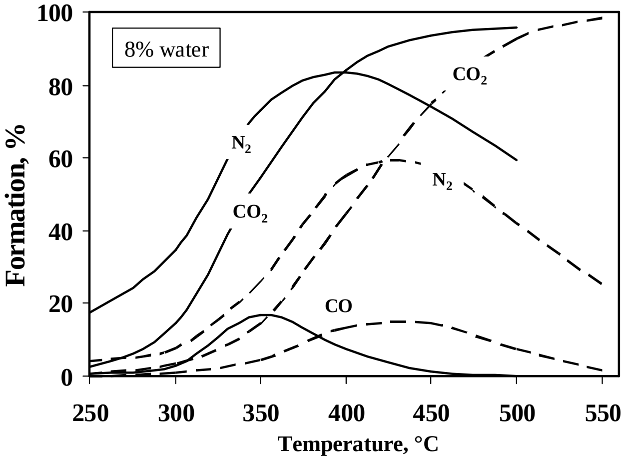


Figure 25. The enhancement of propene-SCR by Mn_3O_4 on In/Al-sg(65) (19:1) and the observed N_2, CO_2 and CO and NO_2 formations in dry and wet conditions (1000 ppm NO; 1000 ppm C_3H_6; 10% O_2; 0/8% H_2O; F/W = 20 dm^3 g^{-1} h^{-1}). Solid lines with Mn_3O_4.

On Ga/alumina, the effect of Mn_3O_4 was dramatic and the operation window was shifted over 100°C to a lower temperature. CO was formed as higher quantities (max. 30%) on Ga/alumina due to its low oxidation activity. NO_2 responses were similar than with In/alumina and higher NO_2 was detected with Ga/alumina in the absence of Mn_3O_4. The formed and present NO_2 had not reacted efficiently on Ga/alumina, but Mn_3O_4 was required to remove NO_2. Unfortunately, the activity of Mn_3O_4 was not studied separately to distinguish its own independent properties. However, it was seen by these results that Mn_3O_4 has an essential role in the NO reduction step in addition to the promotion on NO oxidation. The possible promotion steps are HC-SCR reactions with NO_2 and decomposition of certain formed intermediates or reactants (HNCO, NH_i, NO_x, R-NX). The N_2O formation rate was negligible (< 1% of NO_x) in the absence and presence of Mn_3O_4. N_2O is formed in the presence of adsorbed N. Therefore, the NO or NH_3 dissociation routes to adsorbed N were not proved to be a reason for the observed improvement, even if manganese oxides have a good activity to decompose N_2O.

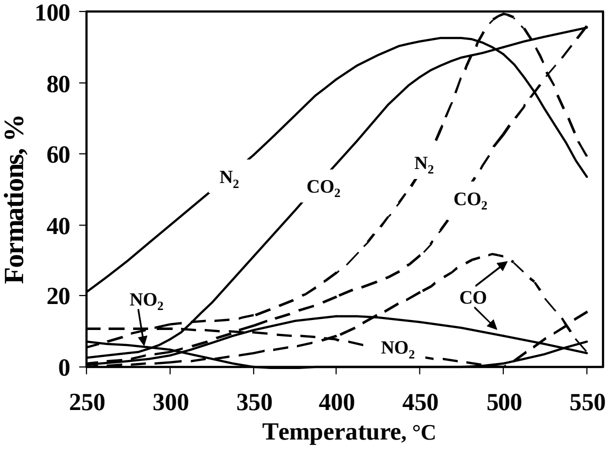


Figure 26. The enhancement of propene-SCR by Mn_3O_4 on Ga/Al-sg(65) (19:1) and the observed N_2, CO_2 and CO and NO_2 formations in dry conditions (1000 ppm NO; 1000 ppm C_3H_6; 10% O_2; F/W = 20 $dm^3\ g^{-1}\ h^{-1}$). Solid lines with Mn_3O_4.

7.2.7 Reaction mechanism for HC-SCR of NO_x

The general reaction mechanism was proposed based mainly on detailed propene-SCR experiments with pure and Co and In loaded sol-gel alumina. A lot of published data exists for HC-SCR and it has been attempted in this thesis to interpret the mechanistic analogies by analyzing literature of HC-SCR, NH_3-SCR, three-way catalysis and NO decomposition both on oxide and zeolite based catalysts. The wide screening of catalysts and HC reductants having varying properties gave a general view about the required chemical properties and reaction paths. The characterizations of catalytically active species on Co and In catalysts gave a view about nano- and molecular-scale properties on active HC-SCR catalysts. The surface intermediates detected in situ by FTIR have been connected to the reaction mechanism. In principle, the reaction mechanism is assumed to be the same on studied alumina supported In, Co, Ga, Sn and Ag catalysts, but the relative rates and the importance of each reaction step can vary. The reaction mechanism in HC-SCR with non-methane hydrocarbons has been proposed in our publications (II-IV) proceeding from general qualitative mechanism proposals to the detailed mechanism and up to quantitative simulations.

Molecules usually react through similar energetic favored intermediates in thermal and catalytic reactions. The reaction mechanism observations in HC activation in thermal conditions have also been utilized to interpret the possible reaction paths on catalyst surface (Eberhard and Howard 1996). It is known that OH radical are able by water formation to activate hydrocarbons to the alkyl radical, which reacts to the alkyl peroxy radical (RO_2) and which is very reactive to oxidize NO to NO_2. Similar reaction mechanisms in hydrocarbon reactions (C_2, C_3) on the hydroxyl groups of metal oxides are relevant, even if catalytic reactions will proceed at significantly lower temperatures than thermal ones.

It was concluded by the studies with In/alumina that the actual reductant (NX) contains a N-H or N-C bonding (III). As soon as these actual reactants are formed, they will react with adsorbed NO. Partially oxidized hydrocarbons and nitro species are intermediates, which precede the final surface reactants in the route to N_2 formation. NCO and CN species observed in many FTIR studies on various HC-SCR catalysts are related mostly to rich and dry conditions. N-H type reductants are more evident in lean and wet conditions, where isocyanates are rapidly hydrolyzed to NH_i on oxide based HC-SCR catalysts (Dümpelmann et al. 1995). The amines and amides are very plausible in reducing NO on active sites (Beutel et al. 1995).

The reaction mechanism, including all surface reactions and possible gas compounds from reactants to the products in propene-SCR on Co/alumina, has been presented by Maunula et al. 1998 and 2000 (IV). In the case of propene, the possible paths before CO_x formation are wide but we have fixed the paths to match the usual hydrocarbon reaction steps, surface observations and the mass balances of chemical compounds. It is essential for HC-SCR to form N containing surface intermediates which have N-C or/and N-H bondings (adsorbed NH_2, H_2NCO; amines and amides) and are able to reduce adsorbed NO in lean conditions. The promotion of NO_2 has been linked to the enhanced formation of partially oxidized hydrocarbon species. NO_2 has a high oxidizing power and it is not able to form the actual reductant (NRO) in a single surface reaction. Nitro species observed in many studies are a reserve of oxidizing compounds similar to RO_2 on catalyst surfaces, but it was proposed that the actual reductant was formed by NO. However, the reaction of NO_2 on catalyst in hydrocarbon oxidation steps might introduce adsorbed NO as a reaction product close to CH_2O, which will react to H_2NCO and further to other actual reductants. Certain reaction steps in the reaction mechanism are more net reactions consisting in reality of two or more single reaction steps. Isocyanate type intermediates observed sometimes on these catalysts are assumed to be hydrolyzed quickly to NRO or NH_i compounds in lean conditions.

The reaction mechanism for HC-SCR has been summarized in Fig. 27 based on the reactions in the publications (III-VI). All the observed reactants and products in gas phase and the defined surface compounds were included in these reaction mechanisms. Six different actual reductants (H_2NCO, HNCO, NCO, NH_2, NH, N) have been proposed to have the potential to reduce adsorbed NO. The lifetime of each intermediate depends on reaction conditions and the catalyst. It can be concluded that within these reductants, NH_2 containing surface intermediates (NH_2, H_2NCO) have the best stability and reduction ability on NO in HC-SCR. HNCO and NCO react quickly to NH_2 in lean and wet conditions. The formation of adsorbed NH and N required particular dissociation ability, which is more relevant in the absence of oxygen and with precious metal catalysts. In fact, H_2NCO can be seen to react by the release of CO_2 through NH_2 intermediates with NO and these reducing intermediates are linked together. Therefore, the difference between them is difficult to distinguish in the experiments and both reductants should explain the reaction dynamics rather similarly. The final nitrogen formation reaction proceeds by the Langmuir-Hinshelwood mechanism.

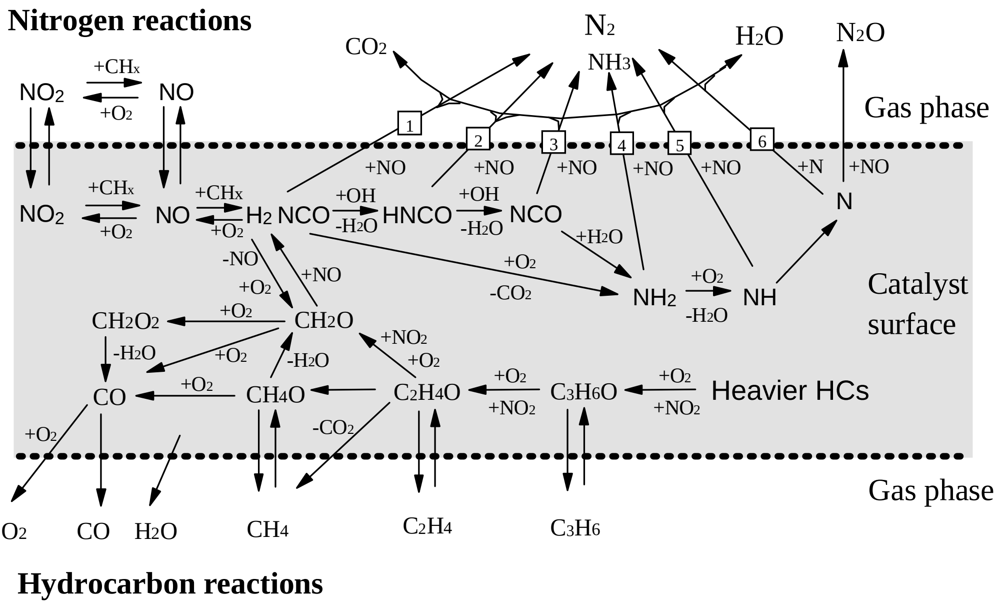


Figure 27. The proposed reaction mechanism for NO_x reduction by hydrocarbons.

In general, the published reaction mechanism proposals for HC-SCR on zeolite or oxide based catalysts are in agreement with this detailed mechanism with NH_i and NRO type final intermediates (Obuchi et al. 1998B, Lukyanov et al. 1995, Liu et al. 2001).

7.2.8 Micro-kinetic model for C_3H_6-SCR of NO_x on Co/alumina

The kinetic equations based on the defined reaction mechanism including all catalytic single surface reaction steps from reactants to the final products were derived (Fig. 27, IV). The kinetic parameters were fitted using the data set with the varying inlet NO, propene and oxygen concentrations (NO-C_3H_6-O_2-He) and residence time in dry steady state conditions on Co/Al-sg(65,700). Many surface and gas phase intermediates are appearing in fast reaction steps as low concentrations and it was not possible to detect them by FTIR analysis, even if they are key compounds in reaction paths. However, reaction mechanistic modeling will include also these undetectable surface compounds and the reaction dynamics are linked to detected responses and mass/vacant balances quantitatively. Many parallel reaction steps are usually proceeding at the same time but in the present model, most of parallel paths has been neglected. Particularly, the path from C_3H_6 to CO_x contains various possibilities but a route which exactly explains the mass balances has been selected based on the experimental and literature observations. The certain important parallel reaction paths have been included in the model like competing O_2 and NO_2 as oxidants and competing oxidation and reduction reactions, which have been seen to have an importance to understand observations in HC-SCR.

The surface reaction equilibrium constants (K_i) have been applied to quasi-equilibrium reactions and the adsorbed reactants (i.e. N_2O, CO_2, H_2O and N_2) in the fast reactions do not exist on catalyst surface. Therefore, these reactants desorb fast from the active site into gas phase. The reactant amounts in the rate equations were defined by the molar concentrations (c_i) in gas phase and surface coverages (θ_i) on active site (*), which was identified to be dispersed Co^{2+} on alumina. The formations of NO_2, N_2, N_2O, RO_2, CO_2 and CO were defined as rate-determining steps in model. Finally, NO is reduced by H_2NCO to N_2 or N_2O leaving oxidized C_1 compounds on active sites (CH_2 denoted to R in IV):

$H_2NCO^* + NO^* \rightarrow N_2^* + CH_2O_2^* \rightarrow N_2 + CH_2O_2^* + {}^*$ main (53)

$H_2NCO^* + NO^* \rightarrow N_2O^* + CH_2O^* \rightarrow N_2O + CH_2O^* + {}^*$ minor (54)

The rate equations were derived and resulted in the dependences on the molar concentrations. The rate equations for N_2 formation and NO reduction can be presented as a simplified correlation function of propene ($P = C_3H_6$), NO, oxygen and NO_2 concentrations or their products with the next powers (the original equation 38 with parameters in IV):

$$r_{NO} \sim r_{N_2} \sim \frac{f(c_p{}^{1/3} \times c_{NO}{}^{2})}{f(c_{NO}, c_{O_2}, c_{NO_2}, c_P{}^{n} \times c_{O_2}{}^{m}, c_P{}^{1/3} \times c_{NO_2} \times c_{O_2}{}^{-1/2}, c_P{}^{1/3} \times c_{NO})} \qquad (55)$$

The reaction rates of other compounds were found in the similar way (IV). The nominator shows the reaction limitations by adsorptions as a function of reactant concentrations.

The proposed model was fitted to the measurements and verified by predicting unmeasured results. Because the condition matrix was limited and the reaction mechanism complicated, the model explained data worse than in the case of CH_4-SCR modeling. However, the dynamics and the main effects of variables were predicted (IV, Fig. 7). The simulations are an efficient and economical way to analyze unmeasured or even unmeasurable conditions in HC-SCR reactions. No earlier micro-kinetic model for propene-SCR was found in literature. Few attempts have been done to model the simpler methane-SCR reactions mostly by power law equations and also by simple mechanistic models (see discussion in chapter 7.3.6).

The reactant and product concentrations as well as the surface coverages were simulated as a function of conditions and catalyst length. The surface coverage of actual reductant (NRO*) was decreasing as a function of temperature in the range of 400-500°C (IV, Fig. 8). The surface coverage of NRO* and PO* dropped to zero, when propene disappeared from gas phase. In contrast, the coverage of NO* decreased about to the one third of the inlet value as a function of the reactor length both at 400 and 500°C. These simulated responses followed common experimental knowledge about these reactions. When the reductant was consumed by fast oxidation, no reducing compounds existed on the catalyst surface. The simulations showed how large catalyst volume was required to fulfill the conversion targets at low temperatures and how small part of reactor volume (catalyst amount) was needed to reach the available N_2 formation at high temperatures (500°C). The simulations were done using propene as a reductant but other light hydrocarbons (e.g. ethene, methane, propanol, ethanol and methanol) can be treated as well as reductants in the model (IV). The reaction initiation is easier with oxygenated hydrocarbons to form PO, EO and RO_x according to IV.

The quantitative micro-kinetic modeling was done only for Co/alumina in propene-SCR but the same reaction schemes and rate equations can be applied for In/alumina or other alumina based catalyst.

7.3 NO_x reduction by methane in lean conditions

7.3.1 NO_x reduction by methane on oxide based catalysts

The catalysts for CH_4-SCR experiments were selected from the active metals known to have an ability to activate methane or NO_x and then possibly catalyze CH_4-SCR reactions. Therefore Co, In and Pd catalysts were evaluated in CH_4-SCR using mainly sol-gel alumina and ZSM-5 (SiO_2/Al_2O_3 = 23) as supports (Table 9). If the activity was low with Al/M = 65 and NO in feed, Al/M = 650 or NO_2 in feed also were attempted to find a deNO_x potential. Because Pd/Al-sg(650) with 0.3% Pd showed still a high methane oxidation activity in dry conditions, it was studied whether water might suppress the oxidation activity and increase HC-SCR activity. However, N_2 formation was negligible also in wet conditions. That experiment showed how the methane light-off temperature (T_{50}) increased from 380 to 475°C when 10% water was added into the feed gas. Because of low methane oxidation activities already in dry conditions, other alumina based catalysts were not studied in wet conditions.

The highest CH_4-SCR activity with alumina based catalysts was found with Al-sg only in dry conditions (14% at 550°C). However, these activities were low compared to ZSM-5 based catalysts, which showed very promising results (V, VI).

Table 9. NO_x reduction to nitrogen by methane and CO_x formation on alumina based catalysts (N_2/CO_x, formation-%).

Sample	Feed	Operation temperature / °C					
	NO_x	300	350	400	450	500	550
Co/Al(65)	NO	-/-	2/1	3/3	4/15	6/41	8/81
	NO_2	-/-	2/1	3/7	4/24	6/51	7/88
Co/Al(650)	NO	-/-	-/-	3/0	6/6	9/24	11/61
In/Al(65)	NO	-/-	3/1	4/4	5/11	6/31	8/67
Pd/Al(65)	NO	3/63	2/98	2/100	2/100	2/100	3/100
	NO_2	3/39	2/93	2/99	2/99	3/100	3/100
Pd/Al(650)	NO	4/3	4/23	6/62	9/92	8/100	7/100
	$NO+H_2O$	-/-	-/-	2/6	2/29	4/72	5/89
Al-sg	NO	-/-	-/-	6/0	8/22	14/69	14/98

1000 ppm NO/NO_2; 1000 ppm CH_4; 10% O_2; 0 or 8% H_2O; 20 $dm^3\ g^{-1}h^{-1}$

7.3.2 NO_x reduction by methane on In/ZSM-5

2.7% indium on protonated ZSM-5 (H-ZSM-5) showed a higher activity in dry conditions than 7.2% indium on sodium containing ZSM-5, which was better in the presence of 8% water (V). Isolated InO^+ in ZSM-5 was seen to act as the active site in CH_4-SCR and its formation from In_2O_3 was favored in dry conditions. This scheme explained the decreasing activity in the presence of water. However, free In_2O_3 present on over-ion exchanged In/ZSM-5 was assumed to have a promoting effect on the activity (V). In situ FTIR analysis in reaction conditions revealed many reaction-inhibiting compounds at lower temperatures and that the coverages of any compounds were low in CH_4-SCR reaction conditions (> 350°C). The oxidized nitrogen (NO_2, NO_3) and carbon species (CO_2, CO_3) have no reducing ability and they are strongly adsorbed and thus they are mostly inhibiting compounds in CH_4-SCR at low temperatures. The main species on surface are carbonaceous compounds but N containing compounds were also detected. These carbonaceous compounds have a key role in having locally reducing conditions to form actual N containing intermediates and reduce NO in net lean conditions. NO_2 had a clear enhancing effect on the activity of In/ZSM-5 and it is an important intermediate. A reason for higher activity with NO_2 in feed is the observation that InO^+ sites strongly chemisorb NO_2 under CH_4-SCR conditions (Ogura et al. 1998B). In/ZSM-5 slightly catalyzed N_2O reduction by methane but N_2O was not a key compound to form N_2. The indium addition on ZSM-5 blocks the Brönsted acidity of ZSM-5 and creates Lewis acid sites. The ratio of Lewis-to-Brönsted-sites correlates with the high CH_4-SCR activity (Beltramore et al. 2003).

ZSM-5 zeolite did not show any CH_4-SCR activity with NO or NO_2 in dry feed gas. Therefore, the limitations in CH_4-SCR are more critical than in propene-SCR, where the use of NO_2 in feed gas created HC-SCR activity on supports.

7.3.3 NO_x reduction by methane on bimetallic catalysts and on the binary catalyst mixtures of In/ZSM-5 and oxidation catalysts

Earlier there have been published good CH_4-SCR results in the presence of water by using bimetallic 4%In-1%Pt/H-ZSM-5 and 4%In-1%Ir/H-ZSM-5, where indium was ion exchanged and the precious metals impregnated (Ogura et al. 1995). It was assumed that Ir and Pt promoted NO_2 formation and NO_x adsorption. Due to a rather low CH_4-SCR activity of In/ZSM-5 in wet conditions, the focus in our studies was also turned to the use of promoters.

Contrary to the promotion presented by Ogura et al. (1995), the addition of Pt or Ir by impregnation decreased the N_2 formation rate on In/ZSM-5 in our studies (VI). The reason for the difference might be related to different reaction conditions, precursors, catalyst preparation methods or active metal loadings.

Because Pt and Ir seemed to disturb the state of In/ZSM-5, these precious metals were added into the catalyst bed as supported on separate, high-surface area sol-gel alumina particles (Al-sg) (VI). The amount of Pt/alumina was optimized to a weight ratio of 19:1 (In/ZSM-5:Pt/alumina, VI, Fig. 1). The CH_4-SCR activity dropped with the ratio of 1:1 due mainly to a lower amount of CH_4-SCR catalyst (50% of In/ZSM-5 in reference level). However, the addition of Ir/alumina with the same ratio (19:1) did not enhance CH_4-SCR (VI, Fig. 2). The addition of that low amount of Pd/alumina (19:1) almost completely destroyed CH_4-SCR activity due to the enhanced CH_4 oxidation rate. Mn_3O_4 showed a high promotion with In/ZSM-5 (19:1) and the maximum N_2 formation was over 90%. Mn_3O_4 was thus an excellent additional catalyst both in propene-SCR with In/alumina and Ga/alumina and in CH_4-SCR with In/ZSM-5. However, even these improved catalyst mixtures had the maximum N_2 formation of only 25% in the presence of 8% water. The effect of F/W was similar on both In/ZSM-5 and In/ZSM-5+Pt/alumina (Fig. 28).

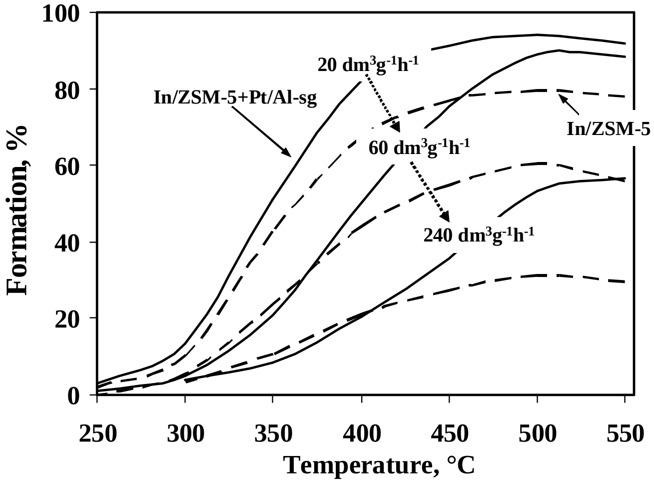


Figure 28. The effect of space velocity on N_2 formation on In/ZSM-5 (broken line) and In/ZSM-5+Pt/Al-sg (19:1) (solid line) in dry conditions (1000 ppm NO; 1000 ppm CH_4; 10% O_2).

The results showed a potential to higher NO_x conversions but the CH_4/NO_x ratio should be higher in wet conditions. These catalysts might also better match to conditions where the raw NO_x concentrations are relatively low (< 300 ppm), where the CH_4/NO_x ratio can be kept high without an excessively high methane consumption as a reductant.

The catalysts were sieved to a particle size fraction of < 250 μm and the average particle size was about 100 μm ($1 \cdot 10^{+5}$ nm), which is a large scale compared to the size of active sites (less than a hundred nanometers) or surface species (about the size of molecules). The size of catalyst particles was significant compared to the scales of the catalyst bed (Diameter of reactor/particle diameter ~ 80:1) (Fig. 29). The amount of active sites on the oxidation catalyst was also low with the mixing ratio of 19:1. Because the reaction rate was enhanced in the mechanical mixtures, the existence of gaseous or very mobile surface intermediates of crucial species is likely.

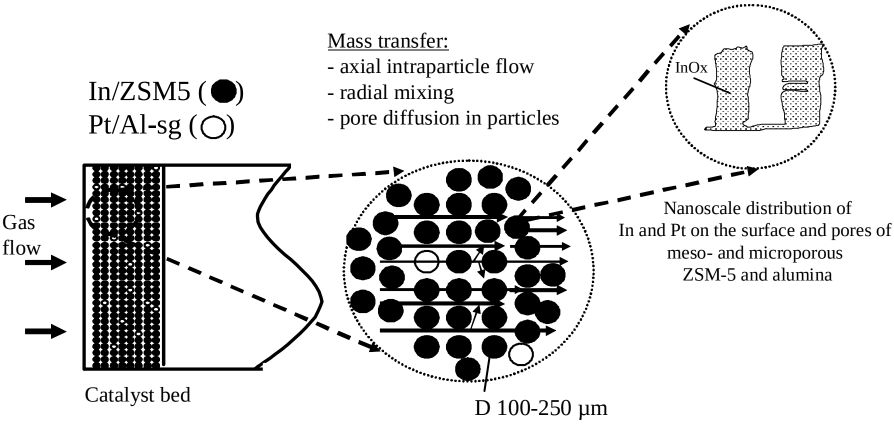


Figure 29. The schematic description of the catalyst and active site distribution in the mixture of two catalyst powders in fixed bed.

The total amount and ratio (In:Pt = In:Ir = 19:1) was exactly the same in In-Pt/ZSM-5, In/ZSM-5+Pt/Al-sg, In-Ir/ZSM-5 and In/ZSM-5+Ir/Al-sg. Therefore, differences are related to the distributions of active compounds (In-Pt or In-Ir) and to supports. The distance between active compounds was low in bimetallic ZSM-5 catalysts and it was possible to have direct surface reactions between adjacent active sites or a short diffusion distance was required in gas or on surface. On the other hand, the presence of Pt or Ir might disturb the active sites of In/ZSM-5, which is sensitive to the preparation method. Alumina itself might have a minor role in reactions but it was not studied independently with In/ZSM-5.

Product formations with bimetallic ZSM-5 and binary catalyst mixtures were analyzed as a function of temperature to find out the reasons for the differences (Fig. 30). A higher NO_2 amount was detected with bimetallic In-Pt/ZSM-5 of a lower deNO_x activity. Therefore, NO_2 formation on these catalysts was not a limiting step but NO_2 utilization and N_2 formation steps.

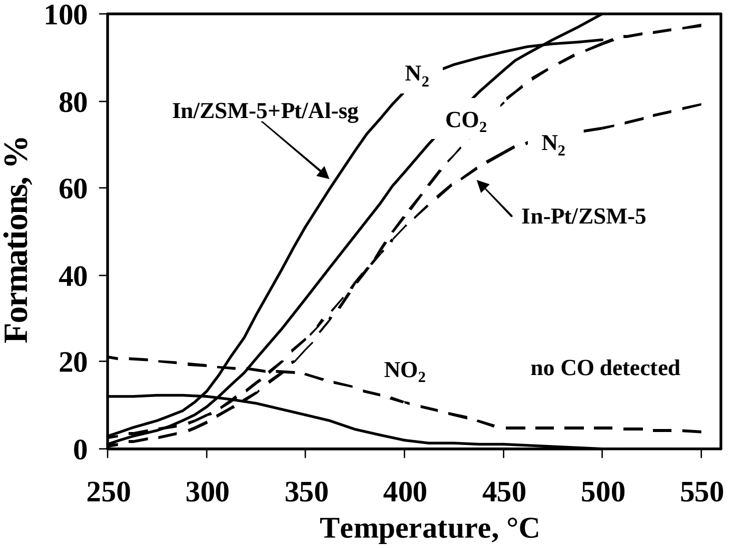


Figure 30. The observed N_2, CO_2 and CO and NO_2 formations in CH_4-SCR with bimetallic In-Pt(19:1)/ZSM-5 (broken line) and the mechanical mixture of In/ZSM-5 and Pt/Al-sg (19:1) (solid line) in dry conditions (1000 ppm NO; 1000 ppm CH_4; 10% O_2; F/W = 20 $dm^3\ g^{-1}\ h^{-1}$).

The mechanical mixture of In/ZSM-5 and Ir/alumina showed a different selectivity than the other catalysts. In the presence of Ir/alumina both not reacted NO_2 (> 25% at 300-350°C) and N_2 formation were higher than with In-Ir/ZSM-5 (Fig. 31). No CO was detected in outlet gas in the presence of Pt or Ir independent off the addition method. The methane oxidation activity was enhanced more by using a separate phase of Pt or Ir on alumina instead of bimetallic ZSM-5 catalysts. Thus, alumina was a better support than In/ZSM-5 for Pt and Ir to catalyze methane oxidation.

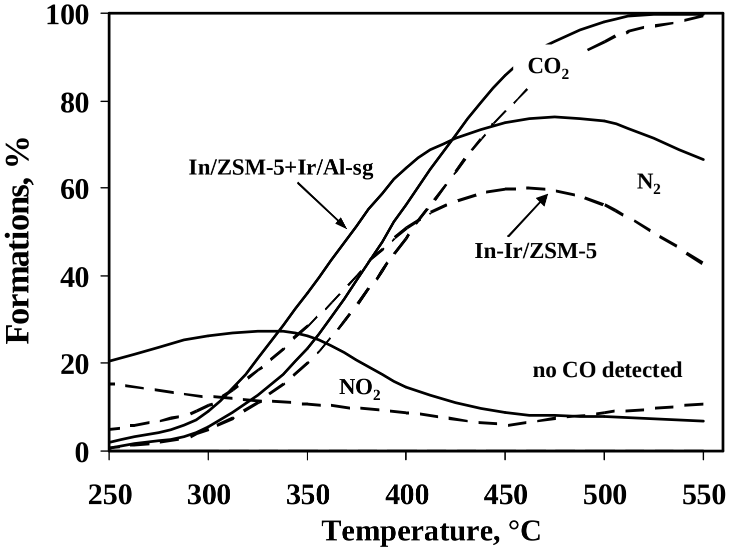


Figure 31. The observed N_2, CO_2 and CO and NO_2 formations in CH_4-SCR with bimetallic In-Ir (19:1)/ZSM-5 (broken line) and the mechanical mixture of In/ZSM-5 and Ir/Al-sg (19:1) (solid line) in dry conditions (1000 ppm NO; 1000 ppm CH_4; 10% O_2; F/W = 20 $dm^3\ g^{-1}\ h^{-1}$).

The product formation analysis of In/ZSM-5+Pt/Al-sg and In/ZSM-5+Mn_3O_4 catalysts, which had the highest observed activities, showed that the only principle difference was the higher N_2O formation in the presence of Pt/alumina (10% at 400°C) (Fig. 32). N_2O formation was the same (max. 5%) in the absence and presence of Mn_3O_4 with In/ZSM-5. NO or NH_i dissociation to adsorbed N is evident and a known property of Pt catalysts (Amiridis et al. 2004). NO was not only dissociated but also the reducing surface species can be adsorbed and be dissociated on Pt sites. Pt and Mn catalysts both enhanced hydrocarbon reactions up to CO_x and the same promotion on the reactions of carbonaceous species to form N containing intermediates is proposed. The morphologies of Pt/alumina and Mn_3O_4 were very different. Pt was dispersed on high-surface area, porous sol-gel alumina but Mn_3O_4 was a low-surface area oxide with Mn_3O_4 crystals without almost any meso- or micropores. Mn_3O_4 has shown rather high activities both in NO and N_2O decomposition, the observation of which might explain the absence of N_2O (Yamashita and Vannice 1996). However, efficient N_2O decomposition below 350°C is not plausible with low space velocities as in our studies. Pt/alumina and Mn_3O_4 both significantly promoted CH_4-SCR with In/ZSM-5 but N_2O responses were evidence that the N_2 formation mechanism differed.

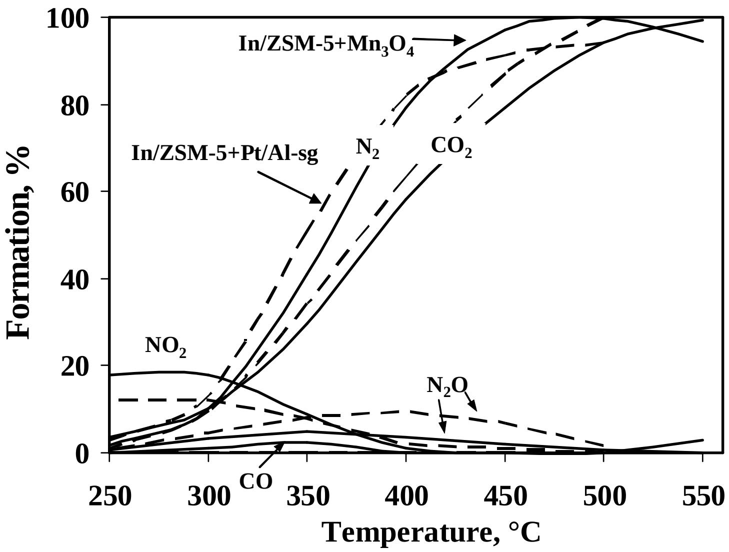


Figure 32. The observed N_2, CO_2 and CO and NO_2 formations in CH_4-SCR in the mechanical mixture of In/ZSM-5 with Pt/Al-sg (broken line) or Mn_3O_4 (solid line) (19:1) in dry conditions (1000 ppm NO; 1000 ppm CH_4; 10% O_2; F/W = 20 $dm^3\ g^{-1}\ h^{-1}$).

7.3.4 In situ FTIR studies on In/ZSM-5, In-Pt/ZSM-5 and In/ZSM-5+Pt/alumina

The surface reactions have been traced by using in situ FTIR on pressed catalyst discs at 200-480°C. The subtraction of He or CH_4-O_2-He spectra from NO-CH_4-O_2-He spectra eliminated a part of the changes caused by temperature increase (V, VI). It was attempted to find the differences between In/ZSM-5+Pt/alumina and In-Pt/ZSM-5 based on FTIR spectra (Fig. 33). The addition of Pt on In/ZSM-5 had stabilized ZSM-5 and hydroxyl groups, which was seen by the smooth spectra of In-Pt/ZSM-5. The peaks at 1601 and 1632 cm^{-1} were the same on both catalysts at low temperatures and that peak pair matched the intense peaks caused by gaseous NO_2. The peak of 2319 cm^{-1} matched also the satellite peak of gaseous NO_2 but the peak height increased as a function of temperature and thus the peak of 2319 cm^{-1} might also be related to other compounds. These peaks were not observed in CH_4-O_2-He or He flow or on evacuated samples. At higher temperatures, those peaks disappeared and the peaks of 1509 and 1540 cm^{-1} were dominant. Adsorbed NO_2 on InO^+ sites has been assigned in the same range at 1619 and 1575 cm^{-1} in earlier studies with In/H-ZSM-5 (Kikuchi and Ogura 1997).

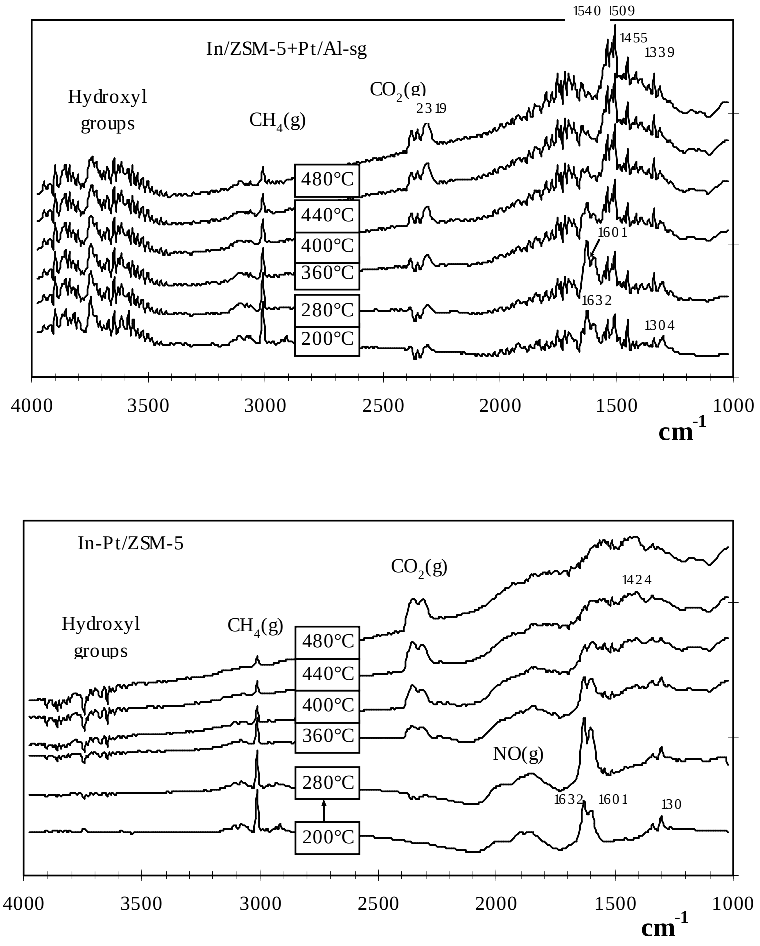


Figure 33. FTIR spectra of In/ZSM-5+Pt/Al-sg and In-Pt/ZSM-5 in NO-CH_4-O_2-He flow in a temperature ramp between 200-480°C.

No larger differences existed between In/ZSM-5 (V, Fig. 6) and In/ZSM-5+Pt/alumina (VI, Fig. 5) in CH_4-SCR at 440-480°C. There were clear differences between static and more realistic dynamic measurements (V). Some of peaks were caused by structural C,H,O,N, because even the He flow was able to change the corresponding intensities (1509, 1540 cm^{-1}). Most of the published studies have been made near to room temperature, where no reactions are yet initiated. It has been proposed that many possible NO_x^- species (nitrate, nitrito or nitro) form the bands in the 1650-1550 cm^{-1} region and even claimed that it is not possible to interpret them by only FTIR analysis (Hadjiinov 2000). Because gaseous NO_2

was present in dynamic experiments in the same range (1600-1630 cm^{-1}), it was difficult to detect the surface NO_x species (Zawadzki et al. 2002). The existence of adsorbed ammonia in the presence of adsorbed NO_x species was not probable, because ammonia reacts immediately to NH_4NO_3 assigned to 1380 cm^{-1}. In the reaction conditions, the adsorption of reactants was higher on ZSM-5 based catalysts than on alumina based catalysts.

In general, the amount of adsorbed surface species was the lowest when reaction rates were the highest. It can be concluded by these FTIR observations that many reaction steps are quick with a negligible coverage of reactants on the catalyst surface at reaction temperatures. However, the dynamics of surface species can be simulated by micro-kinetic models.

7.3.5 Reaction mechanism for CH_4-SCR of NO_x on In/ZSM-5 and the binary mixture of In/ZSM-5 and Pt/alumina

Methane adsorption on In/ZSM-5 or Pt/alumina is an initiation step in the reaction mechanism. NO_2 has an important role as a source of reactive oxygen in reactions. An analogical reaction mechanism including the promotion by NO_2 has also been found in methane activation in gas phase (Tabata et al. 2002). Methane is activated by the fixation of oxygen and the loss of hydrogen. These types of intermediates are generally accepted intermediates of hydrocarbons.

The key step in the reaction mechanism is the formation of actual reductants, which have a N-H or N-C bond (V). The latest mechanism proposed was based on the assumption that the most relevant reductant is adsorbed NH_2, which reacts in a single surface reaction step with adsorbed NO (VI). The reaction steps between more complicated compounds are actually net reactions containing several single reactions. The reaction dynamics can be simulated both by NH_2 (amine) and NRO (amide) paths or possibly by NCO, HNCO, NH or N paths, if NRO was assumed to decompose in the presented sequence. However, HNCO and NCO have a short lifetime in the presence of excess water and oxygen and the existence of adsorbed N requires particular conditions to dissociate NO or NH_i. Often the single steps in sequential reactions are so fast that it is not possible to observe each intermediate on surface or less probable in gas phase. Therefore, FTIR studies are not in contradiction to proposed fast reaction steps, where intermediates have a low coverage on catalyst surface. The main reaction steps include the activation of methane, formation of NO_2, formation of the NH bond containing intermediate and NO reduction on In or Pt

(MnO_x) sites. Carbon and hydrogen in methane are finally oxidized primarily to carbon dioxide and water. N_2O formation is related unambiguously to NO or NH_i dissociation and the formation of adsorbed N, where the presence of a small amount of Pt/alumina catalyst caused significant enhancement. Thus, adsorbed N can be formed also from adsorbed NH_i compounds, not only by the conventional path from NO. Different reaction steps proceed in priority on certain active sites. In fact, In/ZSM-5 and Pt/alumina catalysts consist of four defined active sites on active compounds and supports: In, Pt, alumina and zeolitic sites. Support sites are often also acidic sites, where active compounds are adsorbed during the preparation and a part of these acid sites is lost. These sites can not be treated separately but the interactions between support and active compounds generate completely new catalytic properties. Therefore, it was defined that the reactions occur on two nominated sites: In and Pt sites.

The defined CH_4-SCR reaction mechanisms for In/ZSM-5 and the combination of In/ZSM-5 and Pt/alumina included all surface reaction steps in the chain from the reactants to products and by-products. These reaction mechanisms and the most relevant active sites on each step have been summarized (Fig. 34). Both sites can act in most reaction steps and the reaction rates on them vary by the conditions. The NRO mechanism for methane-SCR (V) followed the presented propene-SCR mechanism (IV) exactly in the last steps in hydrocarbon and completely in NO_x reaction chains. Thus, the reaction mechanism with different hydrocarbons is proposed to join to the same surface reaction steps in the general reaction mechanism for HC-SCR.

The reactions mostly follow the Langmuir-Hinshelwood mechanism and the importance of gas phase reactants was assumed to be low. A possible gaseous reactant might be NO_2, which is known to be a reactive oxidant for adsorbed or solid species. It has been found that NH_3 is efficient in NO reduction over a CH_4-SCR active Gd-Pd/TiO_2 in the absence of oxygen (Watson and Ozkan 2003). In lean conditions, the presence of methane is necessary to create the adsorbed NH_i species but NH_3 in feed was useless because it was oxidized.

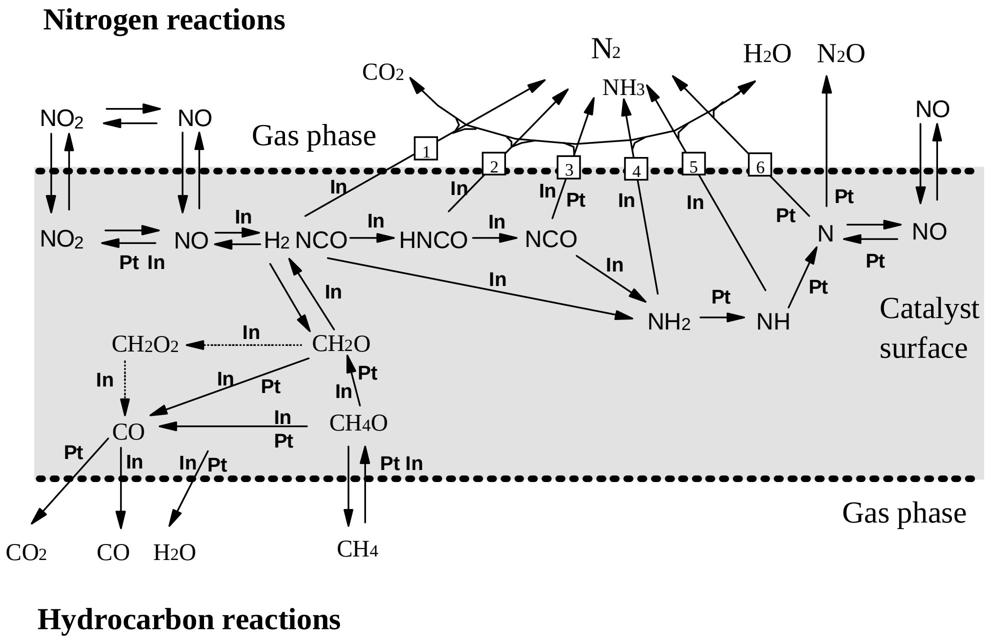


Figure 34. The proposed reaction mechanism for NO_x reduction by methane in lean conditions.

7.3.6 Micro kinetic model for CH_4-SCR of NO_x on In/ZSM-5 and In/ZSM-5+Pt/alumina

Similarly to the case of propene-SCR on Co/alumina, a micro-kinetic model was derived for In/ZSM-5 and for the binary catalyst combination of In/ZSM-5 and Pt/alumina (V, VI). The reaction paths from methane to CO_x are more straightforward than from propene, which simplified models because the parameters in reactions from C_3 to C_1 compounds were not in use. The kinetic parameters were estimated by experimental data where inlet NO, methane and oxygen concentrations (NO-CH_4-O_2-He) and residence time were varied in dry conditions. The model also enables the inclusion and simulation of the undetectable compounds, which have been proposed to be the key compounds in the reaction chains. The competing oxidation reaction by O_2 and NO_2 have been, as in propene-SCR studies, included parallel as oxidants and as well as the selected competing oxidation and reduction reactions, which have an importance in interpreting responses in HC-SCR. A reaction route by adsorbed CH_2O_2 (RO_2) was skipped in the CH_4-SCR reaction model and the same reaction dynamics are explained by the reactions of adsorbed CH_2O (RO). Two different reaction mechanistic models were built for CH_4-SCR on In/ZSM-5 by assuming the NRO or NH_2 mechanisms as final NO reduction steps for N_2 formation on In sites (V, VI):

$H_2NCO^* + NO^* \rightarrow N_2^* + CH_2O_2^* \rightarrow N_2 + CH_2O_2^* + *$ NRO path (56)

$H_2N^* + NO^* \rightarrow N_2^* + H_2O^* \rightarrow N_2 + H_2O + 2\ *$ NH_2 path (57)

The reaction mechanism on Pt sites in N_2 formation was simplified in the kinetic model. The observed catalysis of Pt/alumina in the reduction step was simulated by NO decomposition on Pt sites:

$2\ NO\# \rightarrow N_2 + 2\ O\#$ NO decomposition (58)

However, it was assumed that the Pt site might also catalyze other reaction steps to N_2 and N_2O, such as steps in NRO, NH_i and HNCO hydrolysis (Dümpelmann et al. 1995) and decomposition and as well the reduction of NO by NH_i, NCO, HNCO and NRO, where Pt catalysts are also known be active. Overparametrization is a risk in an excessively complicated micro-kinetic model. In the case of a high number of kinetic parameters, a shorter list of parameters modified by reparametrization can explain data as well. Therefore, the other reduction paths on Pt sites were not included, in order to not add to the number of kinetic parameters. Even if the two-site mechanism explained and predicted data well and simulated the new conditions, the other catalytic steps (hydrolysis of intermediates or NO reduction) could be included in the model to join more of the reaction chains on In and Pt sites together. If NO is assumed to react primarily with adsorbed NH_2 on In sites and decompose solely on Pt sites, it is a risk to have too independent paths to N_2. However, the separate sites are adsorbing and consuming the same carbon and oxygen containing reactants, which fix the chains together.

The variables and parameters are defined in V and VI. The reactant amounts in the rate equations in CH_4-SCR modeling were defined by the partial pressures (p_i) in gas phase and surface coverages (θ_i) on active In (*) and Pt (#) sites. The formation mechanism of partially oxidized hydrocarbon species were differentiated during modeling (adsorbed CH_4O and CH_2O on In sites but CH_4 and CH_2 on Pt sites) but the chemical meaning can be understood by the different oxygen balance on sites ($\# \rightarrow \#' + O$). The oxidation state of both indium and platinum sites changes during the catalytic reactions. It is possible to simulate the reaction dynamics by both carbonaceous intermediates as concluded in Fig. 37 including only adsorbed CH_4O and CH_2O. Because the proposed adsorptions have no direct effect on each others, the different logics had no effect in modeling. The formations of NO_2, N_2, N_2O, CO_2 and CO were defined as rate-determining surface reactions.

The rate equations were derived based completely on surface reactions but the equations were simplified by the reparametrization and sensitivity analysis. The rate equations for N_2 formation and NO reduction can be presented simply as a dependency function of methane, NO, oxygen and NO_2 concentrations or their products with the next powers (the original equations in V and VI).

CH_4-SCR on In/ZSM-5 by NRO mechanism as simplified correlations (V, equations 28-30):

$$\boldsymbol{r}_{N_2}(\boldsymbol{NRO}) \sim \frac{\boldsymbol{f}(\boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{NO}{}^{2})}{\boldsymbol{f}(\boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{NO_2})} \qquad (59)$$

$$\boldsymbol{r}_{CH_4} \sim \frac{\boldsymbol{f}(\boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}) + \boldsymbol{f}(\boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O2}{}^{1/2} \times \boldsymbol{p}_{NO_2})}{\boldsymbol{f}(\boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{NO_2})} \qquad (60)$$

CH_4-SCR on In/ZSM-5 by the NH_2 mechanism resulted in a complicated equations depending on the inlet reactants, p_{NO}, p_{NO2}, p_{CH4} and p_{O2} (VI, equations 29 and 30):

$$\boldsymbol{r}_{N_2}(\boldsymbol{NH}_2) \sim \frac{\boldsymbol{f}(\boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}{}^{1/2} \times \boldsymbol{p}_{NO})}{\boldsymbol{Denom}1} + \frac{\boldsymbol{f}(\boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2} \times \boldsymbol{p}_{NO})}{\boldsymbol{Denom}2} \qquad (61)$$

$$\boldsymbol{Denom}1 \sim \boldsymbol{f}(\boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}{}^{1/2} \times \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{O_2}{}^{1/2} \times \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2} \times \boldsymbol{p}_{NO}) \ (62)$$

$$\boldsymbol{Denom}2 \sim \boldsymbol{f}(\boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2}{}^{1/2} \times \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{O_2}{}^{1/2} \times \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{CH_4} \times \boldsymbol{p}_{O_2} \times \boldsymbol{p}_{NO}) \ (63)$$

CH_4-SCR on a binary catalyst combination with two sites and two N_2 formation mechanisms (NH_2 on In and NO decomposition on Pt sites) resulted in the correlations:

$$\boldsymbol{r}_{N_2}(\boldsymbol{InNH}_2 - \boldsymbol{Pt}) \sim \boldsymbol{r}_{N_2}(\boldsymbol{NH}_2) + \boldsymbol{r}_{N_2}(\boldsymbol{Pt}) \qquad (64)$$

$$\boldsymbol{r}_{N_2}(\boldsymbol{Pt}) \sim \frac{\boldsymbol{f}(\boldsymbol{p}_{NO}{}^{2})}{\boldsymbol{Denom}^{2}} \qquad (65)$$

$$\boldsymbol{Denom} \sim \boldsymbol{f}(\boldsymbol{p}_{O_2}{}^{1/2}, \boldsymbol{p}_{CH_4}, \boldsymbol{p}_{NO_2}, \boldsymbol{p}_{NO} \times \boldsymbol{p}_{O2}{}^{1/2}) \qquad (66)$$

The partial pressures in the nominator show the reaction limitations by adsorptions of the reactant. All three models explained the observed data well in CH_4-SCR but the NH_2 mechanism gave a better fitting ($R^2 > 96\%$ in all cases). The single site mechanism was also attempted for In/ZSM-5+Pt/alumina by assuming NH_2 mechanism on an arbitrary InPt site, which has different kinetic parameters than In sites in the same reaction. It was possible to find a rather good fitting by this model but the real micro-kinetic model was based on two sites and two NO reduction paths. In general, reaction mechanistic models can be applied to wider conditions (extrapolations) than empirical models. Based on the derived models, the partial pressures of reactants and products as well as surface coverages were simulated as a function of conditions and catalyst length. No conflict was found between the detected and simulated surface species. The models were used to simulate unmeasured conditions (V, IV). The ratio of In/ZSM-5:Pt/alumina was simulated by the two-site model. The simulation predicted an increase of the NO_x reduction activity when the amount of Pt/alumina was increased in the presence of a constant amount of In/ZSM-5. However, the experimental results supported the fact that an excessively high amount of Pt/alumina will overly enhance methane oxidation and other reactions, which will decrease N_2 formation. Even if separate parameters were evaluated for the reactions on In and Pt sites and the model is not experimental fitting of the catalyst ratios, the extrapolations should not be extended to very low In/ZSM-5:Pt/alumina ratios (< 9). The experimental conditions (mostly used the catalyst ratio of 19:1) might weigh certain residence time ranges in parameters for both catalysts. Based on the observations and sensitivity analysis, the model can be used in usual lean conditions but not e.g. in near stoichiometric or rich conditions, where the main route can be partly different and NO is reduced mostly by adsorbed hydrogen and CO. The same reaction mechanism and kinetic models can be applied to other CH_4-SCR catalysts but the relative reaction rates and kinetic parameters will vary by the conditions and catalysts.

In previous studies, several reaction mechanism schemes have been presented but real reaction mechanistic models have been missing. A presented reaction of nitromethane (CH_3NO_2) with NO is too complicated and nitromethane too oxidative as a single reaction step to N_2 (Lombardo et al. 1998). Usually power law equations by reactant concentrations were attempted to interpret the NO-CH_4-O_2 reactions on Co/zeolites and H/zeolites (Cowan et al. 1995, Li and Armor 1994B, Ribotta et al. 1997). A kind of mechanistic model was shown for Co/ZSM-5 by nitromethane route (Lukyanov et al. 1996), which was however too straightforward a mechanism by our studies. Power law models depending on the concentrations of methane, oxygen, NO and water were presented also for multifunctional In/ZSM-5 catalysts (CeO_2/In/ZSM-5 and In-Fe_2O_3/ZSM-5) (Sowade et al. 2004, Wang et al. 2000).

8 CONCLUSIONS

In this study, a wide range of scientific methods have been combined to better understand NO_x reduction by hydrocarbons and hydrogen. The catalyst chemistry, various characterizations, reaction studies, in situ surface reaction studies and micro-kinetic modeling were the methods to interpret HC-SCR of NO_x as a whole.

Based on NO-H_2 studies of three-way catalysts, the NO reaction path to N_2 was proposed to proceed by four routes. These paths were categorized by the order of N-O bonding breakage and N-N bonding formation: adsorbed N (First N-O breakage), N_2O (Partly N-O breakage before N-N bonding), ON…NO (First N-N bonding) or NH_i (Partly N-O breakage before N-N bonding) routes. The N_2O formation mechanism was explained by the surface states depending on conditions and NO-H_2 studies were utilized to understand the role of Pt/alumina in the binary combinations in HC-SCR.

The preparation methods were developed to improve NO_x reduction by hydrocarbons in lean conditions in the high temperature range (350-600°C). New or optimized preparation methods were introduced for sol-gel Al_2O_3 supported In, Ga and Co, sol-gel prepared InAl oxide and In/ZSM-5 catalysts, which showed higher HC-SCR activities than usual oxide or zeolite based catalysts. The active compound was Co^{2+} in Co/alumina, In_2O_3 on In/alumina and intrazeolitic InO^+ on In/ZSM-5. The HC-SCR activity was further enhanced by mixing these good HC-SCR catalysts mechanically with a small amount of Mn_3O_4, which was shown to have a very high promotion both in propene-SCR on oxide based catalysts and in methane-SCR on In/ZSM-5.

A general reaction mechanism was proposed for HC-SCR including non-methane and methane reductants on oxide (In, Co, Ga, Ag, Sn) and In/ZSM-5 based catalysts. The NO reduction paths to N_2 with different hydrocarbons as reductants will join the same path beginning from the oxygen containing C_1 surface intermediates (CH_2O). The actual reductant in lean conditions contains a N-C and preferably N-H bond to be able to reduce adsorbed NO. Six potential actual surface reductants were proposed (H_2NCO, HNCO, NCO, NH_2, NH, N), which are able to reduce adsorbed NO. NO_2 promotes hydrocarbon oxidation up to adsorbed CH_2O, which forms the actual reductant with NO. The formed H_2NCO (amide) and preferably NH_2 (amine) were defined to be final reductants with Co/alumina and In/ZSM-5 catalysts in micro-kinetic models. The mechanistic kinetic modeling and simulations were used as a reaction engineering method to interpret the observations. Important surface species (e.g. N containing compounds) had very low coverage on catalyst surface but their dynamics were simulated by models.

The promotion of Pt/alumina and Mn_3O_4 mechanically mixed with the HC-SCR catalysts was explained partly by the enhancement in NO and hydrocarbon oxidations. In addition it was found that these catalysts had an important role in the N_2 formation step. This was observed by a higher N_2O formation in the presence of Pt/alumina, which originates from the decomposition of NO and NH_i species. Mn_3O_4 caused even higher promotion than Pt/alumina but without N_2O formation. The micro-kinetic model and simulations with two sites and two N_2 formation paths (NH_2 on In and NO dissociation on Pt sites) with the mechanical mixture of In/ZSM-5 and Pt/alumina explained the observations well and simulations were used to design catalyst reactors and to optimize the ratio of In/ZSM-5 and Pt/alumina.

9 NOTATION

Acet	acetate (precursors)
Ads	adsorption
A/F	Air/Fuel ratio in combustion (g/g)
^{27}Al-MAS-NMR	Magic Angle Spinning-Nuclear Magnetic Resonance of Al isotope 27
amu	atomic mass unit detected by mass spectrometer
BET	Brunauer-Emmett-Teller method for surface area calculation
c_i	concentration (mol/dm^3)
Chem.	chemisorption
CH_4-SCR	selective catalytic reduction by methane
Coal-N	nitrogen bound in coal
Cpsi	cell per square inch (1 cpsi = 0.096 cells per square cm^2)
deNO$_x$	nitrogen oxide removal (method, conversion) (%)
deSOx	sulfur oxide removal (method, conversion) (%)
D	diameter (mm)
DI	direct injection (diesel engine)
DOC	diesel oxidation catalyst
DPF	diesel particulate filter
E	C_2H_4
ECE-15	urban driving phase in European driving cycle
EDC	European driving cycle
EDTA	ethylenediaminetetraacetic acid
EGR	exhaust gas recycling
ESC	European steady cycle (for heavy-duty vehicles)
ETC	European transient cycle (heavy-duty vehicles)
EU	European Union
EUDC	Extra urban driving cycle, high-way phase in European driving cycle
F	flow rate (dm^3/h)
FTIR	Fourier transform infra red (spectroscopy)
Fuel-N	fuel-bound nitrogen
Fuel-NO$_x$	NO$_x$ emissions originating from fuel-bound nitrogen
GC	gas chromatograph
HC	hydrocarbons
HC-SCR	Selective catalytic reduction by hydrocarbons

H-form	hydrogen form zeolite
H_2-SCR	selective catalytic reduction by hydrogen
$h\nu$	radiation energy
IDI	in-direct injection (diesel engine)
IER	ion exchange ratio
IR	infra red
k_i	reaction rate constants, units depending on reactions
K_i	reaction equilibrium constants, units depending on reactions
L	ligand attached to cation
M	cation or metal in general
MFI	ZSM-5 type zeolite structure
MS	mass spectrometer
NH_i-SCR	Selective Catalytic Reduction by any NH_i compounds (NH_3, urea, etc.)
NH_3-SCR	Selective Catalytic Reduction by ammonia
NO_x	nitrogen oxides
Non-methane	other hydrocarbons than methane
NMR	Nuclear Magnetic Resonance
NSCR	Non-Selective Catalytic Reduction
NSNCR	Non-Selective Non-Catalytic Reduction
NSR	NO_x Storage and Reduction (catalysts)
OBD	On-Board Diagnostics
OSC	Oxygen Storage Capacity
P	Propene, C_3H_6
p_i	partial pressure of a compound i (atm)
PM	Particulate Matter (in exhaust gases)
R-	organic group in general or CH_2 in IV and V
r_i	reaction rate (mol dm^{-3} s^{-1})
s	solid (state)
SCR	Selective Catalytic Reduction
sg	sol-gel, e.g. Al-sg
SNCR	Selective Non-Catalytic Reduction
SO_x	sulfur oxides
T_{50}	temperature corresponding to 50% conversion (°C)
TGA	Thermogravimetric Analysis
TPD	Temperature Programmed Desorption
TWC	Three-Way Catalysts

Urea-SCR	Selective Catalytic Reduction (of NO_x) by Urea
US	the United states (regulations)
US Transient	transient driving cycle for heavy-duty vehicle in USA
UV	Ultra Violet
UV-vis	Ultra Violet visible
W	weight (g)
wt-%	weight-%
x	oxidation state in MO_x compounds
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence
XRD	X-ray difference
Z	zeolite

Greek letters

α	alfa, types of alumina or cobalt
β	beta, type of cobalt
γ	gamma, type of alumina
κ	kappa, type of alumina
χ	ksi, type of alumina
θ	theta, type of alumina
θ_i	coverage of surface species on catalyst
λ	lambda value related to A/F in combustion
δ	delta, type of alumina

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