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**ENVIRONMENTAL CATALYSIS
FOR NO_x EMISSION CONTROL**

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Increasing worldwide effort to decrease the amount of air pollutants (NO_x, CO_x, SO_x, volatile organic compounds etc.) according to strict environmental legislative opens a new worldwide business. Environmental catalysis has seen one of the biggest growth in importance [1]. This report is focused to NO_x emission control. Commercial techniques of NO_x abatement and future NO_x emission control possibilities are discussed. The main stress is given to the selective catalytic reduction of NO with hydrocarbons as one of the promising and attractive systems to NO_x abatement from mobile and stationary sources of NO_x operating in the excess of oxygen.

1 Formation and Noxious Effects of Nitrogen Oxides

There exist seven oxides of nitrogen, namely N₂O, NO, N₂O₃, NO₂, N₂O₄, N₂O₅ and NO₃ [2]. However, anthropological sources of nitrogen oxides produce mainly NO, NO₂ and N₂O. NO represents above 90 % of the total nitrogen oxides emissions [3]. The half-life of nitrogen oxides is approximately 120 years [4].

1.1 NO and NO₂

Emissions of NO and NO₂ are generally defined as NO_x emissions. NO_x are mainly emitted into atmosphere from combustion of fossil fuels and burning of biomass (anthropological sources of NO_x) [5–7]. Natural sources of NO_x coming from lightning and soil microbial productions are insignificant (see Table I). The sources of NO_x might be divided to mobile and stationary and to processes operating under reducing atmosphere and in the excess of oxygen ("lean-burn processes"). Stationary sources of NO_x represent power plants combusting fossil fuels or natural gas, chemical industry, namely in nitric acid production plants and gas turbines. Mobile sources of NO_x represent transport vehicles (light-duty and heavy-duty cars, aircraft, ships and locomotives), whose engines burn gasoline, diesel, natural gas or jet fuel [8].

NO is a precursor for substances of higher toxicity, such as NO₂ and ground level ozone. NO₂ is formed by oxidation of NO at ambient temperature in the atmosphere [9,10]. Ground level ozone is produced by photochemical reactions between NO and hydrocarbons [11]. Although ground level ozone also removes the impurities from air, as ozone is a strong oxidizing agent, it mainly attacks human respiratory system and damages forests.

Nitrogen oxides are a reason of acid rains [12] and formation of photochemical smog. Acid rains originate from acidic gases like nitrogen oxides, sulphur dioxide and hydrochloric acid, which are converted to nitric, sulphurous and sulphuric acids in the atmosphere. The presence of acids in the atmosphere decreases the pH of the rain, snow etc. to ca. 4 – 5. Acid rains are the reason of acidification of rivers, lakes etc., destruction of forests and lower operating life of human structures. Photochemical smog is a mixture of air pollutants like nitrogen oxides, sulphur oxides, carbon monoxide, and fine particulates. It has a strong effect on the ecosystem and on mankind. It is able to reach all parts of the respiratory system.

1.2 N₂O

N₂O has been long time considered as a relatively harmless species. However, during last two decades N₂O has been identified as a relatively strong greenhouse gas [13–15]. Due to its long half-life in the atmosphere, N₂O has 310 and 21 times higher Global Warming Potential than CO₂ and CH₄, respectively [16]. Although, the atmospheric concentration of N₂O increased from 270 ppbv (parts per billion by volume) to 310 ppbv due to human activities [17,18], there are no strict N₂O emission limits now.

N₂O is mainly produced by microbiological natural sources, chemical industry (e.g. nitric acid and adipic acid [19] plants), combustion of coal and it

Table I Global sources of atmospheric NO_x [5–7] and N₂O [15,21] in 1990 – 1995 (Tg N year⁻¹; Tg = 10¹² g)

Source	Emission	
	NO _x	N ₂ O
Anthropological sources		
Fossil fuel use - stationary and mobile sources	21.9	0.2
Biofuel combustion	1.6	0.1
Industrial processes	1.5	0.7
Adipic acid	a	0.5
Nitric acid	a	0.2
Iron and steel. Chemicals. Cement	1.5	a
Land use/waste treatment	a	2.0
Synthetic fertilizer use on arable land	b	1.0
Animal excreta	a	1.0
Post-burning soil emission	a	0.4
Biomass burning	7.7	0.6
Savanna burning	2.9	0.1
Deforestation	1.1	0.4
Agricultural waste burn	2.2	0.1
Total anthropological	31.1 (16 – 46)	3.2 (0.9 – 9.7)
Natural sources		
Soil microbial production	5.5	5.2
Grasslands	b	1.4
Background emission arable land	b	0.9
Atmospheric/stratospheric formation	1.6	0.6
Oceans	a	3.6
Lightning	12.2	a
Total natural	19.3 (6 – 35)	11.7 (4.2 – 18.2)

^a indicates no data available or not identified as a source

^b included in soils under natural vegetation

might be formed by incomplete reduction of NO to N₂ in technologies of NO_x abatement [15,20,21] (see Table I). As the individual N₂O sources exhibit expressive difference in the concentration of N₂O as well as in the process conditions (Table II), the requirements to catalytic system are different. The possibilities for N₂O abatement from nitric acid plants [16,22], adipic acid plants [22,23], coal combustion [14] and agriculture [24,25] have been reviewed in given references.

Utilization of waste N₂O as an oxidizing agent has been intensively investigated during the last decade. It would provide an effective and economic way of N₂O abatement, but it still requires the development of technologies for separating and recovering N₂O cheaply from exhaust gases and the development of technologies for N₂O utilisation. Iwamoto *et al.* [26] discovered a direct partial oxidation of benzene to phenol using N₂O over V₂O₅/SiO₂ catalyst in 1983. Later on, Suzuki *et al.* [27], Gubelmann *et al.* [28] and Panov *et al.* [29] independently

suggested Fe-ZSM-5 catalysts as the most effective ones for direct oxidation of benzene to phenol.

Table II Typical composition of main N₂O emission sources (according to Ref. [22])

Source	<i>T</i> °C	N ₂ O ppm	NO _x ppm	O ₂ %	H ₂ O %	CO ppm
Adipic acid	200 – 300	30 – 50	0.7	4	2 – 3	300
Nitric Acid	180 – 200	300 – 3000	300 – 3000	2 – 4	2 – 3	-

2 NO_x Emission Control

Growing need for NO_x emission control and accepting of strict environmental regulations (Table III) started a worldwide research of abatement system. It opened new billion-dollar worldwide business in the last decades [30].

There are three main strategies to fulfil NO_x limits: (i) minimize problematic processes, for example, replacement of natural gas instead of coal and diesel fuel or research on new technologies, like fuel cells, instead of currently used ones, (ii) process modification (e.g. flue gas recirculation), and (iii) control of exhaust gases (thermal, adsorption and catalytic). This review is focused to the NO_x emission control based on the catalytic reactions. The main advantages of catalytic emission control are simplicity and relatively low cost. On the other hand, dependence of the catalyst performance on temperature, poisoning of the catalyst, deactivation of the catalyst and possible formation of secondary emissions have to be kept in mind.

Table III NO_x emission limits for passenger cars in g km⁻¹ according to European Union Legislative 98/69/EC

		Passenger cars					
		Gasoline			Diesel		
		CO	C _x H _y	NO _x	CO	C _x H _y	NO _x
EURO I	1.7.1992	4.05	0.66	0.49	2.88	0.20	0.78
EURO II	1.1.1996	3.28	0.34	0.25	1.06	0.19	0.73
EURO III	1.1.2000	2.30	0.20	0.15	0.64	0.06	0.50
EURO IV	1.1.2005	1.00	0.10	0.08	0.50	0.05	0.25

2.1 Requirements to Catalytic Emission Control of NO_x

The application of NO_x abatement technique depends on the conditions under which NO_x is emitted and the local (industrial) infrastructure, because the challenge is to reduce NO_x at the process conditions (Table IV). Possibilities of NO_x emission control from mobile [3,31–35] and stationary sources [36–39] have been reviewed in the references given. In contrast to stationary applications, the catalyst for mobile sources of NO_x has to operate under much wider process conditions (temperature, NO_x concentration etc.). While industrial application and stationary engines are characterized by steady-state operating conditions, mobile engines in transport vehicle operate in transient cycles.

Table IV Typical composition of main NO_x emission sources

Source	<i>T</i> °C	NO _x ppm	O ₂ %	H ₂ O %	CO ppm	CO ₂ %	HC ₁ ppm	SO ₂ ppm	H ₂ ppm
Gasoline engines	25 – 800	900	0.5	10	0.5	10	350	20 – 100	0.17
Diesel engines	25 – 600	50 – 2500	3 – 17	2 – 12	~1000	5 – 10	200 – 3000	10 – 150	~600

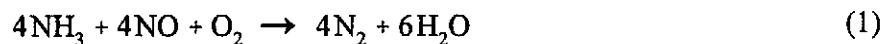
For practical use, exhaust catalytic after-treatment systems are required to be stable, active and selective to N₂ formation. The following process parameters have to be mainly taken in consideration (i) *temperature window*. Temperature window is the range of temperature, which corresponds to high conversion efficiency of the catalyst. Sufficient NO_x conversion has to be found in the whole process temperature range. Mobile sources of NO_x operate under much wider temperature window (200 – 500 °C) than stationary applications. The temperature of the tail-gases of many industrial plants is ca 350 °C and the preheating of the tail-gas to higher temperature is economically disadvantageous, (ii) *space velocities*. Space velocity is defined as the volume of gas measured at standard conditions per unit time per unit volume of the reactor. Most of the stationary and mobile NO_x sources operate from 30 000 to 60 000 h⁻¹, (iii) *NO_x concentration*, (iv) *stability*, (v) *resistance to poisoning*, e.g. sulphur tolerance, and (vi) possible formation of undesirable secondary emissions, e.g. N₂O, CO, ammonia slip etc.

2.2 Commercial Catalytic Systems and Their Limitations

Two commercial catalytic systems are widely used now: (i) noble metal-based three-way catalysts for the purification of automobile emissions from gasoline engines, and (ii) V₂O₅-WO₃/TiO₂ catalyst for the purification of stationary sources of NO_x by selective catalytic reduction with ammonia (NH₃-SCR-NO_x).

Three-way catalyst. Three-way catalyst consists of noble metals (Pt, Rh or Pd) deposited together with alumina washcoat on a ceramic or metallic monolith (for review see Refs [40,41]). The catalyst was developed for NO_x emission control under reducing atmosphere in the mid 1980s and it is widely used in gasoline engines now, where the amount of added air strictly corresponds to the conversion of fuel into CO₂ and water [40,41]. Three-way catalyst simultaneously removes CO, NO_x and hydrocarbons (C_xH_y) by reduction of NO_x to N₂ and by oxidation of CO and C_xH_y to CO₂ and H₂O [40,42]. The catalyst operates only at a stoichiometric mixture of air to fuel, i.e. 14,7 air/fuel ratio [40,41,43], because the conversion of NO_x to N₂ strongly decreases with increasing concentration of oxygen [40,41,44,45]. Modern systems for gasoline engines include electronic sensors to keep the air/fuel ratio close to the stoichiometric point.

NH₃-SCR-NO_x. NH₃-SCR-NO_x (for review see Refs [2,38,39,46,47]) proceeds according to reaction



The most important and critical requirement for commercial catalysts is to combine high activity in the NO_x reduction reaction (1) and very low activity in the oxidation of SO₂ to SO₃, which leads to the deactivation of SCR catalyst. The serious problem also lies in possible formation of explosive ammonium nitrate below 200 °C. Therefore, the reaction temperature can not falls below 200 °C. The majority of commercial installations use V₂O₅-WO₃/TiO₂ catalysts (for review see Refs [48–51]) operating in a wide temperature window from 250 to 450 °C, the optimum for commercial application. Numbers of installations also use zeolite (250-425 °C) and Pt-based (150 – 250 °C) catalysts, but only V₂O₅-WO₃/TiO₂ exhibits resistance to sulphur presence. Moreover, application of Pt-based catalysts requires a precise temperature control system to avoid formation of ammonia nitrate and zeolite-based catalysts exhibits serious stability problems above 500 °C in the presence of water vapour.

NH₃-SCR-NO_x is available for NO_x emission control from stationary sources working in the excess of oxygen (power plants [52], gas turbines, stationary engines, nitric acid plants, chemical plants, gas/coal/oil fired boilers etc.). The disadvantage of NH₃-SCR-NO_x process is the using of ammonia as a reducing agent. It brings serious problems such as storage, transportation, and dosing of ammonia as well as equipment corrosion and necessity of precise system control to prevent ammonia slip, limited to 2 ppm [2]. Therefore, there is a worldwide effort to replace NH₃-SCR-NO_x by another process or using as a reductant another compound less harmful to the environment. The most promising seems to be

selective catalytic reduction of NO_x with paraffin or olefins (see below), although also using of CO [38] and H_2 [38] was discussed in literature.

Limitations of commercial catalytic systems. The main problem of NO_x abatement represents mobile NO_x sources operating in the excess of oxygen, where neither three-way catalyst (it operates only in the reducing atmosphere) nor NH_3 -SCR- NO_x process (problems of ammonia using did not enable its application to mobile sources) can be used.

Diesel engines. Since diesel engines (operates in the excess of oxygen) exhibits better fuel economy than gasoline engines (operates at stoichiometric air to fuel ratio) the interest of automobile industry was addressed to the diesel cars in the last three decades. Nevertheless, three-way catalyst is effective to fulfil the NO_x limits only for gasoline engines and the process for NO_x abatement from diesel engines has not been developed up to now. It should be mentioned that the emissions from diesel engines represent also particulate matter, unburned fuel, hydrocarbons derived from partially burned fuel, metal oxides present in lubricating oil, carbon monoxide, sulphur dioxide, soluble organic fraction, N_2O , dioxins etc. Hydrocarbons, CO and particulate matter can be removed by diesel oxidizing catalyst, which is commercially available [34]. The future limits on particulate matter could be also met by optimising the combustion process or by ceramic filters [34]. Nevertheless, very small particles are not sufficiently removed from diesel exhaust gasses at present. NO content in diesel engine exhaust gas can be significantly reduced by modification of diesel engine, e.g. exhaust gas recirculation, injection rate shaping etc. [34], but NO_x emissions limits cannot be achieved in this way. Thus the research on post-treatment technologies is necessary.

2.3 Future NO_x Emission Control

2.3.1 NO Decomposition

A lot of effort was devoted to the development of catalyst for direct decomposition of NO to its elements without addition of reducing agents (for review see Refs [38,53–56]). Although the reaction



is thermodynamically feasible ($\Delta G_f^0 = -86 \text{ kJ mol}^{-1}$), the reaction rate is low due to very high activation energy (364 kJ mol^{-1}) [57]. The reaction is very attractive and economical due to the absence of reducing agent and undesired combustion

products.

Iwamoto *et al.* [58] discovered NO decomposition in mid 1980s. However, no significant progress has been achieved. The catalyst exhibiting a good activity and stability under realistic conditions has not been proposed in the literature up to now. The highest activity has been reported for Cu ions exchanged in high silica zeolite structures [59–61]. Nevertheless, the reaction rate is still low for the application and excess of water vapour and oxygen as exists in real exhaust gases substantially decreases the activity of catalysts. Therefore, at present decomposition of NO does not seem to be a candidate as future technology.

2.3.2 NO_x Storage Systems

NO_x storage system (for review see Ref. [62]) is based on two modes and its application is possible to mobile and stationary sources operating in the oxidizing atmosphere. Firstly, the engine operates in standard fuel economy mode (in the excess of oxygen). During this mode emitted NO_x is converted to NO₂ over Pt catalyst, followed by trapping and storage of NO₂. The storage components are typically alkali and alkaline earth metal oxides such as BaO or K₂CO₃. The storage compounds are incorporated within γ -alumina washcoat, which is also the main material in three-way catalyst system. Secondly, the engine is switched to a fuel rich mode for a very short time. During this mode, adsorbed NO₂ is desorbed and reduced on Rh in the three-way catalyst. The coupled storage system and three-way catalyst system is known as NO_x traps.

Problem of the application of the NO_x traps is CO₂ and SO_x resistance and thermal deactivation of the catalyst. The presence of CO₂ and SO_x results in competition between NO_x adsorption on the one side and CO₂ and SO_x adsorption on the other side. The most effective NO_x trapping material is BaO. BaO traps are resistant to CO₂ presence (surface carbonates are less stable than surface NO_x species at ambient temperatures [63]). Critical problem is sulphur presence (sulphur oxides are more stable than the nitrates), which reduces the efficiency of both storage and catalytically active materials [64]. At present, the only possible solution to this problem is the use of fuel with low sulphur content (below 10 ppm sulphur).

2.3.3 Non-Selective Catalytic Reduction of NO_x

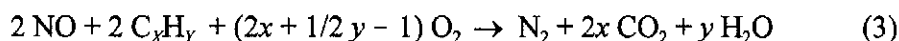
Non-selective catalytic reduction (NSCR) of NO_x is based on the consumption of oxygen in tail-gases so that the application of three-way catalyst can occur. The content of oxygen is reduced by addition of reducing agent (e.g. hydrogen, natural gas, or naphtha) to the tail-gas. NSCR is most likely not a viable option anymore,

due to the high fuel consumption levels, high temperature requiring preheating of the tail-gas when its temperature is too low and high amount of secondary emissions.

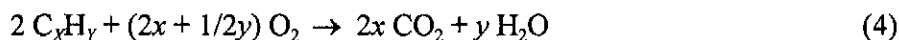
2.3.4 Selective Catalytic Reduction of NO_x with Hydrocarbons

In 1990, Iwamoto *et al.* [65] and Held *et al.* [66] independently discovered that NO_x could be selectively reduced to N₂ with paraffins or olefins in large excess of oxygen [67,68]. This discovery initiated extensive research in this area during last decade (for review see Refs. [30,31,43,46,69]).

Selective catalytic reduction of NO_x with hydrocarbons (HC-SCR-NO_x) in oxidizing atmosphere reduces NO to molecular nitrogen according to the overall reaction



Depending on the reaction conditions and catalyst structure, hydrocarbon is also non-selectively oxidized by molecular oxygen



While conversion of NO exponentially increases with increasing temperature, reaches a maximum and decreases at higher temperature, conversion of hydrocarbon increases with increasing temperature and reaches 100 % value. The maximum of NO conversion is affected by the other competing reaction, which decreases the concentrations of reactants or intermediates. Thermodynamic equilibrium of NO-NO₂ shifts to NO with increasing temperature. Thus, the rate of NO_x reduction decreases, because the oxidation of NO to NO₂ is the first step of the overall reaction (see below). Non-selective oxidation of hydrocarbon leads to insufficient concentration of hydrocarbon able to participate in the reduction of NO_x.

2.3.4.1 Type of Catalysts and Hydrocarbons

Catalysts. The HC-SCR-NO_x reaction might be catalysed by transition (Ag, Cu, Co, Fe etc.) and noble (Pt etc.) metals (i) deposited on inorganic supports such as alumina or silica (for review see Refs [33,70–76]) and (ii) by metal ions exchanged into zeolites matrix (for review see Refs [77–80]). The effectiveness and cost of the catalytic process depend mainly on the type of hydrocarbon, metal ion, and support, method of catalyst preparation and metal content.

Zeolites. Zeolites are three-dimensional microporous crystalline aluminosilicates with well-defined structure and high inner surface area (ca 400 – 800 m² g⁻¹), molecular sieving properties and ion exchange capacity. The term zeolite is used for aluminosilicate-based structures, but other oxides with micropore structure as metallosilicates, silicoaluminophosphates and metalloaluminophosphates are also known [81,82]. Generally, the main advantages of zeolites over conventional supported catalysts are their defined structure forming structurally defined metal ion sites and acid sites of high acid strength located inside pores of various dimensions and architecture. It implies shape-selective effects as well as high sorption capacity for reactants [83].

Hydrocarbons. HC-SCR-NO_x can be realized by injection of hydrocarbon (reducing agent) in front of the catalyst bed ("active" configuration) or by using unburnt hydrocarbons presented in the tail-gasses ("passive" configuration). Active stationary configurations are realized by addition of propane, propene, natural gas, LPG etc. to the tail-gasses. Active mobile configurations are realized by low or high-pressure injection of diesel fuel ahead of the catalyst with the possibility to convert diesel fuel to higher reactive compounds. Although active configurations can achieve higher NO_x conversions than passive systems, because HC-SCR-NO_x activity increases with increasing concentration of hydrocarbon, more favourable for application is the passive system due to its simplicity, reliability, and lower cost. Thus, SCR of NO_x employing methane [84] would be highly important for exhaust gases originated from combustion of natural gas. Methane would also represent a great advantage in comparison to olefins if its release into atmosphere were considered. Lower hydrocarbons, like propane, propene and iso-butane, are interesting for stationary sources, like power plants and chemical industry. Higher hydrocarbons, as octane, decane and toluene, are highly important for exhaust gases originated from diesel engines. Nevertheless, passive systems are limited by insufficient hydrocarbon concentration in the native exhaust.

2.3.4.2 Water Vapour and Sulphur Tolerance

The critical problem of HC-SCR-NO_x application is water and sulphur [85] tolerance as well as stability of the activity. Real exhaust gases from combustion processes consist of approximately 10 –12 vol. % H₂O and between ten and several hundred ppm SO₂ (Table IIB).

Water tolerance. The catalysts might be deactivated in the presence of water vapour reversibly or irreversibly. Nevertheless, most of metal zeolites and metals deposited on alumina support show reversible deactivation in the presence of water vapour [86]. The reversible inhibition by water vapour is most likely to be due to competitive adsorption between water and one or more of the reactants on

the active sites. The high polarity of oxygenates probably explains their greater ability to compete with water for adsorption when compared to hydrocarbons [71,86–88]. The effect of water vapour on the activity decreases with increasing temperatures as the equilibrium adsorption of water on the active sites decreases [89,90]. On the other hand, the promotional effect of water vapour has been also mentioned in literature [91,92]. Haneda *et al.* [91] suggested that the presence of steam (i) decreases the concentration of carbonaceous deposits, which blocks adsorption sites at the surface of the catalyst and (ii) partly inhibits the unselective combustion of hydrocarbon with oxygen.

Sulphur tolerance. Deactivation of the catalyst in the presence of SO₂ proceeds due to the oxidation of SO₂ to SO₃ followed by the formation of thermodynamically stable sulphates on the catalyst surface [93], which reduces the active sites [94,95]. The inhibition of the HC-SCR-NO reaction by sulphur dioxide dramatically depends on the type of the reductant and the sulphur concentration. The solution to this problem is dramatic decrease in the level of sulphur present in the fuel as it is expected during several years.

2.3.4.3 Mechanism

Knowledge of a reaction mechanism of HC-SCR-NO_x is important for the optimum catalyst development as well as for the optimum process performance. Formation of N₂ has appeared in HC-SCR-NO_x to be a multi-step process.

First step. First step is oxidation of NO to NO₂, which preferentially reacts with hydrocarbons. It was evidenced by studies of NO-CH₄-O₂ and NO₂-CH₄ reactions [96–100]. Oxidation of NO was suggested to proceed on Lewis sites [96,101], transition metal cations [102] or dispersed metal oxide clusters [100]. However, trace concentration of Fe was finally evidenced to play an important and critical role in the NO oxidation [103,104]. Nevertheless, the structure of the active Fe sites has not been determined up to now.

Intermediates. Varieties of organic nitroso- and/or nitro- compounds were suggested as intermediates of the HC-SCR-NO_x reaction depending on the type of a hydrocarbon. SCR of NO_x with higher hydrocarbons is much more complex. With ethane, olefin formation was observed due to the interaction of two methyl radicals [98]. With propene, allyl radicals and isocyanate NCO⁻ were formed [105]. On the other hand, if propane was used as a reducing agent isocyanate formation was not observed [106,111], but secondary propyl radical was detected [107]. With decane, cracking of decane to low-chain hydrocarbons and/or their oxo-derivates was mentioned [108,109].

The rate-limiting step. The rate-limiting step in HC-SCR-NO_x is the rupture of C–H bond in hydrocarbon [98,110–115], which proceeds by the reaction of hydrocarbon with adsorbed nitrogen oxides complexes [102,111]. It was

determined by isotopic effect in CH₄- and CD₄-SCR-NO reactions [112,114]. On the other hand, isotopic effect was not observed with *i*-butane [114,116], where the rate-limiting step is assumed to be oxidation of NO or decomposition of the surface N-containing intermediates. Generally, hydrocarbons might be divided into selective and non-selective reductants according to their ability to reduce NO to N₂ on the catalyst [117]. For example, methane is selective reducing agent with Co- [98,110], Pd- [118–122], Ga- and In- [96,123–126] high silica zeolites, but it is not able to reduce NO_x with Cu- [110,117,127] and Fe- high silica zeolites [128,129], where methane is preferentially oxidized to CO_x [113]. With Cu-ZSM-5, adsorbed N-complexes are not able to abstract H atom from methane molecule [130], but they react with higher hydrocarbons like propane [130].

Formation of N₂. It is suggested that formation of N–N bond proceeds in SCR-NO_x by coupling of NO coming from the gas phase, with an adsorbed nitrogen-containing intermediate. It was evidenced by isotopical labelling of N atoms, i.e. ¹⁴N and ¹⁵N, in molecule of NO [107,128].

Although all the reaction mechanisms suggested include similar reaction steps, i.e. the first reaction step, the rate-limiting step, N-compounds as the intermediates, and the step of N–N bond formation (see above), the actual reaction mechanism depends on the type of hydrocarbon and catalyst. Individual mechanisms were proposed, for example, for CH₄-SCR-NO over Pd-ZSM-5 [131], Co-ZSM-5 [132,133], Co-ferrierite [102], Cu-ZSM-5 [133] and Fe-ZSM-5 [133] catalysts, for C₃H₈-SCR-NO over Cu-ZSM-5 [113] and Fe-ZSM-5 [115] catalysts, for C₃H₆-SCR-NO over Cu-ZSM-5 [134] and Ag/γ-Al₂O₃ [95,135] catalysts and for *i*-C₄H₁₀-SCR-NO over Cu-, Co- and Fe-ZSM-5 [116] catalysts. In general, efficient HC-SCR-NO_x catalyst should have high adsorption capacity for hydrocarbons and NO, high rate of NO oxidation, low rate of hydrocarbon oxidation and high reaction rate for NO reduction [136].

2.3.4.4 Active Sites

Generally, HC-SCR-NO activity increases with increasing metal content, reaches a maximum [137–139] and decreases when formation of metal oxides starts. Metal oxides such as PdO [120,140,141], Co₃O₄ [138,142], CuO [130] and Ag aggregates [143] were shown to decrease the HC-SCR-NO_x activity, due to an increase in the rate of non-selective oxidation of hydrocarbon. Although various species were suggested as active species, the structure of active sites is still open as HC-SCR-NO is a complex reaction consisting of several steps. The main concept about the structure of active sites in the most often discussed HC-SCR-NO_x catalysts is described below.

Fe-catalysts. High activity of Fe-ZSM-5 zeolites was explained by the presence of [HO-Fe-O-Fe-OH]²⁺ complexes [144–147], which requires the

presence of two close AlO_4^- units in the framework and the presence of Fe in tetrahedral or deformed tetrahedral position not chemisorbing water molecule [148]. Prins *et al.* [149] and Sachtler *et al.* [144] revealed the structure of Fe species in ZSM-5 zeolites by using EXAFS technique. It is supposed, that Fe-ZSM-5 zeolites contain approximately 20 % of Fe in the form of such Fe-oxo complexes [144].

Co-catalysts. Tabata *et al.* [138,139], Sachtler *et al.* [150,151] and Wichterlová *et al.* [152,153] ascribed high activity of Co-BEA in C_3H_8 -SCR-NO to specific μ -oxo cobalt complexes, Co-oxo species and Co^{2+} ions at α -cationic position [154] and/or cobalt oxo/peroxo species, respectively. In CH_4 -SCR-NO, the Co ions in a main channel, attached to four framework oxygens of the channel wall were suggested as active sites in ferrierite and mordenite zeolite structure, and the Co ions coordinated in six-member ring at the intersection of a straight and sinusoidal channel were suggested as active sites in ZSM-5 zeolite structure [155].

Ag-catalysts. Isolated Ag^+ ions [143,156,157], small Ag^+ -aluminate "clusters" [158] or Ag_2O species [159] were proposed as the active sites in the HC-SCR- NO_x reaction over Ag-catalysts. Recently, the effort is focused on the research of sites responsible for enhancement of the Ag- Al_2O_3 activity after addition of hydrogen (see below).

Pd-materials. Isolated Pd^{2+} ions were suggested as the sites responsible for performance of Pd-zeolites in CH_4 -SCR-NO [118–121,160,161]. Moreover, bifunctional reaction mechanism including isolated Pd^{2+} ions and protons was anticipated [162–164].

2.4 Progress in NO_x Emission Control

The main stress has been given to the research of catalyst material, which should be industrially available, and to the optimisation of various parameters affecting the process performance (temperature window, type of hydrocarbon etc.). However, successful laboratory results of HC-SCR- NO_x cannot be generally taken into consideration, because they often deviate from industrial practice: (i) laboratory tests are predominantly focused on one hydrocarbon, whereas on board reductants, such as gasoline or diesel fuels, contain a mixture of hydrocarbons, (ii) laboratory tests are often performed in the absence of water vapour, although real exhaust gasses contain ca. 10 % water vapour. The reason of it is high requirements for laboratory equipments when the reaction is carried out under water vapor presence. (iii) laboratory tests are often focused on simple reaction mixture (NO , hydrocarbon, O_2 and water vapour), whereas real exhaust systems consist of much more compounds, some of which may poison (SO_2) or inhibit (CO , CO_2) the reaction, (iv) the space velocities used in laboratory micro-reactors are frequently much lower than those in real exhausts systems, (v) laboratory

investigation is focused on powders rather than monoliths.

High and stable NO_x reduction has been reported for (i) Co-beta, Fe-ZSM-5 and Pt-ZSM-5 catalysts using propane and isobutane as reductants, i.e. with potential application in power plants, and for (ii) Ag- Al_2O_3 and Cu-ZSM-5 catalysts using octane and decane, i.e. with potential application in diesel exhaust gasses (see below). Each of these catalysts has its specific drawbacks, related mainly to narrow temperature window, insufficient thermal durability and/or sulphur tolerance. Generally, the advantage of Ag- Al_2O_3 over zeolite-based materials is its hydrothermal stability at high temperature (above 400 °C), because temperature stability of zeolite-based catalysts is still a matter of discussion. On the other hand, zeolite-based catalysts have a chance to be applied in low temperature window (below 350 °C), where metal deposited on supports exhibits non-significant activity. Although, Fe- and Pt-catalysts show high HC-SCR- NO_x activity, they produce high amount of undesirable CO and N_2O , respectively.

Ag- Al_2O_3 . The Ag- Al_2O_3 system appeared to be the most successful catalyst for NO_x abatement from diesel exhaust gases. However, it operates at a temperature window 350 – 550 °C [74,76,85,165,166], which represents an upper limit for diesel exhausts gas application, requiring temperature range 200 – 500 °C. Recently, Daimler-Chrysler [167] and Satokawa *et al.* [168] independently discovered a dramatic positive effect of addition of hydrogen as a co-reductant to hydrocarbons on the conversion of NO_x to N_2 over Ag- Al_2O_3 catalysts in the low temperature range (150 – 350 °C). This positive effect of hydrogen was reported for methane, C_2 and C_3 paraffins and olefins, isobutane [168–170], octane [167,171], decane [157] as well as ammonia [172]. On the other hand, the positive effect of hydrogen on the Ag- Al_2O_3 activity was not reported for any other metal catalysts, and it was not found for Ag supported on other carriers, such as silica, zirconia and titania [169]. This might indicate a specific state of Ag on alumina, and probably some contribution of alumina itself to the reaction [173]. So far, the origin of the effect of hydrogen on the HC-SCR- NO_x reaction is a matter of discussion [157,159,170]. Nevertheless, the addition of hydrogen as a co-reductant represents a promising possibility for NO_x emission control below 350 °C.

Co-zeolites. Eni Technologie and Osaka Gas developed Co-beta catalysts exhibiting high and stable activity in C_3H_8 -SCR- NO_x under real exhaust gas conditions [136,174,175]. Unfortunately, this catalyst achieved only a similar efficiency as the already used V_2O_5 - WO_3 /TiO₂ catalyst in NH_3 -SCR- NO_x . The activity of Co-beta catalyst was later on supposed to be enhanced by group of Wichterlova *et al.* [152]. Sachtler *et al.* developed Co-ZSM-5 catalyst with high and stable activity in *iso*- C_4H_{10} -SCR- NO_x for 100 h [150,151]. However, Tabata *et al.* [136,174,176] showed that longer durability tests lead to a dramatic decrease in Co-ZSM-5 catalyst during 400 h compared to stable activity of Co-beta for 4000 h.

Fe-zeolites. Fe-zeolites were shown as active catalysts in HC-SCR- NO_x , but

high amount of undesirable CO is usually produced [177–179]. The critical factor affecting Fe-zeolite activity is the way of Fe loading into a zeolite. Sachtler *et al.* developed Fe-ZSM-5 catalyst, prepared by sublimation of FeCl₃ over H-ZSM-5, which exhibited high and stable activity in SCR-NO_x with isobutane [128,177] and propane [129]. Analogously, Turek *et al.* [180] reported Fe-ZSM-5 prepared by solid-state ion exchange active in C₃H₈-SCR-NO_x above 300 °C. Hall *et al.* [181] showed high and stable activity of Fe-ZSM-5 prepared by liquid ion exchange using FeC₂O₄ in *iso*-C₄H₁₀-SCR-NO_x in the presence of 20 % H₂O and 150 ppm SO₂ for 2500 h. However, the preparation was not reproduced by other laboratories and by the authors either [182].

Cu-zeolites. Cu-ZSM-5 zeolites have been so far the most investigated HC-SCR-NO_x catalysts [183]. Nevertheless, their activity is negatively affected by water vapour presence (ethane [184], propane [185], propene [186] and *i*-butane [187,188]). Relatively high initial activity of Cu-ZSM-5 was reported with propene [189,190], but significant decrease in the activity appeared already after 40 h of operation [191,192]. Recently, Wichterlová *et al.* [92,108] mentioned possible use of Cu-ZSM-5 catalyst in decane-SCR-NO, where the activity was surprisingly increased by water vapour presence. This high activity has been reported to be stable for 100 h.

Pt-zeolites. Pt-zeolites and Pt-Al₂O₃ are active and stable catalysts in HC-SCR-NO_x even at relatively low temperature window from 200 to 300 °C [72,193–197]. However, as high concentration of N₂O is produced during the reaction [72,195–198], Pt-based catalyst cannot be considered as promising systems.

3 The Fuel Cell

Fuel cells are alternative catalytic technology for both stationary and mobile source applications in the near future (for review see Ref. [199]). They convert chemical energy directly into electrical energy and do not produce any greenhouse gas. Hydrogen gas is electrocatalytically oxidized to hydrogen ions at the anode which pass through an electrolyte to the cathode where they combine with electrocatalytically reduced O₂ (from the air) producing H₂O. The electrons flow through the external circuit and do work.

At the present time H₂ is the only fuel that can be electrocatalytically oxidized at the anode. Hydrogen might be provided by its storage or formation on-board. Storage of H₂ on-board still requires significant breakthroughs in technology, because there is no infrastructure for obtaining hydrogen at the local gas stations or in the home as it is for gasoline or natural gas. Formation of hydrogen on-board is very attractive and safe process to use. The main attention is given to the reforming of liquid fuels such as gasoline and methanol to H₂.

Conclusion

Final configuration of the SCR system for mobile engines has not yet been established. There are a number of differences between systems proposed by different developers and systems evolve with time. However, there is no single catalyst, which would be able to remove NO_x in the excess of oxygen, up to now.

In literature, the most promising way for NO_x abatement in oxidizing atmosphere seems to be selective catalytic reduction of NO_x with paraffin or olefins and NO_x traps. Both technologies might be used at both stationary and mobile sources of NO_x . Although very optimistic results have been given in literature, the reaction rate attained reality is still low and the application of these techniques is still under discussion. Before commercial application of the individual catalysts in the future, mainly the problems of (i) the activity of the catalysts in the whole requiring temperature window, (ii) resistance to poisoning and (iii) formation of secondary emissions, such as N_2O will have to be solved.

At this time, selective catalytic reduction of NO_x with urea remains practically the only option considered for meeting future emission standards of mobile diesel NO_x emissions. Urea is an alternative approach for ammonia injection. The use of ammonia has been practically ruled out, due to safety concerns, and urea appears to be the reductant of choice.

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