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## NITROGEN OXIDES REMOVAL BY SCR PROCESS – STATE OF THE ART

### INTRODUCTION

Air pollution is one of the most important environmental concerns. Due to the increasing awareness in global environmental protection, the government and consumer demands for cleaner emissions and lower fuel consumption grow worldwide. The major primary source of air pollution is combustion of fossil fuels used in power plants, vehicles and other incineration processes. Basic air contaminants are sulfur oxides (especially  $\text{SO}_2$ ), particulate matter, carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides ( $\text{NO}_x$ ). Among them  $\text{NO}_x$  are considered as the primary pollutants of the atmosphere<sup>1</sup>.

Various technologies can be applied for the  $\text{NO}_x$  emissions abatement.  $\text{NO}_x$  storage/reduction (NSR) process is a promising technology for the elimination of  $\text{NO}_x$  from diesel exhausts. This technology is based in the sequential lean-rich changes of the diesel engines, i.e. when the engine is operating in an oxygen excess (lean conditions)  $\text{NO}_x$  is stored on the NSR catalysts in the form of surface nitrates, and then after changing from lean to rich conditions (excess of fuel) the nitrates are catalytically reduced and/or decomposed to  $\text{N}_2$ . Another alternative is the use of the three way catalysts for the removal of  $\text{NO}_x$ , CO and unburned hydrocarbons in spark-ignition engine exhausts; however, it cannot be applied for diesel engines. One promising technology for the elimination of  $\text{NO}_x$  used in electric power stations is a process that is based on the selective catalytic

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<sup>1</sup> K. Skalska, J. S. Miller, S. Ledakowicz, *Trends in  $\text{NO}_x$  abatement: A review*, „Science of the Total Environment” 2010, nr 408 (19), s. 3976–3989.

reduction of  $\text{NO}_x$  with ammonia ( $\text{NH}_3$ -SCR). Recently, this commercial method, in a modified version, was also applied for the elimination of  $\text{NO}_x$  from diesel exhausts<sup>2</sup>.

The aim of this paper is to review the sources of the formation of nitrogen oxides and its influence on the environment and human life as well as different catalytic technologies used for removal of NO. The main point in this short review will be the discussion of SCR technology used for the reduction of NO by utilizing ammonia. The catalysts for this process, including commercial catalysts based on titania, are discussed. Another goal of this review is to present the mixed metal oxides derived from hydrotalcite-like materials as potential catalyst-applicants for the  $\text{NH}_3$ -SCR process in vehicles. In addition, general conclusions and some research directions are given.

## NITROGEN OXIDES POLLUTION PROBLEM

Numerous types of nitrogen oxides, such as  $\text{N}_2\text{O}$ , NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{NO}_3$ , and  $\text{N}_2\text{O}_5$  exist in the environment. The abbreviation  $\text{NO}_x$  refers to the cumulative emissions, mainly of nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ )<sup>3</sup>.  $\text{NO}_x$  emitted in incineration processes typically consist of a mixture of 95% of NO and 5% of  $\text{NO}_2$  due to the thermodynamics of the combustion process<sup>4</sup>.  $\text{NO}_x$  are one of the primary pollutants formed during the combustion of fossil fuels and biomasses in three basic, interdependent processes of the  $\text{NO}_x$  formation<sup>5</sup>: (i) thermal  $\text{NO}_x$  (the Zeldovich mechanism) – direct reaction between air  $\text{N}_2$  and  $\text{O}_2$  at high (flame) temperature, (ii) fuel  $\text{NO}_x$  – oxidation of N-containing compounds present in fuel or biomass, and (iii) prompt  $\text{NO}_x$  – formation of volatile-N (an intermediate gaseous compound) species via the reaction of  $\text{N}_2$  and hydrocarbon radicals in the rich zone of the flame as a primary process, followed by oxidation of HCN to NO, or reduced back to  $\text{N}_2$ .

The contribution of thermal  $\text{NO}_x$  increases with increasing the flame temperature and in the aftermath at high temperatures, thermal  $\text{NO}_x$  usually represents

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<sup>2</sup> N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yojota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, *The new concept 3-way catalyst for automotive lean-burn engine:  $\text{NO}_x$  storage and reduction catalyst*, „Catalysis Today” 1996, nr 27 (1–2), s. 63–69; S. Matsumoto, Y. Ikeda, H. Suzuki, M. Ogai, N. Miyoshi,  *$\text{NO}_x$  storage-reduction catalyst for automotive exhaust with improved tolerance against sulfur poisoning*, „Applied Catalysis B” 2000, nr 25 (2–3), s. 115–124.

<sup>3</sup> K. Skalska, J. S. Miller, S. Ledakowicz, op. cit., s. 3976–3989.

<sup>4</sup> Z. Wang, J. Zhou, Y. Zhu, Z. Wen, J. Liu, K. Cen, *Simultaneous removal of  $\text{NO}_x$ ,  $\text{SO}_2$  and Hg in nitrogen flow in a narrow reactor by ozone injection: Experimental results*, „Fuel Processing Technology” 2007, nr 88 (8), s. 817–823.

<sup>5</sup> F. Normann, K. Andersson, B. Leckner, F. Johnsson, *Emission control of nitrogen oxides in the oxy-fuel process*, „Progress in Energy and Combustion Science” 2009, nr 35 (5), s. 385–397.

most of the total  $\text{NO}_x$  formed. The formation of fuel  $\text{NO}_x$  is independent of the combustion temperature and depends on the nature of N-containing compounds. The formation of prompt  $\text{NO}_x$  has a slight temperature dependence and a short lifetime, and in principle it is only significant in very fuel-rich flames. Accordingly, at high temperatures, thermal  $\text{NO}_x$  usually represents most of the total  $\text{NO}_x$  formed<sup>6</sup>.

$\text{NO}_x$  are blamed for the formation of acid rain, photochemical smog<sup>7</sup>, tropospheric ozone, ozone layer depletion<sup>8</sup>, as well as global warming caused by  $\text{N}_2\text{O}$ <sup>9</sup>. Further,  $\text{NO}_x$  cause many health problems in humans exposed to high concentrations of these gases (e.g. lowering the body's resistance to bacterial infections, eye and respiratory system irritation, problems with breathing, and allergic diseases<sup>10</sup>). Their negative impact both on the environment and on human health led to the legislations that limit  $\text{NO}_x$  emissions from stationary and mobile sources. Limits on emission in most countries have been established by setting standards of  $\text{NO}_x$  concentration emitted in flue gas, in ppm related to 3%  $\text{O}_2$  (reference oxygen concentration on dry basis).

Until now, to control  $\text{NO}_x$  emission several technologies – such as the above-mentioned catalytic reduction of NO in the presence of CO,  $\text{H}_2$  or hydrocarbons as well as decomposition of NO – have been developed to meet the standards<sup>11</sup>. In this work, some technologies for the selective catalytic reduction of NO with ammonia are reviewed.

## SELECTIVE CATALYTIC REDUCTION OF $\text{NO}_x$ WITH AMMONIA

Among flue gas treatment methods, the selective catalytic reduction (SCR) of  $\text{NO}_x$  by ammonia is a well-developed and widespread technology for removing  $\text{NO}_x$  at moderate temperatures (250–500°C) due to its efficiency, selectivity and economics<sup>12</sup>. Generally, the  $\text{NH}_3$ -SCR process is based on the reaction between

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<sup>6</sup> S. Matsumoto, Y. Ikeda, H. Suzuki, M. Ogai, N. Miyoshi, op. cit., s. 115–124.

<sup>7</sup> V. I. Pârvolescu, P. Grange, B. Delmon, *Catalytic removal of NO*, „Catalysis Today” 1998, nr 46 (4), s. 233–316.

<sup>8</sup> X. Tang, S. Madronich, T. Wallington, D. Calamari, *Changes in tropospheric composition and air quality*, „Journal of Photochemistry and Photobiology B” 1998, nr 46 (1–3), s. 83–95.

<sup>9</sup> K. H. Becker, J. C. Lörzer, R. Kurtenbach, P. Wiesen, T. E. Jensen, T. J. Wallington, *Contribution of vehicle exhaust to the global  $\text{N}_2\text{O}$  budget*, „Chemosphere – Global Change Science” 2000, nr 2 (3–4), s. 387–395.

<sup>10</sup> C. Rusznak, S. Jenkins, P. R. Mills, R. J. Sapsford, J. L. Devalia, R. J. Davies, *Mechanism of pollution-induced allergy and asthma*, „Revue Française d'Allergologie et d'Immunologie Clinique” 1998, nr 38 (7), s. S80–S90.

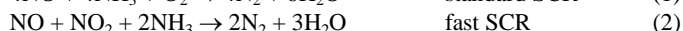
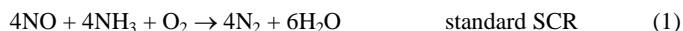
<sup>11</sup> X. Tang, S. Madronich, T. Wallington, D. Calamari, op. cit., s. 83–95.

<sup>12</sup> F. Nakahjima, I. Hamada, *The state-of-the-art technology of  $\text{NO}_x$  control*, „Catalysis Today” 1996, nr 29 (1–4), s. 109–115.

$\text{NO}_x$  (including  $\text{NO}$ ,  $\text{NO}_2$ ) and ammonia ( $\text{NH}_3$ ) or urea ( $\text{CO}(\text{NH}_2)_2$ ), injected into the flue gas stream, to produce  $\text{N}_2$  and  $\text{H}_2\text{O}$ <sup>13</sup>.

Selective noncatalytic reduction (SNCR) has also been applied to control the emission of nitrogen oxides.  $\text{NO}_x$  is selectively reduced in the gas phase by ammonia (or urea, cyanuric acid), which is introduced into the upper part of the boiler<sup>14</sup>.  $\text{NO}_x$  can be reduced into  $\text{N}_2$  and  $\text{H}_2\text{O}$  rapidly and effectively at rather high temperatures (800-1100°C)<sup>15</sup>, which is the major drawback of the SNCR process. In comparison, in the presence of catalysts, the temperature of the reaction depends on the catalysts nature and can be below 250°C for the most active catalysts<sup>16</sup>.

The SCR process is based on the reduction of  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ ) with ammonia into  $\text{N}_2$  and  $\text{H}_2\text{O}$  according to the following main reactions (equations 1-3)<sup>17</sup>:



The standard SCR reaction (equation 1) is the most desirable and it proceeds rapidly at temperatures between 250 and 450°C in excess of oxygen<sup>18</sup>. The fast SCR process (equation 2) was reported to be much faster than standard SCR and can be used in the lower temperature range (180-300°C)<sup>19</sup>. Both fast SCR and  $\text{NO}_2$ -SCR (equations 2-3) play less significant role in technologies of  $\text{NO}_x$  con-

<sup>13</sup> X. Tang, S. Madronich, T. Wallington, D. Calamari, op. cit., s. 83–95.

<sup>14</sup> R. Rota, E. F. Zanoelo, *Influence of oxygenated additives on the  $\text{NO}_x$ OUT process efficiency*, „Fuel” 2003, nr 82 (7), s. 765–770; S. M. Lee, K. N. Park, B. H. Kim, *Characteristics of reducing NO using urea and alkaline additives*, „Combustion and Flame” 2005, nr 141 (3), s. 200–203.

<sup>15</sup> B. K. Gullett, P. W. Groff, M. L. Lin, J. M. Chen,  *$\text{NO}_x$  removal with combined selective catalytic reduction and selective noncatalytic reduction: pilot-scale test results*, „Journal of the Air & Waste Management Association” 1994, nr 44 (10), s. 1188–1193.

<sup>16</sup> B. K. Yun, M. Y. Kim, *Modeling the selective catalytic reduction of  $\text{NO}_x$  by ammonia over a vanadia-based catalyst from heavy duty diesel exhaust gases*, „Applied Thermal Engineering” 2013, nr 50 (1), s. 152–158.

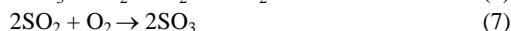
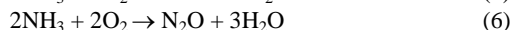
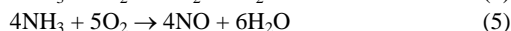
<sup>17</sup> R. Nedyalkova, K. Kamasamudram, N. W. Currier, J. Li, A. Yezerets, L. Olsson, *Experimental evidence of the mechanism behind  $\text{NH}_3$  overconsumption during SCR over Fe-zeolites*, „Journal of Catalysis” 2013, nr 299, s. 101–108.

<sup>18</sup> P. Forzatti, *Present status and perspectives in de- $\text{NO}_x$  SCR catalysis*, „Applied Catalysis A” 2001, nr 222 (1–2), s. 221–236.

<sup>19</sup> J.-Y. Luo, X. Hou, P. Wijayakoon, S. J. Schmieg, W. Li, W. S. Epling, *Spatially resolving SCR reactions over a Fe/zeolite catalyst*, „Applied Catalysis B” 2011, nr 102 (1–2), s. 110–119; A. Grossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, *The chemistry of the  $\text{NO}/\text{NO}_2\text{-NH}_3$  „fast” SCR reaction over Fe-ZSM-5 investigated by transient reaction analysis*, „Journal of Catalysis” 2008, nr 256 (2), s. 312–322.

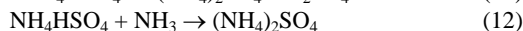
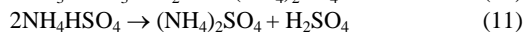
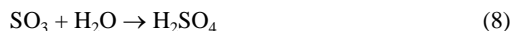
version, since  $\text{NO}_2$  accounts only for 5% of the total  $\text{NO}_x$  in the engine exhaust<sup>20</sup>.

Numerous undesirable oxidation reactions, which can take place alongside the desired ones in the presence of  $\text{NH}_3$ -SCR catalysts, can also lead to the emission of unwanted products and a decrease in  $\text{NO}_x$  conversion<sup>21</sup>. For example, ammonia oxidation reactions (equations 4-6) are undesirable because they imply the consumption of  $\text{NH}_3$ , thus limiting the  $\text{NO}_x$  conversion and partially leading to the formation of  $\text{NO}$  and  $\text{N}_2\text{O}$  as by-products<sup>22</sup>:



In the presence of  $\text{NO}_x$ , these reactions (equations 4-6) become negligible due to the ability of the catalysts and the reducing agent (ammonia) to favor reduction of nitrogen oxides (equation 1)<sup>23</sup>.

In case of sulfur-containing fossil fuels (e.g. coal, oil),  $\text{SO}_x$  ( $\text{SO}_2$  with a minor percentages of  $\text{SO}_3$ ) is generated during combustion in boilers. Further oxidation of  $\text{SO}_2$ , which takes place over the catalysts (equation 7), is highly undesirable.  $\text{SO}_3$  is known to react with water and unreacted ammonia ( $\text{NH}_3$  slip) present in flue gas to form sulfuric acid and ammonium sulfates according to the following reactions (equations 8–12)<sup>24</sup>:



Ammonium sulphates are deposited and accumulated on the catalyst surface, especially if it is working at a low temperature (<300°C), and therefore lead to its deactivation. The deposition of ammonium sulphates on the catalyst's surface

<sup>20</sup> P. Forzatti, I. Nova, E. Tronconi, *Enhanced  $\text{NH}_3$  selective catalytic reduction for  $\text{NO}_x$  abatement*, „Angewandte Chemie“ 2009, nr 121 (44), s. 8516–8518.

<sup>21</sup> F. Normann, K. Andersson, B. Leckner, F. Johnsson, op. cit., s. 385–397.

<sup>22</sup> M. Kobel, M. Elsener, M. Kleemann, *Urea-SCR: a promoting technique to reduce  $\text{NO}_x$  emissions from automotive diesel engines*, „Catalysis Today“ 2000, nr 59 (3–4), s. 335–345; I. Nova, L. dall'Acqua, L. Lietti, E. Giamello, P. Forzatti, *Study of thermal deactivation of de- $\text{NO}_x$  commercial catalyst*, „Applied Catalysis B“ 2001, nr 35 (1), s. 31–42.

<sup>23</sup> Ibidem.

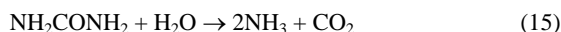
<sup>24</sup> X. Tang, S. Madronich, T. Wallington, D. Calamari, op. cit., s. 83–95; A. Grossale, I. Nova, E. Tronconi, D. Chatterjee, M. Weibel, op. cit., s. 312–322.

can be inhibited upon heating. Apart from the sulfuric acid and ammonium sulphates formation, two additional unselective reactions may occur, namely the formation of ammonium nitrate and  $N_2O^{25}$ . The ammonium nitrate prevails at temperatures below  $200^\circ\text{C}$ , and – similarly to ammonium sulfates – leads to reversible catalyst deactivation<sup>26</sup>. Decomposition of  $NH_4NO_3$  leads to  $NH_3$  and  $HNO_3^{27}$ .

## SELECTIVE CATALYTIC REDUCTION SYSTEM

The catalytic converter is the most important part of SCR system, and its location – together with a system used for ammonia injection – are the critical design parameters<sup>28</sup>.

Ammonia is injected into the flue gas stream through a distribution grid. The source of ammonia is usually 32.5 wt.% urea solution (also referred to as AdBlue)<sup>29</sup>. The SCR systems are designed to produce gaseous mixture of ammonia and carbon dioxide by the hydrolysis reaction of the urea solution (equation 15)<sup>30</sup>:



The hydrolysis reaction is endothermic, and thus requires heat input (it proceeds rapidly at temperature above  $130^\circ\text{C}^{31}$ , temperature flash vaporization<sup>32</sup> or

<sup>25</sup> Ibidem.

<sup>26</sup> Ibidem.

<sup>27</sup> C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, *A „Nitrate Route” for the low temperature „Fast SCR” reaction over a  $V_2O_5$ - $WO_3$ / $TiO_2$  commercial catalyst*, „Chemical Communications” 2004, nr 23, s. 2718–2719.

<sup>28</sup> R. M. Heck, *Catalytic abatement of nitrogen oxides–stationary applications*, „Catalysis Today” 1999, nr 53 (4), s. 519–523.

<sup>29</sup> M. Eichelbauma, R. J. Farrautoa, M. J. Castaldia, *The impact of urea on the performance of metal exchanged zeolites for the selective catalytic reduction of  $NO_x$ . Part I. Pyrolysis and hydrolysis of urea over zeolite catalysts*, „Applied Catalysis B” 2010, nr 97 (1–2), s. 90–97.

<sup>30</sup> P. Forzatti, I. Nova, E. Tronconi, op. cit., s. 8516–8518.

<sup>31</sup> M. A. Isla, H. A. Irazoqui, C. M. Genoud, *Simulation of a urea synthesis reactor. Part I. Thermodynamic framework*, „Industrial & Engineering Chemistry Research” 1993, nr 32 (11), s. 2662–2670; B. Claudel, E. Brousse, G. Shehadeh, *Novel thermodynamic and kinetic investigation of ammonium carbonate decomposition into urea*, „Thermochimica Acta” 1986, nr 102, s. 357–371.

<sup>32</sup> S. Grout, J.-B. Blaisot, K. Pajot, G. Osbat, *Experimental investigation on the injection of an urea-water solution in hot air stream for the SCR application: Evaporation and spray/wall interaction*, „Fuel” 2013, nr 106, s. 166–177.

catalysts<sup>33</sup>). The primary issue is the safety of transportation, storage, and handling of the required bulk reagent.

The required injection molar ratio of ammonia to NO, according to stoichiometry, is 1 (equation 1), although it is generally kept below 1 to avoid ammonia slip at very low values under less than 5 ppm<sup>34</sup>. Besides the NH<sub>3</sub> slip control system, the installation should be equipped with: (i) an effective SCR catalyst, (ii) advanced process control instrumentation, (iii) optimal operating conditions (reaction temperature and the NH<sub>3</sub>/NO feed ratio), and (iv) NH<sub>3</sub> distributor. For the scheme of the commercial SCR process, the reaction kinetics forecasting NH<sub>3</sub> slip must be involved in the model of SCR reactor<sup>35</sup>.

The SCR reactor operating in thermal power plants can be placed according to four different configurations: (i) immediately behind the boiler (high dust arrangement, HD), (ii) upstream of the air preheater unit (low dust arrangement, LD), and (iii) behind the sulfur dioxide removal by a flue gas desulfurization unit (tail end arrangement, TE). More information about the SCR location configuration is available in paper of Forzatti<sup>36</sup> and Heck<sup>37</sup>.

## NITROGEN OXIDE REDUCTION CATALYSTS

Different types of catalytic materials have been considered for use in the selective catalytic reduction of NO with ammonia reaction stationary applications. These catalysts can be divided into three main groups: (i) noble metals, (ii) metal oxides, and (iii) transition metal–modified zeolites. Among these categories, metal oxides based catalysts are the most widely utilized SCR systems nowadays.

Supported noble-metal (mainly Pt, Rh, Pd) catalysts are very active in the SCR reaction in the low temperature region (170–300°C)<sup>38</sup>. Unfortunately, they

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<sup>33</sup> M. Casapu, A. Bernhard, D. Peitz, M. Mehring, M. Elsener, O. Kröcher, *A niobia-ceria based multi-purpose catalyst for selective catalytic reduction of NO<sub>x</sub>, urea hydrolysis and soot oxidation in diesel exhaust*, „Applied Catalysis B” 2011, nr 103 (1–2), s. 79–84.

<sup>34</sup> J. B. Lefers, P. Lodders, G. D. Gerd, *Modeling of selective catalytic DeNO<sub>x</sub> reactors – strategy for replacing deactivated catalyst elements*, „Chemical Engineering & Technology” 1991, nr 14 (3), s. 192–200.

<sup>35</sup> H. J. Chae, S. T. Choo, H. Choi, I. S. Nam, Y. G. Kim, H. S. Yang, H. Ch. Choi, *Direct use of kinetic parameters for modeling and simulation of a selective catalytic reduction process*, „Industrial & Engineering Chemistry Research” 2000, nr 39 (5), s. 1159–1170.

<sup>36</sup> P. Forzatti, I. Nova, E. Tronconi, op. cit., s. 8516–8518.

<sup>37</sup> R. M. Heck, op. cit., s. 519–523.

<sup>38</sup> M. Radojevic, *Reduction of nitrogen oxides in flue gases*, „Environmental Pollution” 1998, nr 102 (1, S1), s. 685–689; A. A. Nikolopoulos, E. S. Stergioula, E. A. Efthimiadis, I. A. Vasalos, *Selective catalytic reduction of NO by propene in excess oxygen on Pt- and Rh-supported alumina catalysts*, „Catalysis Today” 1999, nr 54 (4), s. 439–450.

also effectively oxidize both  $\text{NH}_3$  and  $\text{SO}_2$ <sup>39</sup> and are not sulfur tolerant<sup>40</sup>. For these reasons, and also because of the high cost of this type of materials, noble metal-based catalysts were soon replaced by the second group of catalysts, consisting of transition metal oxides.

Single- and multi-metal oxide catalysts, based on Co, Cr, Cu, Fe, Mn, V<sup>41</sup>, and other oxides, either unsupported or supported on  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and carbon materials, were investigated as potential candidates for  $\text{NO}_x$  reduction by ammonia<sup>42</sup>. Among the various studied oxide compositions,  $\text{V}_2\text{O}_5$  supported on  $\text{TiO}_2$  (in the form of anatase) and additionally promoted with  $\text{WO}_3$  or  $\text{MoO}_3$  showed superior catalytic properties in the selective  $\text{NO}$  reduction with ammonia<sup>16</sup>. These catalysts operate at temperatures significantly higher than noble metals (260–425°C) and additionally present high sulfur tolerance<sup>43</sup>.

Zeolites (e.g. ZSM-5, faujasite – both of X and Y types, mordenite, beta) modified with transition metal ions such as Co, Cu, Fe, Mn, Ce, Ni<sup>44</sup> are another group of materials intensively tested as potential catalysts for stationary SCR applications, mainly in gas-fired cogeneration plants. The studies of zeolite materials as catalysts for the SCR process have resulted in very high  $\text{NO}_x$  conversion, selectivity towards the desired products ( $\text{N}_2$  and  $\text{H}_2\text{O}$ ) even at temperatures as high as 600°C and sulfur tolerance<sup>45</sup>.

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<sup>39</sup> P. Forzatti, I. Nova, E. Tronconi, op. cit., s. 8516–8518.

<sup>40</sup> R. M. Heck, op. cit., s. 519–523

<sup>41</sup> M. F. Irfan, J. H. Goo, S. D. Kim, *Co<sub>3</sub>O<sub>4</sub> based catalysts for NO oxidation and NO<sub>x</sub> reduction in fast SCR process*, „Applied catalysis B” 2008, nr 78 (3–4), s. 267–274; H. E. Curry-Hyde, H. Musch, A. Baiker, M. Schraml-Marth, A. Wokaun, *Surface structure of crystalline and amorphous chromia catalysts for the selective catalytic reduction of nitric oxide I. Characterization by temperature-programmed reaction and desorption*, „Journal of Catalysis”, 1992, nr 133 (2), s. 397–414; G. Centi, S. Perathoner, D. Biglino, E. Giamello, *Adsorption and reactivity of NO on copper-on-alumina catalysts: I. Formation of nitrate species and their influence on reactivity in NO and NH<sub>3</sub> conversion*, „Journal of Catalysis” 1995, nr 151 (1), s. 75–92; G. Ramis, M. A. Larrubia, *An FT-IR study of the adsorption and oxidation of N-containing compounds over Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> SCR catalysts*, „Journal of Molecular Catalysis A” 2004 nr 215 (1–2), s. 161–167; F. Kapteijn, L. Singoredjo, N. J. J. Dekker, J. A. Moulijn, *Kinetics of the selective catalytic reduction of nitrogen oxide (NO) with ammonia over manganese oxide (Mn<sub>2</sub>O<sub>3</sub>)-tungsten oxide (WO<sub>3</sub>)/gamma-alumina*, „Industrial & Engineering Chemistry Research” 1993, nr 32 (3), s. 445–452; M. Takagi, T. Kawai, M. Soma, T. Onishi, K. Tamaru, *The mechanism of the reaction between NO<sub>x</sub> and NH<sub>3</sub> on V<sub>2</sub>O<sub>5</sub> in the presence of oxygen*, „Journal of Catalysis” 1977, nr 50 (3), s. 441–446.

<sup>42</sup> J. Li, H. Chang, L. Ma, J. Hao, R. T. Yang, *Low-temperature selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over metal oxide and zeolite catalysts – A review*, „Catalysis Today” 2011, nr 175 (1), s. 147–156.

<sup>43</sup> R. M. Heck, op. cit., s. 519–523.

<sup>44</sup> J. Li, H. Chang, L. Ma, J. Hao, R. T. Yang, op. cit., s. 147–156; W. Wang, S.-J. Hwang, *Effects of the pretreatment of Cu-Y zeolite catalysts on the reduction of nitric oxide with ammonia*, „Applied Catalysis B” 1995, nr 5 (3), s. 187–197.

<sup>45</sup> R. M. Heck, op. cit., s. 519–523.



More detail and comprehensive review of SCR catalysts was given by Bosch and Janssen<sup>46</sup> (and references herein), Janssen and Meijer<sup>47</sup>, Brandenberger et al.<sup>48</sup>, and Li et al.<sup>49</sup>

## COMMERCIAL METAL OXIDE SCR CATALYSTS

The widely used commercial catalysts for the SCR process in power plants are based on  $V_2O_5$ - $WO_3$ / $TiO_2$  and  $V_2O_5$ - $MoO_3$ / $TiO_2$  oxide systems. Titania in form of anatase is used as high surface area carrier to support the active components (vanadium pentoxide, tungsten trioxide or molybdenum trioxide)<sup>50</sup>. Anatase shows activating properties in the supported  $V_2O_5$ , which makes for a very active catalyst, more active than those obtained with other supports. This type of support is only weakly and reversibly sulfated under conditions of SCR reaction, and this sulfation even enhances the SCR catalytic activity<sup>51</sup>.  $V_2O_5$  is an active phase and is responsible for high activity and selectivity to  $N_2$ <sup>52</sup> and for undesired oxidation of  $SO_2$  to  $SO_3$  in case of sulfur-containing fuels. The content of vanadium oxide is usually below 1 wt.% in high sulfur applications.  $WO_3$  or  $MoO_3$  are introduced into the  $V_2O_5$ / $TiO_2$  catalyst structure in larger amounts (ca. 10 and 6 wt.%, respectively)<sup>53</sup>. It is proposed that  $WO_3$  is added to improve stability of the catalysts. The  $V_2O_5$ - $MoO_3$ / $TiO_2$  catalyst was found to be more resistant to thermal deactivation and poisoning by metal oxides (e.g.  $As_2O_3$ ) in comparison to  $V_2O_5$ / $TiO_2$ . Additionally, the  $V_2O_5$ - $MoO_3$ / $TiO_2$  catalyst is less

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<sup>46</sup> H. Bosch, F. Janssen, *Formation and control of nitrogen oxides*, „Catalysis Today” 1988, nr 2 (4), s. 369–379.

<sup>47</sup> F. Janssen, R. Meijer, *Quality control of DeNO<sub>x</sub> catalysts: Performance testing, surface analysis and characterization of DeNO<sub>x</sub> catalysts*, „Catalysis Today” 1993, nr 16 (2), s. 157–185.

<sup>48</sup> S. Brandenberger, O. Kroecher, A. Tissler, R. Althoff, *The state of the art in selective catalytic reduction of NO<sub>x</sub> by ammonia using metal-exchanged zeolite catalysts*, „Catalysis Reviews Science and Engineering” 2008, nr 50 (4), s. 492–531.

<sup>49</sup> J. Li, H. Chang, L. Ma, J. Hao, R. T. Yang, op. cit., s. 147–156

<sup>50</sup> S. Brandenberger, O. Kroecher, A. Tissler, R. Althoff, op. cit., s. 492–531.

<sup>51</sup> P. Forzatti, I. Nova, E. Tronconi, op. cit., s. 8516–8518; B. Roduit, A. Wokaun, A. Baiker, *Global Kinetic Modeling of Reactions Occurring during Selective Catalytic Reduction of NO by NH<sub>3</sub> over Vanadia/Titania-Based Catalysts*, „Industrial & Engineering Chemistry Research” 1998, nr 37 (12), s. 4577–4590.

<sup>52</sup> M. Takagi, T. Kawai, M. Soma, T. Onishi, K. Tamaru, *The mechanism of the reaction between NO<sub>x</sub> and NH<sub>3</sub> on V<sub>2</sub>O<sub>5</sub> in the presence of oxygen*, „Journal of Catalysis” 1977, nr 50 (3), s. 441–446.

<sup>53</sup> G. Busca, L. Lietti, G. Ramis, F. Berti, *Chemical and mechanistic aspects of the selective catalytic reduction of NO<sub>x</sub> by ammonia over oxide catalysts: A review*, „Applied Catalysis B” 1998, nr 18 (1–2), s. 1–36.

active in undesired oxidation of  $\text{NH}_3$  and  $\text{SO}_2$ <sup>54</sup>. The introduction of  $\text{MoO}_3$  prevents the catalyst's deactivation in the presence of As-containing compounds in flue gases, even as the mechanics of the process is not fully understood<sup>55</sup>. Finally, other inert compounds (e.g. aluminosilicates, fiberglass) are used in commercial catalysts as additives to improve its mechanical resistance<sup>56</sup>.

The NO conversion obtained over the  $\text{V}_2\text{O}_5$ - $\text{TiO}_2$  commercial catalysts depends on the vanadium pentoxide loading: e.g. for high  $\text{V}_2\text{O}_5$  loading, the temperatures about 327°C is needed for total removal of NO. At higher temperatures, the NO conversion slowly decreases due to the side process of ammonia oxidation<sup>57</sup>.

The SCR catalyst forms are represented mainly by honeycomb monoliths, plates and coated metal monoliths. These catalyst forms are preferred because of: (i) lower pressure drop, (ii) higher geometric surface areas, (iii) abrasion resistance, and (iv) lower tendency to fly ash plugging<sup>58</sup>. Many studies are focused on design and modeling of the honeycomb-type monolith reactor for the SCR process [e.g.<sup>59</sup>].

If we consider the applications of the SCR technology to vehicles, there is a clear trend in the automobile industry to replace V-based SCR catalysts with zeolite or other catalytic materials, mainly due to narrow operating temperature

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<sup>54</sup> J. P. Chen, R. T. Yang, *Role of  $\text{WO}_3$  in mixed  $\text{V}_2\text{O}_5$ - $\text{WO}_3$ / $\text{TiO}_2$  catalysts for selective catalytic reduction of nitric oxide with ammonia*, „Applied Catalysis A” 1992, nr 80 (1), s. 135–148; L. J. Pinoy, L. H. Hosten, *Experimental and kinetic modeling study of  $\text{DeNO}_x$  on an industrial  $\text{V}_2\text{O}_5$ - $\text{WO}_3$ / $\text{TiO}_2$  catalysts*, „Catalysis Today” 1993, nr 17 (1–2), s. 151–158; L. J. Pinoy, L. H. Hosten, *Experimental and kinetic modeling study of  $\text{DeNO}_x$  on an industrial  $\text{V}_2\text{O}_5$ - $\text{WO}_3$ / $\text{TiO}_2$  catalysts*, „Catalysis Today” 1993, nr 17 (1–2), s. 151–158.

<sup>55</sup> F. Hilbrig, H. E. Göbel, H. Knözinger, H. Schmelz, B. Langelier, *Interaction of arsenious oxide with  $\text{DeNO}_x$ -catalysts: An X-ray absorption and diffuse reflectance infrared spectroscopy study*, „Journal of Catalysis” 1991, nr 129 (1), s. 168–176; F. C. Lange, H. Schmelz, H. Knözinger, *Infrared-spectroscopic investigations of selective catalytic reduction catalysts poisoned with arsenic oxide*, „Applied Catalysis B” 1996, nr 8 (2), s. 245–265.

<sup>56</sup> P. Forzatti, I. Nova, E. Tronconi, op. cit., s. 8516–8518.

<sup>57</sup> P. Forzatti, L. Lietti, E. Tronconi, *Nitrogen oxides removal-industrial*, „Encyclopedia of Catalysis” 2002, s. 1–57.

<sup>58</sup> H. J. Chae, S. T. Choo, H. Choi, I.-S. Nam, Y. G. Kim, H. S. Yang, H. Ch. Choi, *Direct use of kinetic parameters for modeling and simulation of SCR process*, „Industrial & Engineering Chemistry Research” 2000, nr 39 (5), s. 1159–1170.

<sup>59</sup> E. Tronconi, P. Forzatti, *Adequacy of lumped parameters models for SCR reactors with monolith structure*, „AIChE Journal” 1992, nr 38 (2), s. 201–210; E. Tronconi, L. Lietti, P. Forzatti, S. Malloggi, *Experimental and theoretical investigation of the dynamics of the SCR- $\text{DeNO}_x$  reaction*, „Chemical Engineering Science” 1996, 51 (11), s. 2965–2970; A. Berretta, C. Orsenigo, N. Ferlazzo, E. Tronconi, P. Forzatti, *Analysis of the performance of plate-type monolithic catalysts for selective catalytic reduction  $\text{DeNO}_x$  applications*, „Industrial & Engineering Chemistry Research” 1998, nr 37 (7), s. 2623–2633.

window of the  $V_2O_5/TiO_2$  catalysts<sup>60</sup>, anatase to rutile phase transformation under reaction conditions<sup>61</sup>, and vanadium pentoxide toxicity<sup>62</sup>.

## LAYERED DOUBLE HYDROXIDES AS SCR CATALYSTS

One group of the potential catalysts for SCR application in vehicles suggested by research is the layered double hydroxides (LDHs) referred also as hydroxalite-like materials (HTs). They are either natural or synthetic minerals described with the general formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]A^{n-}_{x/n} \cdot zH_2O$ , where  $M^{II}$  is a divalent cation (e.g.  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  etc.),  $M^{III}$  is a trivalent cation (e.g.  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  etc.),  $A^{n-}$  can be organic or inorganic anion (e.g.  $CO_3^{2-}$ ,  $Cr_2O_7^{2-}$ ,  $Mo_7O_{24}^{6-}$  etc.),  $x$  can generally have values between  $0.2 < x < 0.4$  and  $z$  is normally 4-5. Hydroxalite-like compounds are very interesting materials due to highly developed surface area ( $>200 \text{ m}^2/\text{g}$ ), homogeneous dispersion of components, and high thermal stability<sup>63</sup>. Different composition of mixed metal oxides obtained from hydroxalite-like material such as Mg-Cu-Al<sup>64</sup>, Mg-Co-Al, Mg-Cu-Co-Al<sup>65</sup>, Mg-Cu-Fe<sup>66</sup> have been studied. Among them, the highest catalytic activity in the SCR process was observed for the series of Mg-Cu-Al mixed oxides.

In order to improve the catalytic activity and selectivity of the Cu-containing materials (Mg/Cu/Al=66/5/29), further modifications of the catalysts composition with small amounts of: (i) noble metals (0.2 wt.% of Pd, Rh, Pt), and (ii) alkaline metal (2 wt.% of K) were carried out. According to research data

<sup>60</sup> R. M. Heck, op. cit., s. 519–523.

<sup>61</sup> E. Abi Aad, A. Aboukaïs, *Characterization by EPR spectroscopy*, „Catalysis Today” 2000, nr 56 (4), s. 371–378.

<sup>62</sup> F. Liu, H. He, Ch. Zhang, *Novel iron titanate catalyst for the selective catalytic reduction of NO with NH<sub>3</sub> in the medium temperature range*, „Chemical Communications” 2008, nr 17, s. 2043–2045.

<sup>63</sup> F. Cavani, F. Trifiro, A. Vaccari, *Hydroxalite-type anionic clays: Preparation, properties and applications*, „Catalysis Today” 1991, nr 11 (2), s. 173–301.

<sup>64</sup> M. Trombetta, G. Ramis, G. Busca, B. Montanari, A. Vaccari, *Ammonia adsorption and oxidation on Cu/Mg/Al mixed oxide catalysts prepared via hydroxalite-type precursors*, „Langmuir” 1997, nr 13 (17), s. 4628–4637; B. Montanari, A. Vaccari, M. Gazzano, P. Käbner, H. Papp, J. Pasel, R. Dziembaj, W. Makowski, T. Lojewski, *Characterization and activity of novel copper-containing catalysts for selective catalytic reduction of NO with NH<sub>3</sub>*, „Applied Catalysis B” 1997, nr 13 (3–4), s. 205–217; L. Chmielarz, P. Kuśtrowski, A. Rafalska-Łasocho, D. Majda, R. Dziembaj, *Catalytic activity of Co-Mg-Al, Cu-Mg-Al and Cu-Co-Mg-Al mixed oxides derived from hydroxalites in SCR of NO with ammonia*, „Applied Catalysis B” 2002, nr 35 (3), s. 195–210.

<sup>65</sup> Ibidem.

<sup>66</sup> L. Chmielarz, A. Węgrzyn, M. Wojciechowska, S. Witkowski, M. Michalik, *Selective catalytic oxidation (SCO) of ammonia to nitrogen over hydroxalite originated Mg-Cu-Fe mixed metal oxides*, „Catalysis Letters” 2011, nr 141 (9), s. 1345–1354.

such selected metals are the most often used to increase activity and selectivity of the catalysts in the SCR process. The influence of the composition modifications on the catalytic activity and selectivity to  $N_2$  over prepared catalysts has been examined. Examples of the catalytic results are presented in Fig. 1. More results of the catalytic studies of the SCR process for a series of the Cu-containing samples doped with noble metals were presented in a paper given by Chmielarz et al.<sup>67</sup> The deposition of noble metals enhanced the activity of the catalysts in the low temperature range; however, such modification of the Mg-Cu-Al oxide system decreased selectivity to  $N_2$ . On the contrary, the deposition of potassium promoter decreased both activity and selectivity of the Mg-Cu-Al oxide catalysts, which could be related to the changes in the redox properties of copper oxide species<sup>68</sup>. At higher temperatures for all the catalysts, the NO conversion decreased due to the side process of ammonia oxidation.

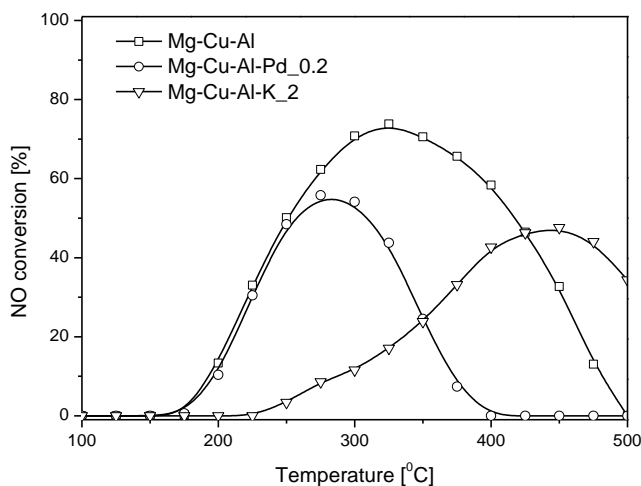


Fig. 1. Selective catalytic reduction of NO with ammonia performed for Mg-Cu-Al oxides and its modifications with Pd/K. Conditions: mass of catalysts = 100 mg,  $[NH_3] = [NO] = 0.25\%$ ,  $[O_2] = 2.5\%$ ,  $[He] = 97\%$ , total flow rate =  $40 \text{ cm}^3/\text{min}$ , linear heating of  $10^\circ\text{C}/\text{min}$ .

<sup>67</sup> L. Chmielarz, M. Jabłońska, A. Strumiński, Z. Piwowarska, A. Węgrzyn, S. Witkowski, M. Michalik, *Selective catalytic oxidation of ammonia to nitrogen over Mg-Al, Cu-Mg-Al and Fe-Mg-Al mixed metal oxides doped with noble metals*, „Applied Catalysis B” 2013, nr 130–131, s. 152–162.

<sup>68</sup> L. Chmielarz, Z. Piwowarska, M. Rutkowska, M. Wojciechowska, B. Dudek, S. Witkowski, M. Michalik, *Total oxidation of selected mono-carbon VOCs over hydrotalcite originated metal oxide catalysts*, „Catalysis Communications” 2012, nr 17, s. 118–125.

The results revealed that Mg-Cu-Al oxides derived from hydrotalcite-like material could be considered as potential SCR catalysts in the vehicle application. Further studies and longer tests in the presence of typical exhaust gases ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ) are still required. The reaction mechanism over this type of catalysts should be determined to specify the role of the individual components in the process and to identify the key properties of the catalytic systems that determine their activity. Moreover, the comparison with the vanadium-containing reference catalyst should be carried out.

## SUMMARY AND CONCLUDING REMARKS

Nowadays,  $\text{NO}_x$  reduction has become one of the major issues in environmental protection. Looking for an active and selective catalyst is one of the challenges. Up to now, tungsten and molybdenum promoted  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts exhibit the best performance in the  $\text{NO}_x$  reduction process, and these catalysts have already been industrialized. For the vehicle applications there is a trend for considering other catalysts due to some drawbacks of titania-supported catalysts. Application of Cu-containing mixed metal oxides obtained from hydrotalcite-like materials as catalysts for this process could be a potential solution; however, further research in real operating conditions is needed.

## USUWANIE TLENKÓW AZOTU METODĄ SCR – PRACA PRZEGLĄDOWA

W pracy omówiono źródła powstawania tlenków azotu, wpływ  $\text{NO}_x$  na środowisko i życie człowieka, jak również katalityczne reakcje ich usuwania. W szczególności omówiono technologię procesu selektywnej katalitycznej redukcji NO amoniakiem (proces  $\text{NH}_3$ -SCR), w tym stosowane w procesie komercyjne katalizatory oparte na tlenku tytanu oraz mieszane tlenki pochodzenia hydrotalkitowego. Uzyskane wyniki jednoznacznie wskazują na duży potencjał materiałów hydrotalkitowych jako katalizatorów technologii SCR.

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