1. Introduction

Nitrogen oxides (NO_x) comprise species like N_2O, NO, NO_2, N_2O_3, N_2O_4, NO_3, and N_2O_5. Among these most abundant are nitrous oxide (N_2O) as a relevant greenhouse gas and the important air pollutants nitric oxide (NO) and nitrogen dioxide (NO_2) (Skalska et al. 2010). The latter two are commonly summed in the term NO_x.

Although NO_x are also emitted in biological and geological processes, the vast majority (83%) of NO_x in the atmosphere are anthropogenic (Delmas et al. 1997). In 2010 the worldwide NO_x emissions were 67 million tons, whereas emissions of the second important air pollutant SO_2 sum up to 56 million tons (UNSD 2009). Together with sulfur oxides, NO_x are the main air pollutant and responsible for phenomena like the so called “acid rain” (Hameed & Dignon 1992).

The largest part of NO_x emissions (about 38%) stem from road transport, especially from Diesel engines (see Fig. 1) (Bradley & Jones 2002; European Environment Agency 2011). While more than 90% of the NO_x emissions from these fossil fuel power units are NO, it is quickly oxidized at the atmosphere to NO_2 (Neathery et al. 1997). NO_2, however, is even more harmful to human than NO (Pietrzak & Bandosz 2007).

In the European Union, Iceland, Liechtenstein, Norway, Switzerland and Turkey the NO_x emissions have been decreased by 41% between 1990 and 2009, primarily due to the broad introduction of three-way catalysts and NO_x-abatement technologies (European Environment Agency 2011). So far, the control of NO_x emissions from light-duty engines has been successful in many ways and the perspective in the future is a focus on reducing emissions from heavy-duty engines (McDonald et al. 2012).

In addition to NO_x emission reductions, direct NO_x removal in human workspace would be a great progress. In automobiles, incumbent cabin air filters usually remove dust particles, pollen grains and also some pollutant gases, but modification of these filters to add catalytic NO_x conversion would be favorable. For such application the operational temperature would be preferentially at room temperature or – by use of waste heat from the car engine – at about 373 K. A broad introduction in human workspace would require inexpensive and nontoxic materials. Hence, modification and adaption of commercial catalysts for low temperature application seems to be a preferential path.

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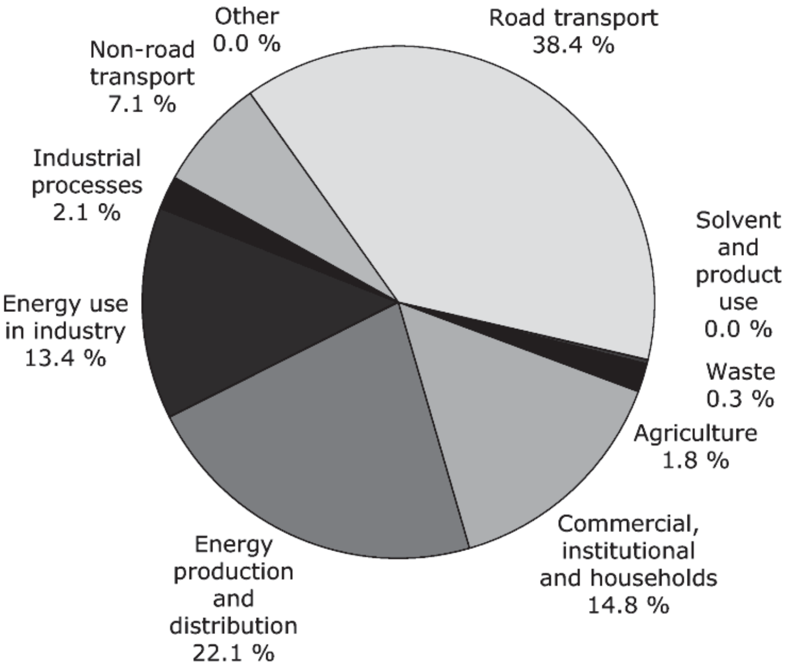

Fig. 1. Sector share of NO_x emissions in European Union and Iceland, Liechtenstein, Norway, Switzerland, Turkey; adapted from (European Environment Agency 2011)

The objective of this work is to prepare and characterize an appropriate catalyst system for low temperature removal and conversion of nitrogen oxides in human workspace. On the route, two separate questions need to be answered: Which catalyst system is most efficient in NO_x removal at low temperature? And which catalyst is most efficient in NO_x decomposition at low temperature?

This work is focused on carbon- and zeolite-based catalysts as promising candidates with a high load of catalytically active species. The chosen catalyst preparation via chemical vapor infiltration is expected to confer these catalysts with a higher infiltration load and different species than common wet chemistry techniques (Pieterse et al. 2004). Samples from either preparation method are likely to differ structurally and chemically, which is often associated with a difference in their catalytic performance (Aksoylu et al. 2003; Capek et al. 2005; Pérez-Ramírez & Gallardo-Llamas 2005).

Subsequent to an overview of the state of the art in NO_x conversion, important theoretical aspects are introduced. Experimental methodologies and procedures are explained and reference catalyst systems are defined. The results and discussion part is subdivided into a section for activated carbon-based catalysts and another for zeolite-based catalysts. Each catalyst is characterized in structure, chemical composition, NO_x adsorption and NO_x conversion. Finally, the work is summarized and conclusions from the discussion are drawn. The work finishes with a prospect and further research recommendations.

1.1. State of the art of NO_x conversion

1.1.1. History of NO_x removal and conversion

The investigation of the catalytic decomposition of NO_x has a long history going back to the beginning of the 20th century when the earliest attempts were carried out with pure platinum

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catalysts (Jellinek 1906; Green & Hinshelwood 1926). A first report on reduction and conversion of N_2O and NO with activated carbon has been published by Shah (Shah 1929a; 1929b). In the following decades an abundant number of catalyst systems have been screened, mainly comprising supported and unsupported noble metals, transition metals and their oxides (Elving & McElroy 1941; Shelef et al. 1969; Bosch & Janssen 1988). Several catalytic and non-catalytic NO_x removal technologies have been developed with a special focus on combustion processes (Gohlke et al. 2010).

Today, catalytic and non-catalytic NO_x abatement technologies are well established and broadly deployed. They mainly comprise three-way catalysis (TWC) (Farrauto & Heck 1999; Roy et al. 2009), the selective catalytic reaction (SCR) by addition of ammonia or hydrocarbons (Burch & Millington 1995; Shelef 1995; Heck 1999; Burch et al. 2002) and technologies which aim at minimizing the synthesis of NO_x already during combustion like low NO_x burners (LNB) (Ballester et al. 1997). However, most of these technologies require either high temperature, or they apply harmful additives.

1.1.2. Overview of NO_x removal catalysts

The common catalyst materials for NO_x decomposition include a large number of noble metals, transition metals, their oxides, combinations and alloys (Bosch & Janssen 1988). Typical catalysts for the SCR reaction are Fe_2O_3, Fe_2O_3-Cr_2O_3, Fe_2O_3-WO_3 and Fe_2O_3 or V_2O_5 supported on $A1_2O_3$ (Nakajima & Hamada 1996). The mechanisms for their adsorption behavior, catalytic decomposition reaction and reaction kinetics have been elaborately investigated (Parvulescu et al. 1998; Garin 2001; Al-Abadleh & Grassian 2003).

The additive-free direct removal of NO_x still suffers from slow reaction kinetics. Substantial conversion rates require high temperature (Jobson 2004). A number of transition metal oxides have been investigated at elevated temperatures (573-1073 K), the most promising being an unsupported Co_3O_4 catalyst, even outperforming a platinum catalyst (Shelef et al. 1969).

Starting from the late 1980s, zeolite-based catalysts have been considered for NO_x decomposition. Transition metal ion-exchanged zeolites proved to be good catalysts for selective and direct catalytic NO_x removal (Iwamoto et al. 1986; Centi & Perathoner 1995; Konduru & Chuang 1999; Garin 2001; Tang et al. 2002; Kumar et al. 2004). In their function as molecular sieves they selectively adsorb NO_x from waste gas (Sundaresan et al. 1967).

The first reports on ZSM-5, highly exchanged with copper, revealed very promising results in direct NO decomposition (Iwamoto et al. 1986). In Cu-ZSM-5 direct decomposition of NO is notable above 493 K (Teraoka et al. 2000). The adsorption of NO is increasing with higher exchange level. Among various transition metals for ion exchange in zeolites, copper and iron have been identified to be among the most promising candidates (Bosch & Janssen 1988; Centi & Perathoner 1995).

While zeolite catalysts in the SCR reaction are well investigated (Bosch & Janssen 1988; Heinrich et al. 2002; Schwidder et al. 2005), studies on direct NO_x decomposition with zeolites other than ZSM-5 remain scarce. Recent studies try to elucidate for example the low temperature direct removal of N_2O by iron-exchanged zeolites (Pieterse et al. 2004; Bulushev et al. 2005).

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Drawbacks in the application of the SCR technology include the considerably high reaction temperatures (> 573 K) and the possible slip of unreacted reactants (Neathery et al. 1997; Illán-Gómez et al. 1999; Shirahama et al. 2002). Harmless reactants like carbon may be preferential in human workspace applications and the working temperature of activated carbon based catalysts can be considerably lower than required in the efficient selective catalytic reaction (SCR) with ammonia (Busca et al. 1998; Skalska et al. 2010).

A good activity of an activated carbon catalyst is often correlated with a good activity in carbon decomposition with oxygen, producing a loss of carbon material in a NO_x-polluted air flow (Illán-Gómez et al. 1999). The addition of oxygen has a positive effect on NO decomposition with copper-infiltrated activated carbon (Yamashita et al. 1993), but the effect of copper could rather be attributed to the catalytic conversion of carbon with oxygen than to the catalytic NO decomposition itself (Aarna & Suuberg 1997).

1.1.3. Availability, application, problems and limitations of the described processes

On the other hand, oxidation of the carbon catalyst surface during NO_x decomposition is often responsible for catalyst deactivation (Illán-Gómez et al. 1996). Catalyst deactivation is also observed at low temperatures for zeolite catalysts due to the accumulation of oxygen at the catalyst surface (Iwamoto et al. 1981; Modén et al. 2002; Cejka et al. 2012). At temperatures above 873 K zeolites like ZSM-5 tend to lose alumina which can destabilize their framework structure (Grinsted et al. 1993).

Several authors have studied the effects caused by co-adsorption of other reactants – e.g. H_2O (Sager & Schmidt 2009), CO (Aarna & Suuberg 1999) or SO_2 (Rubel & Stencel 1997) – which may be present in common flue gases. For example, the co-adsorption of water vapor with NO_2 or NO can easily lead to formation of nitric acid, which may decompose the zeolite support (Richter et al. 1990; Kong & Cha 1996):

$$4\,NO_2^{ads} + 2\,H_2O + O_2 \leftrightarrow 4\,HNO_3^{ads} \tag{1}$$

Larger quantities of water vapor seem to bear an inhibiting effect on the catalytic conversion of NO on activated carbon catalysts (Stegenga et al. 1993). Excess oxygen in the gas phase can limit NO conversion in copper-exchanged zeolites, since it prohibits the reduction of Cu^{2+} species to the more active Cu^+ (Li & Hall 1991).

In the last years, the NO_x-storage-reduction (NSR) has been developed as a new concept (Takahashi et al. 1996; Gómez-García et al. 2005; Liu & Gao 2011). In this two-step-process NO_x from flue gas is first stored in the catalyst system under lean burn conditions and it is subsequently decomposed under fuel rich combustion. Promising further attempts of direct NO_x conversion include investigation of perowskites, like $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$, and rare earth oxides like Ba/CeO_2-MnO (Imanaka & Masui 2012). However, all investigation is performed at temperatures well above 973 K. In general, recent studies on direct NO_x conversion became scarce.

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1.2. Motivation of this work

The review of the literature shows that elaborate research has been performed in order to limit NO_x emissions or to decompose these harmful flue gases. Progress in the catalytic decomposition with additives, or at high temperature and the modification of fuel combustion processes leads to a lower rise of NO_x emissions, than without these actions.

However, air pollution by nitrogen oxides remains a major issue of industrial environments and road traffic, which cannot be eliminated in short term. Hence, the removal of emitted nitrogen oxides at least from ambient air at human workspace is a topic of high priority, thus leading to the motivation of the present work.

Complementary to the state of the art, this work is focused on the removal and decomposition of nitrogen oxides close to ambient temperature and avoiding the use of any harmful additives. The expectable chemical reactions at such conditions are likely to be kinetically much slower than at their maximum efficiency temperature. Hence, the applied measurement methods need to be adapted to slow chemical conversion processes and to the investigation of possibly different reactions than at higher temperature.

The proposed solution in this thesis includes the stabilization of nano particles of catalytically active transition metals and their oxides, well dispersed in microporous matrix materials, in order to achieve a large number density of active sites per unit volume of catalyst material. Therefore, activated carbons and zeolites are infiltrated with different metal organic precursors via chemical vapor infiltration and liquid ion exchange processes. The resulting catalyst materials are investigated in a recycle flow reactor regarding their decomposition behavior of nitrogen oxides at low temperature.

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2. Theoretical background

2.1. Heterogeneous catalysis

2.1.1. Definition and history of heterogeneous catalysis

The concept of catalysis dates back to works of Berzelius in the beginning of the 19th century (Boreskov 2003, p. 1ff; Deutschmann et al. 2009, p. 5ff). According to Boreskov, catalysis is the "change of the rate of chemical reactions under the action of certain substances – catalysts, which repeatedly enter intermediate chemical interactions with the reactants and restore their chemical composition after each cycle of intermediate interactions" (Boreskov 2003, p. 1). Hence, for a given temperature and pressure, not the equilibrium of a reaction is shifted, but the kinetics to achieve equilibrium are accelerated.

Depending on the phase of the reactants a catalytic process may be homogeneous or heterogeneous. In homogeneous catalysis the reactants and the catalyst have the same phase, i.e. both are gaseous or liquid. In heterogeneous catalysis – like in this work – the reactants and the catalyst have different phases, e.g. gaseous reactants and a solid catalyst (Boreskov 2003, p. 38).

2.1.2. Principles of heterogeneous catalysis

Catalytic conversion of gaseous reactants in a porous catalyst can be described as a process in five steps (Ponec & Bond 1995, p. 247):

1) The reactants diffuse from the gas atmosphere to the catalyst surface or into catalyst pores.
2) The reactants adsorb at the active centers.
3) The chemical reaction proceeds.
4) The adsorbed products desorb from the catalyst surface.
5) The products diffuse from the catalyst surface or out of the pores into the gas atmosphere.

Steps 1 and 5 are interparticle or intraparticle transportation processes, depending of the location of the reaction site inside the pores or on the external surface of the catalyst. Steps 2, 3 and 4 are usually comprised in one step and one rate equation, although each of the steps can be rate limiting for the overall catalytic throughput.

The Langmuir-Hinshelwood reaction mechanism of adsorbed species is the most common mechanism in heterogeneous catalysis. It is based on the Langmuir equation, describing the surface coverage of the catalyst by an adsorbent as an equilibrium between adsorbing and desorbing species at a certain temperature and partial pressure (Langmuir 1918). Hinshelwood suggested an interaction of the reactant species in the adsorbed state (Hinshelwood 1940, p. 187ff; Ponec & Bond 1995, p. 268ff). The overall reaction rate can be limited by the adsorption kinetics of reactants, the chemical reaction itself or by the desorption rate of products.

In contrast to the Langmuir-Hinshelwood mechanism, the mechanism described by Eley and Rideal assumes the participation of at least one reactant directly from the gas phase without adsorption on the catalyst (Schwab 1928; Rideal 1939; Eley & Rideal 1940).

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2.1.3. Role of the catalytically active species

Taylor introduced the concept after which not the entire catalyst surface, but only certain surface sites participate in the reaction (Taylor 1925). These active centers can be high energy sites like defects, step sites, vacancies, locally unsaturated or oversaturated sites. At these sites foreign molecules can adsorb, dissociate, change their oxidation state or change their polarity. The surface number density of active centers is typically larger in small particles due to their high surface to volume ratio and due to the defects induced by surface lattice tensions or interaction of surface molecules with the support material.

Adsorption of specific reactants and subsequent chemical reactions can be highly sensitive to the geometric or electronic nature of the active site (Norskov et al. 2008), the local composition of the material and to the catalyst particle size (Bell 2003). The particle size effect plays a large role for nano particles as for example the electron binding energy quickly decreases with decreasing cluster size (Ponec & Bond 1995, p. 227ff).

2.1.4. Role of the support

Catalytically active materials are often supported by a foreign material. The role of this support includes the stabilization of the catalytically active material in a well dispersed form even under chemically harsh conditions, facilitating the adsorption of reactants or the desorption of reaction products, facilitating diffusion kinetics, i.e. exchange of reactants and reaction products, and to prevent attrition upon mechanical stress (Ponec & Bond 1995, p. 320ff).

Many catalysts have a monolithic macro-form with many smaller, possibly interconnected passages inside the material (Cybulski & Moulijn 1994). Inside these passages the actual catalytically active material is incorporated or deposited on the surface. Support materials with very narrow passages are porous and according to IUPAC nomenclature the pore sizes can range from microporous (< 2 nm) to mesoporous (2 – 50 nm) and macroporous (> 50 nm) (Smith et al. 1994).

Additionally, charged sites of the support - e.g. unsaturated surface atoms in activated carbons or Brønsted acidic sites in zeolites – may impose changes in polarity to neighboring small catalyst particles, thus changing the catalytical properties (Ponec & Bond 1995, p. 234ff).

2.1.5. Adsorption of reactants at the catalyst surface and desorption of products

The adsorption of reactants at the catalyst surface is classified as physisorption and chemisorption, according to the binding energy of the adsorptive. Physisorbed species are weakly bonded to the surface, mainly as the result of van der Waals forces and Pauli repulsion, whereas chemisorbed species form a rather strong bond (typically more than 40 kJ mol^{-1} binding energy) (Chorkendorff & Niemantsverdriet 2007, p. 217ff). Chemisorption of molecular reactants is often associated with dissociation, if the molecule in its dissociated state has a lower potential energy compared to the adsorbed molecule (Ertl 2010, p. 7ff).

The desorption of reaction products from the catalyst surface to the atmosphere usually requires activation and is essential in catalytic steady-state processes (Thomas et al. 1997, p. 94ff). The catalytic activity will decrease if the active centers become inaccessible for reactants due to coverage by accumulating reaction products.

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The rate of the catalytic reaction strongly depends on the interaction of reactants with the catalyst surface. Interactions between catalyst and reactants, which are too weak, prevent adsorption or reactant dissociation of the species (Chorkendorff & Niemantsverdriet 2007, p. 264). Interactions, which are too strong, may prevent desorption of reaction products and consequently inhibit the overall reaction after some time. Hence, there is an optimum heat of adsorption for a specific catalyst material, known as Sabatier's principle. It is typically depicted in a volcano plot, the ordinate showing some measure of the reaction rate and the abscissa showing some measure of the interaction energy, e.g. the heat of adsorption. For NO decomposition over metal catalysts the corresponding volcano plot is displayed in Fig. 2 (Falsig et al. 2007).

In addition to the accumulation of surface species, catalysts can be deactivated due to thermal or chemical degradation, fouling, poisoning or mechanical wear (Forzatti & Lietti 1999; Bartholomew 2001). Many of these causes are reversible and the catalytic activity may be restored after chemical or thermal recovering.

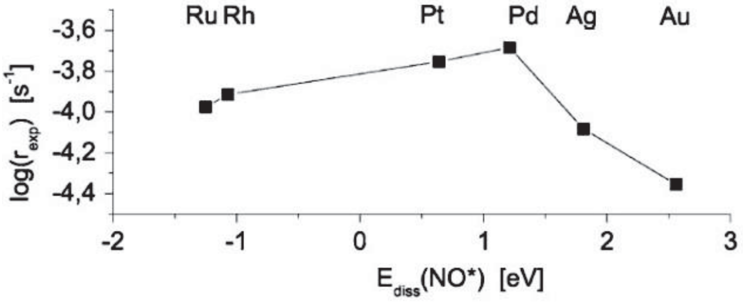

Fig. 2. Experimental activities (log r_{exp})/s of metal catalysts on $MgAl_2O_4$ support versus the dissociation energy $E_{diss}(NO^*)$ of adsorbed nitric oxide, T = 873-923 K, taken from (Falsig et al. 2007)

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2.2. Characterization of catalysts

Table 1. Common methods of catalyst characterization for physical and chemical properties (Chorkendorff & Niemantsverdriet 2007, p. 129ff; Deutschmann et al. 2009, p. 52ff)

Catalyst property	**Measurement technique**	**Comments**
Physical properties		
Accessible surface area	Low temperature nitrogen adsorption*	
Surface topology	Atomic force microscopy (AFM)	
	Scanning tunneling microscopy (STM)	Limited to conducting materials
Sample porosity	Low temperature nitrogen adsorption*	
Particle size	Scanning electron microscopy (SEM)*	Limited to a small part of the sample
	Transmission electron microscopy (TEM)*	Limited to a small part of the sample
	X-ray diffraction (XRD)*	Limited to crystalline species and provides average particle size
Crystal structure and phase	XRD*	
	High-resolution electron transmission microscopy (HRTEM) followed by fast-fourier transform (FFT)*	Provides only information of a small part of the sample
Catalyst dispersion in matrix material	SEM*	Typically inspection of the surface or cross section of the particle
	TEM*	Typically inspection of a cross section or thin lamella of the particle
	STM*	Typically inspection of the surface of the primary particle; only for conducting materials, but allows spatial resolution even of atoms
Local coordination of atoms	Extended X-ray absorption fine structure (EXAFS)	Requires synchrotron radiation
Chemical properties		
Elemental analysis and	Energy-dispersive X-ray spectroscopy (EDX)*	Elemental composition in spatial resolution
	Inductively-coupled plasma mass spectrometry (ICP-MS)	High accuracy of elemental quantification
	X-ray photoelectron spectroscopy (XPS)	Surface-sensitive
	Auger electron spectroscopy (AES)	Surface-sensitive
Oxidation state of elements	XPS	Surface-sensitive
	AES	Surface-sensitive
	Mössbauer spectroscopy	Limited to investigation of some elements (e.g. iron, cobalt)
	X-ray Absorption Near Edge Structure (XANES)	Allows analysis of elemental composition and oxidation states
Surface groups	Diffuse reflectance infrared fourier transform spectroscopy (DRIFT)	Not exclusively sensitive to surface groups
	X-ray photoelectron spectroscopy (XPS)	
Chemical and structural environment	Nuclear magnetic resonance (NMR) spectroscopy	Applicable for example for investigation of ion accomodation in zeolites
Acid/base properties	Adsorption of probe molecules combined with microcalorimetry	Interesting for example for zeolites
Thermal analysis	Thermal gravimetric analysis (TGA)*	Information on mass change of catalyst upon thermal treatment
	Differential thermal analysis (DTA)*	Information on enthalpy changes upon thermal treatment
	Temperature programmed desorption spectroscopy (TPD)	Information on desorbing species upon thermal treatment by means of mass spectrometric analysis, can be combined with isotope-labelling

*) measurement technique applied in the present work

Many catalyst systems react very sensitive to small variations of the experimental conditions and the actual mechanisms are not yet thoroughly understood. An overview of the most common scientific characterization methods of catalysts is provided in Table 1 (Chorkendorff &

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