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Advances in selective catalytic oxidation of ammonia to dinitrogen: a review

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Abstract:

Ammonia emission to atmosphere is an important environmental problem. A significant increase in ammonia emission is expected in automotive and energy production sectors in the near future. It is related to the spreading of technologies that use ammonia for NO_x conversion in flue gases (e.g. DeNOx, DEF) and combustion of nitrogen rich fuels (e.g. biogas, biomass). Among the various methods of ammonia elimination from flue gases, its catalytic selective oxidation to dinitrogen seems to be the most promising one. Different types of the catalytic systems active in selective ammonia oxidation were presented and discussed. Moreover, the possible mechanisms of ammonia oxidation and the concept of bifunctional catalyst were discussed and analysed. Finally, the future trends in these studies were suggested.

1. Introduction

Ammonia (NH_3) is a colourless gas with a characteristic pungent smell. Pure ammonia was first synthetized by Joseph Priestley in 1774, while its exact chemical composition was determined by Claude-Louse Berthollet in 1785. The main commercial method used for ammonia production in industrial scale is based on the Haber-Bosch process,[1] which involves the direct reaction of elemental hydrogen and elemental nitrogen:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3 \quad (1)$$

This process is performed under high pressure (up to 100 MPa) and elevated temperature (400-550°C). Moreover, this reaction requires an active catalyst. Typical industrial catalysts for ammonia synthesis are based on iron oxide doped with alkali metal oxide promotors. Ammonia is one of the world's most produced chemicals and its global industrial production in 2012 was estimated to be about 200 million tons.[2] Due to high nitrogen content, ammonia is mainly used as a fertilizer or as material for the production of other fertilizers, such as urea - $(NH_2)_2CO$ or anhydrous ammonium nitrate - NH_4NO_3. Thus, ammonia manufacturing is important for intensification of food production. On the other hand emission of ammonia into atmosphere is hazardous to human live and may result in degradation of environment. Exposure to low concentrations of ammonia may result in skin or eye irritation. Higher concentrations of ammonia may cause severe injury and burns, especially dangerous in case of burning of respiratory tract. It may cause bronchiolar and alveolar edema as well as airway destruction resulting in respiratory distress or failure. Ammonia has a negative impact on environment, especially on aquatic life. Its accumulation in the organism may cause alteration of metabolism. Different species of fish can tolerate different levels of ammonia. They may suffer a loss of equilibrium, hyperexcitability, increased respiratory activity and oxygen uptake, and increased heart rate. At extreme ammonia levels, fish may experience convulsions, coma and death.

Global emission of gaseous ammonia into the atmosphere was estimated to be about 44 million tons per year (without the oceanic sources).[3] The major sources of ammonia emission into atmosphere are related to agriculture activities, mainly volatilization from livestock wastes and losses from agriculture crops, especially when nitrogen fertilizers are used. It was estimated that about 75% of the global emission of ammonia (without the oceanic sources) is related to agriculture.[3] The remaining 25% of the ammonia emission from non-agriculture sources is poorly documented, however it was estimated that about 13% is a result of biomass burning (including biofuels), about 0.2% is related to fossil fuel combustion and about 0.5% to ammonia emission from industrial processes.[3] The last two sources of ammonia emission, fossil fuel combustion and industrial processes, apparently seem to have a negligible role in the global NH_3 emission, however it is anticipated that contribution of these sources will be increasing in the future, especially in the case of fuel combustion by cars.[4] It is related to common application of catalytic three-way converts for flue gases purification (CO and hydrocarbons oxidation to CO_2 as well as NO_x reduction to N_2), which increases ammonia formation. Average ammonia emission from gasoline European car not equipped with catalytic converter is 2.2 mg NH_3/km, while for European car with catalytic converter increases to 85 mg NH_3/km.[5] In case of diesel cars even higher increase in ammonia emission is expected. It is related to implementation of diesel exhaust fluid (DEF) technology, commonly referred in Europe as AdBlue and standardized as ISO 22241.[6] The DEF technology is used to lower nitrogen oxides ($NO_x = NO + NO_2$) concentration in exhaust emissions from diesel engines. In the first step an aqueous urea solution made with 32.5% high-purity urea and 67.5% deionized water is thermally or catalytically hydrolysed to produce ammonia and carbon dioxide:

$$(NH_2)_2CO + H_2O \rightarrow 2\ NH_3 + CO_2 \qquad (2)$$

Then ammonia, similarly to the classical DeNOx process, is used as reducing agent for catalytic conversion of NO_x to N_2:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O \qquad (3)$$

$$2\ NO_2 + 4\ NH_3 + O_2 \rightarrow 3\ N_2 + 6\ H_2O \qquad (4)$$

There is a risk, that ammonia unconverted in reactions (3) and (4) will be present in exhaust gases of diesel car. In 2010, the U.S. Environmental Protection Agency (EPA) brought in new emissions standards requiring medium- and heavy-duty vehicles to significantly reduce engine emissions, particularly NO_x and particulate matter (PM).[7-9] A lot of vehicle manufacturers use DEF technology to meet these standards. Thus, this new became more and more widespread and therefore increased emission of ammonia by diesel cars is expected.

Other important sources of ammonia emission are NO_x converts, in which ammonia is used as reducing agent for conversion of nitrogen oxides to N_2 according to equations (3) and (4). This technology, called DeNOx, is used for NO_x conversion in exhaust gases produced in large utility boilers, industrial boilers and municipal solid waste boilers. Typical efficiency of nitrogen oxides reduction to dinitrogen in the DeNOx converter is in the range of 80-90%.[10] There are two possible options of the DeNOx process: (i) selective non-catalytic reduction (SNCR) of NO_x with ammonia and (ii) selective catalytic reduction (SCR) of NO_x with ammonia. In SNCR technology the NO_x conversion (equations 3 and 4) is thermally induced and takes place at high temperatures (1073-1373 K),[11] whereas in the SCR process, which is performed in the presence of catalysts, NO_x can be reduced to N_2 and H_2O (equations 3 and 4) rapidly and effectively at moderate temperatures (520-680 K).[12] More detailed comparison between SNCR and SCR technologies was presented in papers.[13,14] The technical problem of both those technologies is a risk of NH_3 slip, which in industrial applications is restricted to 10 ppm.[15] Above this limit excessive air heater plugging and fly ash contamination may occur, mainly due to a possible formation of ammonium sulphate salt.[16,17] The SCR technology is more environmental friendly than SNCR due to nearly five times lower NH_3 slip.[17] Because of ammonia slip risk, the majority of the SCR installations operates with the NH_3/NO ratio below 1 ($\approx$ 0.90-0.95), so with ammonia content below stoichiometry of the reactions (3 and 4). Thus, the effectiveness of the SCR process is not optimal and complete NO_x conversion is impossible.[18] A strategy for improving the efficiency of NO_x emission abatement together with keeping the goal of low NH_3 slip can consist of increasing the inlet NH_3 feed in the SCR reactor to stoichiometric or even higher ammonia content and selective oxidation of unreacted ammonia to nitrogen down-stream of the DeNOx converter.[19]

2. Methods for ammonia emission control

Removal of ammonia can be classified to elimination of ammonia from liquid or gas phase. However, in the paper only removal of gaseous ammonia will be discussed. Several abatement techniques to treat waste gases containing ammonia, such as absorption, adsorption, condensation, biofiltration, catalytic combustion, catalytic decomposition, thermal and catalytic oxidation were widely studied and used. Unfortunately, none of these methods cannot be a universal solution, because of their technical and/or economic limitations in ammonia removing from waste gases. In particular, it seems that the main parameter in ammonia removal that should be taken into account is its concentration in waste gases. General review about various methods for ammonia removal from waste gases was given by Busca and Pistarino,[20] while reviews of particular methods can be also found in papers.[21-26] Therefore, only a general overview of these methods is presented in this paper.

Absorption (scrubbing)

Absorption is used to remove ammonia from gas phase by its transferring into liquid non-volatile phase. Ammonia is highly soluble in pure water and inorganic acid solutions such as HCl, HNO_3, H_2SO_4).[27] The Henry's law constant (H) for NH_3 is $5.33 \cdot 10^1$ $M \cdot atm^{-1}$ at 298 K, and it is relatively high compared to other gases such as CO_2, CH_4 and H_2S with H values of $3.47 \cdot 10^{-2}$, $1.50 \cdot 10^{-3}$, $1.00 \cdot 10^{-1}$ $M \cdot atm^{-1}$, respectively. During this process, ammonia is adsorbed in a diluted acidic solution and converted to NH_4^+.[28]

Packed-bed and spray wet scrubbers are widely used for reduction of ammonia emission because of their high efficiency. Acid-packed scrubbers reached efficiency on the level of 90-99% for treatment of inlet NH_3 concentrations ranging from 8 to 29 ppm.[21] For the higher ammonia concentration (100-400 ppm) acid spray wet scrubber was able to reduce NH_3 by about 75-85%. In spray wet scrubber, air containing ammonia can react counter-current or cross-current, with a dilute acidic solution in the form of liquid droplets. The spray droplets hit the scrubber walls and form a liquid film. Typically, spray scrubbers operate in a closed loop in which the sprayed liquid is collected in a tank and recirculated back to the spray nozzles using pumps.[28] Process control with pH measurements, usually at a value below 4, and automatic water discharge can guarantee sufficient ammonia removal.[21]

Finally, the formed valuable products such as ammonium sulphate and ammonium phosphate, can be used either as a fertilizer upon further purification or disposed of in some way. Other possibility is regeneration by air stripping at high temperature or reboiling.[20] Subsequently, ammonia is not destroyed and further processing or disposal is necessary. Additionally, the investment and operational cost of scrubbers can be quite high as it was given by Melse and Ogink.[21]

Adsorption

Adsorption can take place by ammonia physisorption and chemisorption. Physisorption or non-specific adsorption is related to a micropores filling driven by van der Waals forces and relies on the porosity of the adsorbent. Chemisorption leads to much stronger interactions than physisorption and it involves chemical reactions between the species to be adsorbed and the adsorbent surface. Therefore, much more selective adsorption process is possible in this case.[29] Adsorption can be successfully applied to a mixture containing besides NH_3 also H_2, N_2, Ar and CH_4, which can be regarded as non-adsorbing gases. However, this does not seem applicable to water vapour containing gases due to competition for the same adsorption sites.[30]

Ammonia molecules with a relatively small size and its basic and polar nature can be strongly adsorbed at ambient conditions by adsorbents with very small pores and acidic surface.[31,32] The most widely used adsorbents are activated carbons, zeolites, alumina and silica.[32-35] Typically ammonia adsorption occurs near room temperature, while adsorbent regeneration can be obtained at low pressure (Pressure Swing Adsorption, PSA) or even vacuum (Vacuum

Swing Adsorption, VSA) and high temperatures (Temperature Swing Adsorption, TSA). E.g. TSA in the range of 323-473 K, and PSA between 10 and 40 kPa were used for regeneration of surface treated active carbon and ion-exchanged Y zeolite.[36]

Condensation (liquefaction)

Ammonia can be separated from other incondensable gases by pressure increase, temperature decrease or combination of both these parameters. Ammonia boiling point is 240 K at 0.1 MPa. For ammonia liquefaction at 298 K a pressure of about 1 MPa is required.[23] Condensation of ammonia is used mainly in ammonia synthesis plant to its separation from the circulating gas. Usually, pressure about 15 MPa and temperature near 273 K is used for ammonia condensation. Apart from ammonia also other components of waste gases (e.g. water vapour) can be condensated under these conditions.[20]

Biofiltration

Biofilters are biological reactors, which use microorganisms that colonize porous media to decompose pollutants from air stream.[37] Biofiltration has been successfully applied for treating large air streams with low ammonia concentration and high flow rates.[38-40] Biofilters, based on a wide variety of support materials, either organic or inorganic, permit usually around 95-98% efficiency of ammonia removal.[20] Lava rock, compost, plastic rings, activated carbon, ceramics rings, polyurethane foams and perlite are the most often used packing materials for microorganisms.[41,42] Efficiency of biofiltration is relatively high, e.g. biofilter with wood chips was able to remove ammonia with efficiency of 79-81%.[43]

The general technical concept of this method is based on using of biofilter in the form of packed bed. Contaminated air passes through such bed and ammonia is removed from the air stream by adsorption onto the biofilter. Then ammonia is oxidized through microbial nitrification, which is the aerobic conversion of NH_3 to nitrite (NO_2^-) and nitrate (NO_3^-).

Subsequently, nitrite and nitrate are autotrophically or heterotrophically denitrified to NO, N_2O and finally to N_2.[44]

Although, biological treatments have become an effective and inexpensive alternative to other ammonia treatment systems,[45,46] this method has several disadvantages. Biofilters operate under specific conditions, such as moisture content, pH, light, oxygen availability, nutrient limitation and temperature that strongly affect their performance.[45,47]

Catalytic decomposition

Studies of ammonia decomposition have been undertaken primarily to acquire insights into the ammonia synthesis process. However, it was further successfully applied in the generation of clean hydrogen for fuel cells. Conventional processes, such as stream reforming, catalytic biomass gasification, coal gasification, autothermal reforming and partial oxidation produce large amounts of CO_x.[48-50] These by-products may be harmful not only for the environment but also for hydrogen cells. Therefore, catalytic decomposition of ammonia seems to be CO_x-free alternative.[51,52] Decomposition of ammonia is endothermic process. The equilibrium conversion of NH_3 under normal pressure and at 673 K reaches 99.1%, while above this temperature conversion is less temperature dependent. In scientific literature, there is a wide variety of catalytic materials that were proved to be effective even below 673 K,[53,54] but some still require high operating temperatures (e.g. 973-1173 K) and the presence of reducing gases.[55,56] Therefore, this method does not seem applicable to oxygen containing gases. Among different catalytic systems studied for ammonia decomposition, such as containing Fe,[57] Ni,[58] Pt,[59] Ir,[60] and Pd,[59] the ruthenium containing catalysts were reported to be the most catalytically active.[24]

Thermal oxidation

Thermal oxidation of ammonia takes place in the Claus process used in oil refining and gas processing to recover sulphur and destroy contaminants formed in upstream processing.

Ammonia is formed as a by-product of dinitrogen operations such as hydrocracking and hydrotreating. After sour water striping, sour gas stream containing NH_3, is directed to the sulphur recovery facility for destruction at temperature higher than 1473-1523 K.[61] Efficiency of thermal oxidation of ammonia depends on temperature, residence time and gas composition. Ammonia conversion was found to increase with both temperature and residence time.[62] E.g. NH_3 conversion through oxidation was in the range of 1-50% for temperatures between 1123 and 1223 K, while significantly higher conversion up to 90% was obtained at 1323-1473 K under the same conditions (residence times: 50-700 ms, O_2/NH_3: 0.85-2.55).[61] Thus, this method can be used only for elimination of ammonia from hot waste gases.

Catalytic combustion

Catalytic combustion of ammonia was considered mainly in gasified biomass (biogas) used for gas-turbine (GT) applications operating below 1473 K.[63] Biogas has a complex composition and contain apart from N_2, CO_2 and H_2O significant amounts of CO, H_2, NH_3, H_2S, CH_4 and other hydrocarbons.[64] The problem of this method is the formation apart from N_2 also nitrogen oxides as ammonia oxidation products. Depending on the catalyst used, different contribution of NO_x was found. One of the most widely studied materials were transition metals substituted (Mn, Cr, Co, Ni, Fe) hexaaluminates, which were reported to be the high-temperature stable combustion catalysts.[65,66] Another group of effective catalysts are alumina-supported metals (e.g. Ag, Pd, Pt, Rh, Cu).[67,68]

Low-temperature selective catalytic oxidation (NH_3-SCO)

Selective catalytic oxidation of ammonia concerns mainly the treatment of oxygen containing waste gases after SCR process from both stationary and mobile sources.[69-73] Therefore, it is an attractive method, especially for treatment of large gas flows containing low concentration of ammonia. The advantage of this process is fact that it proceeds between components of waste gases (NH_3, O_2), therefore there is no need for supplying of additional reactants for ammonia conversion. Appropriate catalyst can promote oxidation in shorter reaction time under milder operation conditions. Catalyst for selective ammonia oxidation is referred also as the Ammonia Slip Catalyst (ASC), ammonia guard catalyst or Ammonia Oxidation Catalyst (AMOX). Such catalyst is placed down-stream of the SCR catalyst, either as a short zone on the same monolith or as a separate brick.[74,75]

For use in power plant applications the target temperature is in the range of 523-673 K. On the other hand, temperature of exhaust gases emitted by diesel engines varies in a broad temperature range and can increase up to 873 K (in cycle of diesel particulate filter regeneration). Therefore, different parameters of operation are expected for the catalysts dedicated for treatment of waste gases emitted from these sources. It should be also mentioned that although AdBlue technology already has been introduced for heavy trucks and buses, where the size of catalytic converters could be relatively large, it is necessary to develop more efficient catalysts for exhaust gas purification process in passenger cars, for which the size of the catalytic converters has to be much smaller.

The selective catalytic oxidation of ammonia to dinitrogen as a method for ammonia removal from waste gases is discussed in this paper**.**

3. Selective catalytic oxidation of ammonia to dinitrogen

Selective oxidation of ammonia to dinitrogen (equation 5) is one of the most promising technologies for elimination of NH_3 from exhaust gases emitted by cars, especially diesel cars equipped with DEF converters, as well as boilers (down-stream DeNOx converter).

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O \qquad (5)$$

Such gases contain small amounts of oxygen, which is an oxidizing agent for ammonia conversion, and therefore there is no need to introduce of any additional reactants into flue gases. The problem is related to the possible formation of NO (equation 6) and N_2O (equation 7) as side-products of ammonia oxidation:

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

$$2\ NH_3 + 2\ O_2 \rightarrow N_2O + 3\ H_2O \qquad (7)$$

All the reactions of ammonia oxidation are strongly exothermic. From figure 1A, presenting temperature dependence of Gibbs free energy for the reactions of ammonia oxidation, it can be clary seen that the formation of dinitrogen is much more thermodynamically favourable than oxidation of ammonia to NO or N_2O. Moreover, the formation of N_2O is more thermodynamically favourable at temperatures below 1000 K in comparison to ammonia conversion to NO, while at higher temperatures the formation of NO is more favourable. Figure 1B presents temperature dependence of equilibrium constant (K_{eq}) for the reaction of ammonia oxidation. It can be seem that for all these reactions the values of K_{eq} are relatively high in a broad temperature range. Thus, apart from dinitrogen also nitrogen oxides can be formed as side reaction products. Therefore, beside high efficiency of ammonia conversion, the selectivity of the process is a very important issue, which should be controlled by conditions of ammonia oxidation as well as suitable catalytic systems.

Fig. 1

The catalysts for the selective oxidation of ammonia should operate in a relatively low-temperature range (450-680 K) in order to reduce costs of additional heating of exhaust gases. Moreover, the effective catalysts of this process should be stable in the presence of water vapour and other typical components of waste gases (CO_x, SO_x).[68,76,77]

Different types of catalysts have been tested for the low-temperature process of ammonia oxidation into nitrogen and water vapour. The number of papers related to this process gradually increases. Catalytic materials tested in oxidation of ammonia can be classified in three main groups, such as: (i) noble metal based catalysts, (ii) transition metal oxide based catalysts and (iii) modified zeolites.

3.1. Noble metals

Noble metals were found to be active catalysts in the low-temperature process of ammonia oxidation. In general, noble metal based catalysts effectively operate at temperatures 470-630 K,[74,78-81] what fulfil expectations necessary for their applications in systems for waste gases treatment in cars and boilers. On the other hand noble metals, due to their redox properties, direct ammonia oxidation not only to N_2 but also to nitrogen oxides, which are products of deeper oxidation of NH_3. Another problem is related to a relatively high cost of noble metals, what make this group of the catalysts less attractive for potential large-scale applications. This problem can be partially solve by preparation of the supported catalysts, containing small amount of well dispersed noble metal species deposited on high surface area supports. The problem is also a relatively high volatility of some noble metals, what may result in fast deactivation of the catalysts.

Among noble metals the most promising results in the low-temperature process of selective ammonia oxidation to nitrogen were reported for platinum,[76,78,82-84] palladium,[18,82] rhodium,[18,67,85] iridium,[81,86,87] and ruthenium,[18,88] as well as multicomponent noble metal systems (e.g. Pt-Rh or Pt-Pd-Rh).[79,89-92]

Different types of catalytic supports, including Al_2O_3, TiO_2 or SiO_2, were used for deposition of various noble metals.[74,76,93] The Pt/Al_2O_3 catalysts were reported to be the most active in NH_3 oxidation process, however also low selective to dinitrogen.[74,80] Li and Armor studied catalytic activity of platinum, palladium and rhodium deposited on ZSM-5 and γ-Al_2O_3.[76] The loading of noble metal was in the range of 2.5-4.2 wt.%. It was reported that studied catalytic systems presented high efficiency in the ammonia oxidation process, however the selectivity to dinitrogen was not fully acceptable. The platinum based catalysts were non-selective (only

36 and 42% selectivity to N_2 at 573 K for Pt-ZSM-5 and PtO/Al_2O_3, respectively), while much higher selectivity to N_2 was found for palladium (81 or 87% at 573 K for Pd-ZSM-5 and PdO/Al_2O_3, respectively) and rhodium (84 or 82% at 573 K for Rh-ZSM-5 and RhO/Al_2O_3, respectively) based catalysts. Moreover, it was shown that catalytic performance of the studied samples is only slightly modified in the presence of wet reaction mixture (5 vol.% of water vapour) at higher temperatures. Analysis of the support influence on the catalytic performance of the studied samples leads to the conclusion that Pd and Rh deposited on ZSM-5 are more active comparing to the catalysts based on γ-Al_2O_3. However, it must be noted that various method were used for deposition of noble metals. In case of ZSM-5 ion exchange method, most often resulting in deposition of monomeric metal cations and possibly also other low-aggregated metal oxide species, was used, while in case of γ-Al_2O_3 impregnation method, possibly leading to more aggregated metal oxides species, was applied. Unfortunately, this effect as well as an influence of surface acidity of the supports used on catalytic performance of the studied samples was not discussed by authors. This gap was partially fulfilled by Sobczyk *et al.*, who studied ammonia oxidation in the presence of platinum doped γ-Al_2O_3.[78,83,94] First of all, it was reported that platinum supported on γ-Al_2O_3 was significantly less catalytically active in the low-temperature process of ammonia oxidation (below 400 K) than pure platinum sponge and larger platinum aggregates are more active compared to smaller Pt-species. It should be noted that in contradiction to the presented above studies of Li and Armor[76] higher selectivity to N_2 in the presence of the studied platinum based catalysts was reported. Moreover, it was suggested that N_2 is fast produced when there is a low surface coverage of the platinum surface with ammonia molecules, while in the case steady-state conditions, when the surface is fully covered relatively slow production of N_2 and N_2O was detected. Decreased activity of the Pt/γ-Al_2O_3 catalyst was explained by a preferential sorption of ammonia on the acidic alumina support, which was

found to be inactive in ammonia oxidation. Preferential sorption of oxygen occurs on the platinum surface and resulting in its fast covering by oxygen species, which together with strongly adsorbed NH_x species deactivate catalyst. In the temperature range of 400-520 K ammonia adsorbs on oxygen-rich platinum surface and therefore the reaction rate increases. Moreover, it was reported that oxygen spill-over to the alumina support is rather small. At temperatures higher than 520 K adsorbed oxygen and NH_x species are removed from the catalyst surface and efficiency of ammonia oxidation increases.

More detailed information about the nature of adsorbed species and their interaction with the platinum surface in the Pt(1 1 1) orientation was reported by Daramola and Botte, who analysed their structural, electronic and vibrational properties using Density Functional Theory (DFT) for the model Pt_{20} cluster.[95] The adsorption energies of the various possible surface species followed the trend: $H_2O < NH_3 < OH < NH_2 < NH < N$, with the weakest bonds formed by charge transfer and the strongest bonds formed by orbital overlap of unpaired electrons of the radicals and the d orbital of adjacent Pt atoms. Reported calculated frequency vibrations showed sufficient agreement with experimental observations. The obtained results are fully supported by the presented above studies of Sobczyk *et al.* who suggested that the surface NH_2 and NH species are so strongly bounded to the platinum surface that are responsible for catalyst deactivation.[94]

Long and Yang reported high catalytic activity of palladium doped ZSM-5 in the process of selective oxidation of ammonia to dinitrogen.[96] The catalyst was obtained by ion-exchange method using a solution of $Pd(NO_3)_2$ as palladium precursor, with the final Pd loading of 5.51 wt.%. Ammonia conversion obtained at 573 K was about 80% with a relatively low selectivity to dinitrogen (73%). Much better results were obtained for palladium introduced to Y zeolite.[97] A series of Pd-doped Y zeolites, with different noble metal loading (0.05-2.5 wt.%), were prepared by impregnation method using $PdCl_2$-HCl solution. The catalytic activity of modified zeolites increased with an increase in noble metal loading. Opposite order was found for selectivity to nitrogen, which decreased with an increase in palladium content (Fig. 2). Optimal catalytic properties were found for the samples with palladium loading of 1.0 and 1.5 wt.%, which at 573 K was able to convert 100% of ammonia with 96 and 95% of selectivity to dinitrogen, respectively. Studies of dispersion and aggregation of palladium species introduced to zeolite proved that for higher noble metal loading part of them exist in the form of aggregated species, which were found to be less active and selective in comparison with more dispersed palladium species. Moreover, important parameters of the studied catalyst are the low Si/Al molar ratio of 2.6 and therefore high concentration of the surface acid sites (about 1.3 mmol/g) as well as their high specific surface area (813-993 m^2/g) that allow for high dispersion of noble metal. It must be stressed that Pd-doped Y zeolites[97] seem to be the most promising in a group of the noble metal containing catalysts due to selective and effective ammonia oxidation to dinitrogen in a relatively low temperature range.

Fig. 2.

Burch and Southward studied Al_2O_3-supported noble metals as catalysts for selective oxidation of ammonia to dinitrogen in gases produced by biomass combustion.[67] It was reported that under conventional combustion conditions nitrogen oxides were the main product of ammonia oxidation. In contrast, it was shown that under oxygen deficient conditions it is possible to convert ammonia to dinitrogen with the Rh- or Ir-based catalysts, whereas for the Pt- or Pd-containing catalysts significantly lower selectivity to N_2 was obtained. These differences in selectivities were attributed to various state of noble metal surface under operating conditions. For the Rh- and Ir-based catalysts it was shown that under fuel-rich conditions, surface carbon (C_{ads}), derived from the dissociative adsorption of CO, results in self-poisoning toward CO and H_2 oxidation at low temperatures. However, at higher temperatures methanation of the C_{ads} is possible thought the surface reaction with H_{ads}, so that O_{ads} can react with NH_3 in a highly specific manner resulting in nitrogen oxides, which in the subsequent step are reduced by CO to N_2.

Chmielarz *et al.* studied noble metals (Pt, Pd and Rh) supported on calcined Mg-Al hydrotalcite.[98] Small amounts of noble metals (0.05-0.09 wt.%) were deposited by incipient wetness impregnation using acetylacetonates of suitable metals as precursors of catalytically active components. The highest conversion of ammonia was obtained in the presence of the Pt-containing catalysts (98% at 573 K), however selectivity to N_2 was relatively low (48% at 573 K). The Pd- and Rh-containing catalysts were less active (NH_3 conversion at 573 K was 89 and 66%, respectively) and more selective to N_2 (58 and 72% at 573 K, respectively). Thus, the selectivity of these catalysts was not acceptable. Moreover, it should be also noted that, similarly to previously presented studies,[76] the Pt-based catalysts were reported to be significantly less selective to dinitrogen in comparison to the Pd- and Rh-containing catalysts. Thus, it seems that platinum, independently on support used for its deposition, is non-selective in ammonia oxidation to dinitrogen.

Hung *et al.* studied multicomponent noble metal catalysts. An example is binary Pt-Rh system supported on γ-Al_2O_3 with a molar Pt:Rh ratio of 3:1.[79,89-92] Complete oxidation of ammonia, with only 56% selectivity to dinitrogen, was obtained at 673 K in the presence of this catalyst. Thus, as it was shown above,[76,98] the Pt-containing catalysts are non-selective in ammonia oxidation to dinitrogen and there is not significant modification of this feature for the binary noble metal systems containing platinum.

Gang *et al.* compared catalytic activity of powder silver and silver deposited on Al_2O_3 and SiO_2 in the process of low-temperature selective ammonia oxidation.[80] The supported catalysts were prepared by incipient wetness impregnation of $AgNO_3$ solution to obtain 10 wt.% of silver loading. Polycrystalline silver was prepared from Ag_2O powder. In a group of the silver-based catalysts, the highest activity was reported for Ag/Al_2O_3, especially for the hydrogen pre-treated sample (473 K). Complete ammonia oxidation with N_2 selectivity about 83% was obtained at 433 K in the presence of the reduced form of Ag/Al_2O_3.

Ammonia oxidation activity at low temperature was related to the catalyst ability to dissociative or non-dissociative adsorption of oxygen.[80] Authors reported at least four types of oxygen species produced when silver was oxidized (adsorbed molecular oxygen, adsorbed atomic oxygen, subsurface oxygen and bulk dissolved oxygen). Thus, it was suggested that a well-dispersed, high surface area silver catalyst with abundant lattice defects favours the low-temperature ammonia oxidation. Moreover, it was suggested that dissociation of oxygen is the rate-controlling step for ammonia oxidation over silver-based catalysts.[99] The selectivity to N_2, N_2O, and NO is mainly determined by the surface oxygen coverage and by reaction temperature. The adsorbed NO and N_2O species are actually inhibitors for ammonia oxidation and lower the surface oxygen coverage. The selectivity to dinitrogen is improved with the increasing surface concentration of these adsorbed species.

Studies of Ag/Al_2O_3 (with Ag loading of 10 wt.%) obtained by various methods (impregnation, incipient wetness impregnation and sol-gel) as catalysts for the selective ammonia oxidation were reported by Zhang *et al.*[100] It was suggested that the activity of silver catalysts is related mainly to the states of Ag species. Ag^0 was found to be the main active species at low temperature (T<413 K). On the other hand, Ag^+ was suggested to be the active species at higher temperatures. The catalysts with high surface areas and well-dispersed Ag^0 particles favoured greater activity at low temperatures, whereas their N_2 selectivity was not good. This effect is in full agreement with the presented above studies of Gang *at al.*, who showed that pre-reduction of the Ag/Al_2O_3 catalyst increased its activity in ammonia oxidation.[80] Moreover, it was reported that the catalysts with large Ag^0 particles provided higher N_2 selectivity but lower activity in the low-temperature range.[99] Thus, both silver particle size and the states of the Ag species seem to be important factors that influence the activity and N_2 selectivity of the catalysts in the process of ammonia oxidation.

Concluding this part, it could be stated that the noble based catalysts are catalytically active in a relatively low-temperature range (430-630 K) but selectivity to dinitrogen, reported for majority of these catalysts, is not fully rewarding. However, it must be stressed that among the noble metal based catalysts there is some very promising catalytic systems. Among them the most promising seems to be palladium deposited on H-form of Y zeolite, which combined high activity and selectivity in a broad temperature window (Fig. 2).[97] High efficiency of these catalysts is possibly related to high dispersion of palladium species on the zeolite surface (authors reported higher catalytic activity of monomeric Pd species than aggregated clusters) and optimal acidity of Y zeolite (Si/Al = 2.6) responsible for ammonia accumulation on the catalyst surface. It seems possible that ammonia chemisorbed on the zeolite surface is protected against unselected oxidation. On the other hand such chemisorbed ammonia molecules could be transported from acid sites of Y zeolite into reactive Pd-species by desorption – re-adsorption cycles.

Other promising catalysts are the supported Rh/Al_2O_3 and Ir/Al_2O_3 samples, which were effective in the selective conversion of NH_3 in gases produced by biomass combustion. More detailed studies of these catalytic systems should be done in the future. Catalytic results of various noble metal based systems for selective ammonia oxidation are compared in Table 1.

The main objectives in these studies of noble based catalysts for selective ammonia oxidation are: (i) increasing selectivity to N_2 in the low-temperature range; (ii) development of the catalysts stable under conditions of real waste gases converters; (iii) development of active, selective and stable catalytic systems with decreased loading of noble metals in order to reduce the cost of the catalysts; (iv) testing of catalytic systems in the structured from (e.g. monolith).

3.2 Modified zeolites

Zeolites have been intensively studied as catalysts and catalytic supports for selective oxidation of ammonia to dinitrogen. Attractiveness of zeolites as catalytic materials is related to their uniform microporous structures with different size and shape of pores and caves, presence of surface acid sites of uniform strength and location as well as ion-exchange properties, which allow introducing catalytically active components in highly dispersed form. Recent studies are focused, among other, on the synthesis of zeolitic materials with the hierarchical micro- and mesoporous structure with improved internal diffusion of reactants, especially in case of larger bulky molecules,[102,103] as well as selective incorporation of the catalytically active components into the zeolite framework.[104,105]

The selective oxidation of ammonia to dinitrogen in simulated biogas containing a large excess of CO and H_2 was examined using zeolite catalysts.[106] Among the examined zeolitic materials the highest N_2 yield (about 85% at 750-850 K) in the presence of Beta zeolite, lower dinitrogen yield (75% at 847 K) was obtained for ZSM-5, while HY was both less active and selective. It was suggested that N_2 is formed via an internal selective catalytic reduction between nitrogen oxides, derived from direct oxidation of NH_3, and NH_3 adsorbed on Brønsted sites of zeolite. Thus, it could be concluded that zeolites non-modified with metal species effectively operate in the process of selective ammonia oxidation only in the high temperature range, and therefore could be considered for ammonia conversion only in hot flue gases.

Modifications of zeolites with metals activate them for the low-temperature ammonia oxidation. In a previous section some examples of noble metal modified zeolites were presented and discussed.[76,95,97] More results of selective catalytic oxidation of ammonia in the presence of transition metal modified zeolites are presented in this section.

Catalytic performance of various transition metals introduced to Y zeolite by ion-exchange method in the process of selective ammonia oxidation was compared few decades ago by II'chenko.[82] The following activity order of metals introduced to Y zeolite was reported: Cu > Cr > Ag > Co > Fe > Ni ~ Mn. The selectivities to dinitrogen were relatively high and typically above 95% (with exception of AgY and CrY catalysts). High catalytic activity of copper introduced to Y zeolites was also reported by Gang *et al.*[107] Catalysts were prepared by introduction of copper to NaY zeolite (Si/Al = 2.4) by ion-exchange method using a solution of $Cu(NO_3)_2$. Depending on copper loading (3.7 or 8.4 wt.%) various ammonia conversion (54 and 88 %, respectively at 573 K) and selectivity to N_2 (98 % for both catalysts at 573 K) were obtained. Treatment of the catalysts with NaOH solution significantly increased ammonia conversion (100 % at 573 K for both the catalysts with 3.7 and 8.4 wt.% of copper loadings), while the high selectivity to dinitrogen was not changed. This activation effect was related to the formation of $[Cu\text{-}O\text{-}Cu]^{2+}$-like species or small copper oxide aggregates, which likely are the forms of the catalytically active centres operating at low-temperatures.

Similar studies, however with ZSM-5 zeolites as the catalytic support for deposition transition metal species, were reported by Long and Yang.[95] The catalysts were prepared by ion-exchange procedure using solutions of metal salts as precursors of catalytically active components and NH_4-ZSM-5 (Si/Al = 10) as support. The following activity order was reported: Fe > Cu > Cr > Pd > H-ZSM-5 > Mn > Ni ~ Co. For two most active catalysts, Fe-ZSM-5 and Cu-ZSM-5, very high selectivity to N_2 was obtained (at 723 K for both catalysts selectivities to N_2 were 100%, while ammonia conversions 99 and 97%, respectively). It was shown that although iron cations were exchanged with NH_4-ZSM-5 as Fe^{2+} ($FeCl_2$ was used for iron introduction) most of iron cations in Fe-ZSM-5 is present as Fe^{3+} ions after calcination, leaving only a small amount of Fe^{2+}. It was also been reported that both Cu^+ and

Cu^{2+} cations are present in Cu-ZSM-5. Thus, iron and copper in these catalysts exist in various oxidation states and the Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} ratios in the zeolite samples depend on the content of transition metal and preparation procedure. Moreover, it was suggested that the variable valence of metal cations in these two catalysts may be beneficial to oxygen adsorption and activation. Therefore, their high activity in the process of selective ammonia oxidation could be expected. On the other hand relatively lower activities, observed for Mn, Co, and Ni exchanged ZSM-5, could be attributed to their stabilized valence in zeolites, which is not favourable for oxygen activation. Both Fe-ZSM-5 and Cu-ZSM-5 were sensitive to the presence of SO_2 in reaction mixture but only Cu-ZSM-5 was deactivated in the presence of water vapour. The catalytic performance of Fe-ZSM-5 was only slightly affected when wet reaction mixture was used.

It should be noted that the activity order reported by II'chenko[82] for metals deposited on Y zeolite and Long and Yang[96] for zeolite ZSM-5 doped with transition metals species is not fully compatible. It could be related to the important role of the supports used (e.g. differences in nature, density and strength of surface acid sites and in porous structure) as well as form and aggregation of deposited metal species[107].

The important problem of the role of the zeolitic support on the overall catalytic performance of iron catalysts was analysed by Qi *et al.* [108] The following activity order was reported for zeolites modified with iron by $FeCl_3$ sublimation: Fe-ZSM-5 ≈ Fe-mordenite ≈ Fe-clinoptilolite > Fe-Y ≈ Fe-beta > Fe-ferrierite ≈ Fe-chabazite. Among the tested catalysts, the highest selectivity to N_2 was obtained for Fe-ZSM-5 (100% at 673 K with complete NH_3 conversion). The other Fe-modified zeolites were characterized by lower selectivity and activity. Also in this case authors related high catalytic activity of iron ions to their simultaneous existence in various oxidation states (Fe^{3+} and Fe^{2+}). Moreover, the highest activity of the Fe-ZSM-5 catalyst was related to a unique pore structure that consists of two intersecting channel systems with 10-member ring elliptical openings (0.52–0.57 nm in diameter). It was suggested that such narrow pore structure favours ammonia oxidation to dinitrogen. Another important feature is a relatively high stability of the Fe-ZSM-5 catalysts in the presence of SO_2 and water vapour, especially that obtained by $FeCl_2$ sublimation followed by two-step calcination (in He at 823 K for 6 h and then in air for 6 h).[109] For the Fe(2.5 wt.%)-ZSM-5 catalyst the ammonia conversion at 673 K decreased from 90 to about 84% after introduction of water vapour (2.5 vol.%) and SO_2 (500 ppm) in to reaction mixture. The NH_3 conversion was almost unchanged during next 5 h on-stream in the presence of water vapour and SO_2.[109] The inhibition effect of water vapour is possibly related to its competition with ammonia for these same adsorption sites.

It was suggested that the process of selective ammonia oxidation in the presence of the Fe-ZSM-5 catalysts proceeds by the formation of NO, as an intermediate, which in the next step is converted to N_2 by NH_3 (unreacted in the first step) according to equation 3.[108,109] This mechanism called internal selective catalytic reduction (i-SCR) is presented and discussed in chapter 4.

The consequence of the presented above results was a deeper analysis of the Fe-ZSM-5 catalysts, including the influence of kind of iron salts used for deposition of this metal.[109] Iron was deposited on NH_4-ZSM-5 using three different iron salts ($FeCl_2$, $FeSO_4$ and $Fe(NO_3)_3$) by incipient wetness impregnation method. Two calcination procedures were used: (i) one-step - calcination in air atmosphere and (ii) two-step - calcination in helium followed by calcination in air. It was reported that iron deposited using $FeCl_2$ as its precursor was more active comparing to other iron salts. Moreover, the catalysts obtained using two-step calcination procedure, especially in case of the sample obtained from $FeCl_2$, were more active in comparison to the catalysts calcined only in air atmosphere (one-step calcination). In this case 99% of ammonia conversion with 100% selectivity to dinitrogen was obtained at 723 K.

Detailed analyses of forms and aggregation of deposited iron species showed that applied methods resulted in introduction of iron cations in ion-exchange positions as well as more aggregated iron oxide species. Authors suggest that monomeric iron ions, formed in larger amounts during calcination in helium atmosphere (two-step calcination), are responsible for high catalytic activity of the studied catalysts. Moreover, simultaneous co-existence of Fe^{3+} and Fe^{2+} ions, which are able to form active oxygen ad-species (e.g. O_2^-, $O_2^{\delta-}$ where: $1 < \delta < 2$, O_2^{2-}) was reported. Authors showed high catalytic activity of the studied catalysts in the DeNOx process (equation 3) and suggested that the process of selective ammonia oxidation proceeds according to the internal selective catalytic reduction mechanism, i-SCR (see chapter 4).

The studies of iron modified zeolites as catalysts for selective ammonia oxidation were continued by Akah *et al.,* who compared studied ~~catalytic~~ activity of a series of Fe-zeolites prepared by incipient wetness impregnation, ion exchange and hydrothermal synthesis.[110] ZSM-5 and Beta zeolites as well as Amorphous Silica-Alumina (ASA) were used as supports for iron deposition. It was shown that the Fe-ZSM-5 catalysts prepared by incipient wetness impregnation were the most active for NH_3 conversion (e.g. 88% at 673 K for 2 wt.% of Fe loading) and selectivity to N_2 (100% at 673 K for 2 wt.% of Fe loading). Fe-ASA and Fe-Beta were less active and selective. Activity was found to depend on the amount of Fe and the nature of Fe species as well as the method used for the catalyst activation (reducing > inert > oxidizing). High activity of the studied catalysts was related to the simultaneous presence of Fe^{3+} and Fe^{2+} cations. It must be mentioned that the studied catalysts were deactivated in the presence of water vapour, which possibly rival with ammonia for these same adsorption sites.

The studies reporting zeolites modified with iron species as catalysts for selective oxidation of ammonia to dinitrogen show that the zeolitic support plays a very important role in catalytic activation of deposited iron species. The presented above studies report ZSM-5 as the most appropriate zeolitic support.[96,108-110] Moreover, an important issue is high dispersion of iron species, that should contain redox pairs Fe^{3+}/Fe^{2+} responsible for the catalytic activation of surface oxygen species. [95,108-110]

Fig. 3

Apart from iron and noble metal (presented in a previous chapter) doped zeolites also copper modified zeolites were reported to be effective catalysts for selective ammonia oxidation. An example are studies of Curtin and Lenihan, who reported high catalytic activity of copper exchanged Beta zeolites.[111] Catalytic activity increased with increasing copper loading. The most promising feature of these catalysts seems to be their high selectivity to dinitrogen (e.g. for the catalyst containing 6.6 wt.% Cu, the complete ammonia oxidation with selectivity to N_2 about 96% was obtained at 573 K). Moreover, introduction of water vapour into reaction mixture did not affect the selectivity to dinitrogen.

Catalytic results of various zeolite based systems for selective ammonia oxidation are compared in Table 2.

Table 2

Concluding, modified zeolites seem to be very interesting catalysts for selective oxidation of ammonia. The most promising catalytic system seems to be ZSM-5 modified with iron or copper. It was shown that method used for catalytically active component deposition is very important for the synthesis of the catalysts with optimal properties. The studied zeolite based catalysts, especially those modified with iron and copper, presented high selectivity to dinitrogen. However, the main problem is related to rather lower activity in the low-temperature range ($T < 673$ K). Another important issue that should be taken into account is the need to increase the tolerance of the zeolite based catalysts for water vapour and SO_2.

It must be remind that zeolites modified with noble metals, presented in a previous chapter, were active at temperatures below 673 K but were not enough selective to dinitrogen.

3.2. Transition metal oxides

A broad series of various metal oxides was compared with respect to their catalytic activity in the process of ammonia oxidation in early studies of Il'chenko, who reported the following activity order: MnO_2, Co_3O_4 > CuO > NiO > Bi_2O_3 > Fe_2O_3 > V_2O_5 > TiO_2 > CdO > PbO > ZnO > SnO_2 > ZrO_2 > MoO_3 > WO_3.[82] Similar activity order was proposed few years earlier by Germain *et al.*: Co_3O_4 > MnO_2 > Cr_2O_3 > Fe_2O_3 > CuO > NiO > V_2O_5 > MoO_3 > U_3O_8 > ThO_2 > WO_3 > SnO_2 > ZrO_2 > ZnO > Nb_2O_5 > Sb_2O_4 > Ta_2O_5.[112] It must be mentioned that in case of Co_3O_4 and MnO_2, which showed high catalytic activity, N_2O was the main product of ammonia oxidation.[82] There is a lot of more recent studies focused on the CuO and Fe_2O_3 based samples, which were reported to be simultaneously active and selective catalysts in early studies of Germain *et al.*,[112] and Il'chenko.[82]

Gang *et al.* studied the supported CuO/Al_2O_3 catalysts obtained by incipient wetness impregnation using a $Cu(NO_3)_2$ solution as copper precursor.[107] A series of three catalysts containing 5, 10 and 15 wt.% of copper was prepared. The best catalytic results in the process of selective ammonia oxidation were obtained for the sample doped with 10 wt.% of Cu (90% of NH_3 conversion with 97% selectivity to N_2 at 573 K). The samples with lower and higher copper content were significantly less catalytically active. This effect was explained by the formation of the surface $CuAl_2O_4$-like species, active in selective ammonia oxidation, which dominated in the catalyst containing 5 and 10 wt.% of copper. Most of the Cu^{2+} ions in these species are in a distored octahedral geometry, unlike bulk $CuAl_2O_4$, where about 60% are tetrahedral and 40% octahedral. An increase in copper loading to 15 wt.% resulted in the formation of bulk-like CuO, which was found to be less active comparing to $CuAl_2O_4$. Liang *et al.* extended these studies for analysis of copper based catalysts obtained by impregnation of Al_2O_3 with various copper salts - $Cu(NO_3)_2$, $CuSO_4$ and $(CH_3COO)_2Cu$ (Fig. 4).[113] In all the samples copper loading was 10 wt.%. It was found that crystalline CuO aggregates existed in the samples calcined at 673-1073 K. Calcination at 1073 K and higher temperatures resulted in gradual decrease in CuO and formation of the spinel $CuAl_2O_4$ phase. It was suggested that the $CuAl_2O_4$ phase is formed in the following thermal solid-solid reaction: $CuO + Al_2O_3 \rightarrow CuAl_2O_4$. Moreover, it was reported that type of copper precursor influences the contribution of various copper oxide species deposited on alumina support. The acetate precursor favoured the formation of crystalline CuO more than the nitrate precursor, while more $CuAl_2O_4$ phase was formed when sulphate precursor was used. Moreover, in contradiction to Gang *et al.*, it was suggested that CuO is more catalytically active in the process of selective ammonia oxidation than the $CuAl_2O_4$ phase.[107] Examples of the catalytic studies for the Cu/Al_2O_3 catalysts obtained from various precursors are presented in figure 4. It should be noted that Cu/Al_2O_3 is one of the most promising catalyst with respect to low-temperature activity and high selectivity to dinitrogen in a group of the transition metal based samples.

Fig. 4

The studies of the CuO/Al_2O_3 catalytic system were continued by Curtin *et al.,* who compared the influence of various promoters on catalytic performance of the supported CuO/Al_2O_3 sample (4.3 wt.% of CuO introduced by incipient wetness impregnation).[114] PbO (1 wt.%), NiO (1 wt.%), CoO (1 wt.%), SnO (0.6 wt.%) or Cr_2O_3 (0.4 wt.%) were tested as catalytic promotors. The positive influence was found for all tested promoters with an exception of Cr_2O_3. The best results were found for the $SnO-CuO/Al_2O_3$ and $CoO-CuO/Al_2O_3$ catalysts. Moreover, it was reported that addition of sulphur dioxide to the reaction stream sharply reduces the level of ammonia conversion, but has a beneficial effect on selectivity to nitrogen. This effect was explained by the formation of surface $CuSO_4$ and therefore limitation of the lattice oxygen availability for NH_3 to NO oxidation. Addition of water vapour to the reaction stream has a lesser effect on activity but is equally beneficial in terms of selectivity to dinitrogen. Authors suggest that it is related to competitive adsorption of H_2O and NH_3 molecules and therefore, restricted access of ammonia to surface oxidation sites. The internal selective catalytic reduction (i-SCR) mechanism was postulated for the process of selective ammonia oxidation in the presence of the studied catalysts.

Jones *et al.*,[115] and Darvell *et al.*,[68] compared catalytic performance of CuO (10 wt.%) deposited on Al_2O_3 with other metal oxides - NiO (10 wt.%), CoO (10 wt.%), Cr_2O_3 (10 wt.%), MnO_2 (7 wt.%) and Fe_2O_3 (8.5 wt.%) supported on alumina. Metal oxides were deposited on the Al_2O_3 support by impregnation method using solutions of suitable metal salts as their precursors. The catalysts were tested in the process of selective ammonia oxidation in gas stream simulating real gases produced by biomass combustion. Thus, reaction mixture apart from NH_3 and O_2 contained CO, CO_2, CH_4, H_2, H_2O, toluene and alternatively H_2S. The highest ammonia conversion in the absence of H_2S was obtained for Cr_2O_3/Al_2O_3 and NiO/Al_2O_3, which was 77 and 44% respectively at 973 K. The obtained results clearly show that additional components introduced to reaction mixture participate in the process of ammonia oxidation and therefore activity orders proposed by Il'chenko,[82] and Germain *et al.*,[112] are not fully consistent with the activity order presented in this work.[115] A very interesting effect was observed for CuO/Al_2O_3 after introduction of H_2S to the reaction stream. In this case ammonia conversion increased from 40 to 90% at 973 K. This effect was explained by oxidation of H_2S to SO_2 and then to SO_3 catalysed by CuO/Al_2O_3, which finally can be bind to the catalyst surface in the form of sulphates. Authors suggest that the surface sulphate species increase the activity of Cu/Al_2O_3 in NH_3 oxidation.[115] Moreover, it was suggested that the mechanism of the NH_3 oxidation reaction is possibly depend on the availability of oxygen through the relative rates of H_2, NH_3 and H_2S oxidation reactions.

Similar studies, including the influence of various components of flue gases, were reported by Kušar *et al.,* who compared catalytic performance of various metal oxides deposited on Al_2O_3

in selective oxidation of ammonia under fuel-lean and fuel-rich conditions in a monolith laboratory scale reactor.[116] The catalysts were obtained by deposition of Fe_2O_3 (5 wt.%), MnO_2 (5 wt.%), CuO (20 wt.%), Pt-CuO (1 and 20 wt.%, respectively) and Rh (2 wt.%) on Al_2O_3 by impregnation method using solutions of suitable metal nitrates (in case of platinum - $Pt(NH_3)_4(OH)_2$) as precursors of catalytically active components. Gas stream apart from NH_3 and O_2 contained: N_2, H_2, CO, CO_2, CH_4 and alternatively H_2O. The main difference between fuel-lean (F-L) and fuel-rich (F-R) conditions was related to different contribution of oxygen in gas streams (18.2 vol.% for F-L and 1.2 vol.% for F-R). Oxidation of ammonia performed under F-L conditions resulted mainly in the formation of NO and N_2O. An exception was Fe_2O_3/Al_2O_3, which presented relatively high selectivity to N_2 (93% for NH_3 conversion of 65% at 633 K). On the other hand, for the process performed under F-R conditions in the presence of CuO/Al_2O_3 and $Pt\text{-}CuO/Al_2O_3$, the selectivities to dinitrogen were much higher but ammonia conversions much lower in comparison to F-L conditions. For CuO/Al_2O_3 the selectivity to N_2 was 99% for NH_3 conversion of 75% at 573 K, while for $Pt\text{-}CuO/Al_2O_3$ the selectivity to N_2 was 88% for NH_3 conversion of 36% at the same temperature. Thus, introduction of platinum to CuO/Al_2O_3 decreased both NH_3 conversion and N_2 selectivity. Moreover, it must be mentioned that Fe_2O_3/Al_2O_3 surprisingly was less selective to N_2 under F-R conditions then under F-L conditions, while Rh/Al_2O_3 was catalytically inactive under F-R conditions at temperatures below 873 K. The differences in the performance of the studied catalysts under F-R and F-L conditions are related to activity and selectivity of the catalysts not only in selective ammonia oxidation but also in oxidation of CO, H_2 and CH_4. In case of F-R conditions, where the oxygen content in reaction mixture is very low, O_2 is fully consumed for CO and H_2 oxidation and possibly also for CH_4 oxidation at higher reaction temperatures. On the other hand, when the experiment was performed under F-L (oxygen excess) the performance of the catalyst and its interaction with various components of the reaction mixture determine ammonia conversion and distribution of the reaction products.

These studies again clearly show that efficiency of the catalytic systems in selective ammonia oxidation strongly depends on composition of the reaction mixture and the results obtained for the gas mixture containing only NH_3 and O_2 diluted in inert gas cannot be simply extrapolated for real flue gases (e.g. produced by biomass combustion or car engines).

An interesting concept of the catalyst for the low-temperature ammonia oxidation, based on CuO-CeO_2 oxide system was proposed by Hung. [117,118] Cerium dioxide in copper catalyst can be assumed to promote the formation of the active phase of CuO under the conditions of ammonia oxidation. Moreover, CeO_2-based materials, due to the Ce^{3+}- Ce^{4+} redox couple, can act as oxygen buffers by storing/releasing O_2.[119] The samples with different CuO:CeO_2 molar ratios (6:4, 7:3, 8:2 and 9:1) were prepared by co-precipitating copper nitrate and cerium nitrate using K_2CO_3 as precipitating agent, followed by calcination of the obtained precipitates at 773 K.[117,118] The highest ammonia conversion (99% at 673 K) and selectivity to N_2 was obtained for the sample with the CuO:CeO_2 molar ratio of 6:4. Author reported that the efficiency of ammonia conversion increased with reaction temperature and as the residence period was reduced. Moreover, a Langmuir-Hinshelwood model incorporating a first-order reaction was suggested to adequately represent the NH_3 oxidation, which showed fairly good agreements with experimental data. The apparent activation energy, determined by authors, is 27.8 kJ/mol.

One of the main drawbacks of the co-precipitated CuO-CeO_2 studied by Hung was their relatively low surface area that limited the rate of ammonia conversion.[117,118] This problem was solved by Wang *et al.,* who studied CuO-CeO_2 oxide system obtained by the surfactant directed method.[120] Cetyltrimethyl ammonium bromide (CTAB) was used as surfactant, while $Cu(NO_3)_2$ and $Ce(NO_3)_3$ solutions were used as precursors of mixed metal oxides. The samples with the Cu content of 6, 8, 10 and 12 wt.% were calcined at various temperatures (673, 773, 873 and 973 K). The BET surface area the samples calcined at 673 or 773 K is above 130 m^2/g. The $CuO-CeO_2$ oxide system obtained by the surfactant directed method was more catalytically active in the process of selective ammonia oxidation than the analogous oxide system prepared by conventional wet impregnation method. In a series of the catalysts obtained by the surfactant directed method the highest activity was found for the sample containing 10 wt.% of Cu calcined at 773 K. The complete NH_3 conversion with selectivity to N_2 above 95% was obtained at about 523 K, thus this catalyst operates at temperatures lower than the co-precipitated $CuO:CeO_2$ catalysts studied by Hung. [117,118] The high catalytic activity of this sample was ascribed to the high molar ratio of the finely dispersed CuO species and small particle size of CeO_2 as well as strong synergetic interaction between copper oxide species and ceria particles. It was suggested that this synergetic interaction between CuO and CeO_2 changes the chemical state in near-surface region and the strong electron state interaction enhances the adsorption and activation of NH_3 molecules. The activation of ammonia by ceria led to the formation of N_2 and NO_x, followed by reduction of NO by NH_3 to N_2 selectively catalysed by CuO. Moreover, the lattice oxygen provided by Cu-O-Ce solid solution could also react with the activated ammonia intermediates (NH_x) to produce N_2 and N_2O. When the lattice oxygen was completely consumed, oxygen from gas phase could refill the oxygen vacancies in Cu-O-Ce solid solution to maintain the Ce^{4+}- Ce^{3+} redox couple. Thus, the presence of the Cu-O-Ce solid solution promotes the activation of oxygen from gas phase as well as the formation and migration of the lattice oxygen, which is an important for the effectiveness of the selective ammonia oxidation process.

Hung *et al.* continued the studies of two-component copper oxide containing systems for the low-temperature ammonia oxidation by replacing for CeO_2 by La_2O_3.[121] A series of $CuO-La_2O_3$ mixed metal oxides with various Cu:La molar ratios (6:4, 7:3, 8:2 and 9:1) was prepared by co-precipitation method using $Cu(NO_3)_2$ and $La(NO_3)_2$. The best catalytic results were obtained for the sample with the Cu:La molar ratio of 8:2 (93% of NH_3 conversion with selectivity to N_2 about 53% at 673 K). Thus, the obtained catalytic results due to low selectivity to dinitrogen are significantly less promising in comparison to $CuO-CeO_2$ oxide system.[116,118]

Interesting studies of the mesoporous CuO/RuO_2 system in the role of catalyst for selective ammonia oxidation were reported by Cui *et al.*[122] Mesoporous RuO_2 and CuO/RuO_2 materials were prepared by one-step co-nanocasting method using KIT-6 as hard template. KIT-6 template was impregnated with a methanol solution of $Cu(NO_3)_2{\cdot}3H_2O$ and $RuCl_3$. After ethanol evaporation, the ruthenium-copper/silica composite was kept under ammonia vapour to convert ruthenium precursor into metal hydroxide. In the next step the obtained sample was calcined at 773 K. Finally, the silica template was removed by treatment of the sample in NaOH solution. The CuO/RuO_2 catalysts with CuO content in the range from 0 to 30 wt.% were synthetized. The obtained samples were characterized by BET surface area about 100 m^2/g and pore volume in the range of 0.19-0.28 cm^3/g. In general, this type of catalytic materials presented a very promising catalytic performance with respect to high catalytic activity in the low-temperature ammonia oxidation, high selectivity to dinitrogen and high catalytic stability. Among the studied catalysts the best results were obtained for the CuO/RuO_2 catalysts containing 10 wt.% of CuO (complete NH_3 oxidation with selectivity to N_2 about 95% was achieved at 453 K). Thus, this catalyst is one of the most active and selective reported in scientific literature. Authors suggest that the enhanced catalytic activity of CuO/RuO_2 system is related to the synergetic catalytic effect between CuO and RuO_2.[122] The (1 1 0) surface of stoichiometric RuO_2 is highly susceptive to NH_3 molecules because it possesses numerous dangling bonds and exposes coordinatively unsaturated $Ru_{\text{-cus}}$ atoms able to adsorb NH_3 molecules ($NH_{3\text{-cus}}$) and oxygen atoms ($O_{\text{-cus}}$).[123] The interaction between these adsorbed species may result in the formation of N_{-cus} and H_2O. In the next step two N_{-cus} species may recombine with the formation of N_2 molecule or N_{-cus} may react with neighbouring O_{-cus} into NO_{-cus}. Finally, NO_{-cus} species can be reduced by NH_3 with the formation of N_2 and H_2O. The last reaction is catalysed by CuO.

Recently, these studies were extended for RuO_2-CuO/Al-ZrO_2 composite with the hierarchical porous structure containing RuO_2 and CuO nanoparticles homogeneously dispersed on the support surface.[124] The composite catalyst, synthesized by the hydrothermal and wet impregnation method, presented high and stable catalytic activity for the process of selective ammonia oxidation (NH_3 was completely oxidized with 100% N_2 selectivity at 468 K in the presence of the Ru(20 wt.%)-Cu(20 wt.%)/Al-ZrO_2 catalyst). Thus, the catalytic performance of this catalysts is similar to CuO (10 wt.%.) deposited on mesoporous RuO_2 reported in earlier studies of Cui *et al*. [122] The high performance of the RuO_2-CuO/Al-ZrO_2 composite catalyst was attributed to the synergetic catalytic effects of the Al-ZrO_2 matrix and RuO_2 nanoparticles, which are able to activate the oxygen and ammonia molecules into O_{-cus} and NH_{3-cus} by the large number of oxygen vacancies in the Al-doped matrix and the active (1 1 0) surface of RuO_2, respectively. Subsequently, CuO plays a successive role of catalysing the NO reduction, an undesired intermediate during the NH_{3-cus} oxidation by O_{-cus}, into N_2.

Other interesting studies reporting application of the copper oxide base catalysts for selective oxidation of ammonia were presented by Song and Jiang, who deposited CuO on carbon nanotubes (CNTs).[125] Before CuO deposition CNTs were treated with concentrated HNO_3 (at 353, 373, 393, 413 or 433 K for 5 h) in order to produce surface defects. Copper was introduced in the form of $Cu(CH_3COO)_2$ solution, which during calcination (623 K in He) was transformed to CuO. In general, the CuO/CNT catalysts presented excellent catalytic properties in the low-temperature ammonia oxidation with respect to high activity and selectivity to dinitrogen. It was reported that the CuO/CNT samples with the highest concentration of defeats in CNTs were the most catalytically active and selective. E.g. for the CuO supported on CNT treated with concentrated HNO_3 at 413 K complete ammonia conversion occurred at about 450 K with selectivity to N_2 above 98%. Authors suggest that CNTs with high defect density facilitated the reduction of CuO due to profound impact of the defects upon electronic transport properties and production of electron acceptor-like states within graphitic materials. Thus, the defects could promote electron transfer in the reduction process, which destabilizes the Cu-O bonds and facilitates the reduction of CuO to Cu^0 and therefore, activate CuO in the ammonia oxidation process. It should be noted that although the CNT based catalysts presented excellent catalytic properties in the low-temperature ammonia oxidation process there is a serious risk of carbon nanotubs destruction in case of catalyst overheating in a presence of oxygen containing gases.

Mayer *et al.* studied an effect of pressure on reaction path and distribution of reaction products in the ammonia oxidation process over the polycrystalline copper foil by means of in-situ NEXAFS (near-edge X-ray absorption fine structure) spectroscopy in the soft X-ray range.[126] It was shown that at temperatures 570 and 670 K and at a total pressure of 40 Pa a fast deactivation of copper in the ammonia oxidation occurred due to surface nitride formation, whereas at 120 Pa no decrease in activity was observed and no copper nitride was formed. During reaction carried out under a pressure of 120 Pa no surface imide species was detected. Moreover, authors suggest that CuO is the active phase in NH_3 oxidation to NO, whereas Cu_2O catalyses ammonia oxidation to dinitrogen.

In the next step Mayer *et al.* extended their studies for deposited copper clusters prepared with the inert gas aggregation technique.[127] It was reported that copper (I) nitride, which is responsible for deactivation of copper, was formed on both copper polycrystalline foil as well as copper clusters. Thus, it was assumed that the experiments and results obtained with copper foil as a model catalyst in ammonia oxidation was exemplary for the reaction behaviour of copper clusters or small particles.

There are some papers reporting studies of pillared layered clay minerals in the role of catalysts for selective ammonia oxidation.[128,129] Chmielarz *et al.* studied alumina pillared vermiculite and phlogopite as supports of the catalysts for selective ammonia oxidation.[128] Copper and iron were introduced to pillared clays by an ion exchange method using aqueous solutions of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ as precursors of catalytically active components. In the calcined samples (723 K) copper was present mainly in the form of mononuclear ions, while iron formed oligomeric and bulky metal oxide species. The best catalytic performance presented pillared vermiculite modified with copper. However, the catalysts effectively operated only in the high temperature range (complete ammonia oxidation with nearly 100% of N_2 selectivity was obtained at 773 K).

In order to increase the surface area and porosity of the clay mineral based catalysts another way of their pillaring, based on surfactant directed method, was applied by Chmielarz *et. al.*[129] Synthetic saponite was intercalated with silica pillars by surfactant directed method using hexadecyltrimethylammonium chloride and hexadecylamine as surfactants and co-surfactants, respectively, while tetraethyl orthosilicate (TEOS) was used a silica source. The obtained materials, called porous clay heterostructures (PCHs), directly after calcination were treated with ammonia in order to protect ion-exchange properties of the modified clay samples. Copper and iron were introduced to the PCH support by an ion exchange method using aqueous solutions of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ as precursors of catalytically active components. In the calcined samples (823 K) copper and iron were present in highly dispersed forms (monomeric cations and small oligomeric metal oxide aggregates). The PCH supports modified with transition metals were found to be the active catalysts of selective oxidation of ammonia. The Cu-containing samples, especially the catalyst with higher copper loading, operated at lower temperatures (complete NH_3 oxidation at 673 K) than PCHs modified with iron (complete NH_3 oxidation at 823 K). The selectivity to dinitrogen obtained over the studied catalysts was very high and did not drop below 90% in the studied temperature range (423-823 K).

Thus, it could be concluded that the studied clay based catalysts are very interesting for potential application in conversion of ammonia in hot gas streams, mainly due to high selectivity to dinitrogen in a broad temperature range.[128,129]

Recently, a lot of attention was paid on hydrotalcite-like materials as possible catalysts or precursors of mixed metal oxide catalysts for various processes, including selective ammonia oxidation.[98,130-132]

Hydrotalcites, also called layered double hydroxides (LDHs), are characterized by the brucite-like structure [$Mg(OH)_2$], where the octahedra of Mg^{2+} (six-coordinated to OH^-) form doubled layers, which are held by hydrogen bonding. In case of hydrotalcite part of Mg^{2+} ions is replaced by trivalent Al^{3+} cations, what results in a positive charging of the brucite-like layers. This positive charge is compensated by anions (typically CO_3^{2-}), which together with water molecules are located in the interlayer space of the material. Furthermore, some of the Mg^{2+} as well as Al^{3+} ions can be replaced by other di- (e.g. Cu^{2+}) and trivalent- (e.g. Fe^{3+}) cations, respectively. Such samples are called hydrotalcite-like materials. Calcination of hydrotalcite-like materials results in their decomposition and formation of thermally stable mixed metal oxides characterized by a relatively high surface area and homogeneous distribution of metal cations.[133] Taking into account these properties and additionally, a large number of various metals, which can be incorporated into the brucite-like layers, the hydrotalcite-like materials are very promising for the possible applications in catalysis.

Chmielarz *et al.* studied hydrotalcite derived mixed metal oxides containing apart from Mg^{2+} and Al^{3+} cations also other ions: Cu^{2+} (5, 10, 20 mol.%), Co^{2+}(5, 10, 20 mol.%), Ni^{2+} (10 mol.%), Fe^{3+} (10 mol.%) and simultaneously both Cu^{2+}- Co^{2+} (2.5-2.5, 5-5, 10-10 mol.%).[130] Hydrotalcite-like materials were transformed into mixed metal oxides by calcination at 773 K. The highest activity in the process of selective ammonia oxidation was observed for the copper containing catalysts (e.g. for the catalysts with 5 mol.% Cu complete ammonia oxidation with 88% selectivity to N_2 was obtained at about 673 K). The samples modified with cobalt were less active, while the catalysts modified with nickel or iron showed poor catalytic performance in the studies reaction. Distribution of ammonia oxidation products strongly depends on transition metal loading. The highest selectivities towards nitrogen were obtained for the catalysts with the lowest transition metal content. An increase in transition metal content resulted in a decrease of the selectivity to dinitrogen and an increase in the selectivity to nitric oxide. The reaction temperature is also a very important factor affecting distribution of ammonia oxidation products. Dinitrogen was a dominant reaction product at lower temperatures, while at higher temperatures the selectivity to NO increased. The studies of reaction mechanism showed that distribution of ammonia oxidation products is dependent on reducibility of transition metal oxide dispersed in Mg-Al-O matrix. In the low-temperature range parallel scheme of product formation was proposed, while at higher temperatures NO is reduced by ammonia with the formation of N_2 and N_2O (i-SCR mechanism).

In the next step of these studies hydrotalcite originated metal oxide Mg-Cu-Fe system containing two transition metals was prepared and tested in selective ammonia oxidation. [134] A series of hydrotalcite-like materials, obtained by co-precipitation method, with the Mg:Cu:Fe molar ratios of 2:1:1, 2:0.75:1, 2:0.5:1, 2:0.25:1, and 2:0:1 was calcined at 873 K. MgO, CuO, Cu_2O, Fe_3O_4 and $MgFe_2O_4$ phases were identified in the calcined samples. For all the copper containing catalysts high activity in the process of low-temperature selective ammonia oxidation, which only slightly increased with an increase in Cu content, was reported. Also copper content in the studied catalysts slightly influence their selectivity to N_2.

Moreover, the Mg-Cu-Fe mixed metal oxide catalysts were only slightly deactivated in the presence of water, which possibly competes with ammonia for the same adsorption sites. Similarly to the presented above studies of the hydrotalcite originated Cu-Mg-Al catalysts,[130] also for Mg-Cu-Fe the i-SCR mechanism of the ammonia oxidation process was suggested. Copper oxide species played a role of components active in selective reduction of NO with ammonia to dinitrogen.

The presented above studies were extended for the other hydrotalcite originated Cu-Mg-Al, Cu-Mg-Fe and Cu-Zn-Al mixed metal oxide catalysts.[132] The samples with the Cu:Mg(Zn):Al(Fe) molar ratio of 0.6:1.4: 1.0 were obtained by co-precipitation method. Cu-Mg-Fe and Cu-Zn-Al hydrotalcite-like materials calcined at 873 K CuO, MgO, Fe_2O_3, ZnO and mixed oxides with spinel phases were identified. An increase in calcination temperature to 1173 K resulted in a significant increase in the crystallinity of the phases formed at lower temperatures and additionally, the formation of Cu_2MgO_3 phase. The highest catalytic activity was reported for Cu-Mg-Al, Cu-Zn-Al and Cu-Mg-Fe oxides systems calcined at 873 K. For these samples the complete NH_3 conversion was obtained at about 650 K with selectivities to N_2 about 90%. The samples calcined at 1173 K were significantly less active probably due to sintering of crystallites and formation of less active transition metal containing spinel phases. Catalytic performance of the studied samples was related mainly by the presence of copper oxide phases and their redox properties. The catalysts containing easily reduced copper oxide species presented not only catalytic activity at lower temperatures but also significant decrease in selectivity to dinitrogen at higher temperatures.

Apart of copper containing catalysts, which are the most intensively studied in a group of transition metal based catalysts for selective ammonia oxidation, there is also some reports presenting other metal oxide catalytically active in this process. Selected examples of such catalytic systems are presented below.

Lee *et al.* studied manganese ore (composed of β-MnO_2 as main component and small amounts of Fe_2O_3, Al_2O_3, CaO, MgO and SiO_2) as catalyst for selective low-temperature ammonia oxidation.[135] As the reference catalysts pure manganese oxides such as MnO_2 and Mn_2O_3 were used. The catalytic activity of manganese ore was relatively high (complete NH_3 oxidation with N_2 selectivity about 75% at 500 K) and was related to the promoting effect of minor components (e.g. Fe_2O_3, Al_2O_3). At temperature below 520 K, selectivity into N_2 was in the following order: Mn-ore>MnO_2 >Mn_2O_3, while the reverse order was reported for catalytic activity.

The promotional effect of vanadium on Ce/TiO_2 catalyst for the selective catalytic oxidation of NH_3 to N_2 was studied by Lee and Hong.[136] The vanadium doped Ce/TiO_2 catalysts were prepared by a wetness impregnation method, using commercial anatase (TiO_2) as support and solutions of ammonium metavanadate (NH_4VO_3) and cerium nitrate hydrate ($Ce(NO_3)_3·6H_2O$) as precursors of vanadium and cerium, respectively. Vanadium or cerium were deposited by subsequent impregnations (e.g. 10Ce/2V/TiO_2, catalysts containing 10 and 2 wt.% of Ce and V, respectively) or co-impregnation (e.g. 10Ce-2V/TiO_2). It was found that the addition of vanadium on the Ce/TiO_2 catalyst greatly enhanced its activity (96% of NH_3 conversion with 90% N_2 yield over 10Ce/2V/TiO_2 catalyst at 573 K). Addition of vanadium to Ce/TiO_2 resulted in increased dispersion of Ce^{4+} species on TiO_2. Moreover, vanadium enhanced the redox properties, which was beneficial to the selective ammonia oxidation. It was suggested that abundant adsorbed NH_2 species have a promoting effect on the formation of NO_x species, and it could accelerate the reaction with adsorbed NH_3 or NH_2 species and NO_x species, according to the internal SCR (i-SCR) mechanism. Finally, it must be mention that addition of vanadium to the Ce/TiO_2 catalyst, not only improved its catalytic activity but also greatly improved its SO_2 tolerance.

Catalytic results of various transition metal oxide based systems for selective ammonia oxidation are compared in Table 3.

Table 3

Concluding, transition metal based catalysts are very promising for application is selective oxidation of ammonia to dinitrogen. Among them the most interesting are the alumina supported copper catalysts (CuO/Al_2O_3). It was shown that various parameters of the catalysts synthesis, including type of copper salt used as precursor of active phase, content and type of copper species present in catalyst, presence of promotors, strongly influence their catalytic performance in the studied process. Majority of the presented studies is focused on low-temperature activation of the transition metal based catalysts as well as development catalysts operating under specific real conditions (e.g. conversion of ammonia in gases produced by biomass combustion) to fulfil requirements necessary for their commercialization.

4. Mechanisms of the ammonia oxidation process

Determination of the ammonia oxidation mechanism in the presence of various types of catalysts is an important scientific problem studied by many researchers. Such studies should result in better understanding of the chemical nature of this process as well as in determination of the catalyst properties responsible for their high activity, selectivity and stability. Various reaction mechanisms have been proposed for different types of the catalytic materials and processes performed under different conditions, however, in general there is agreement that the first step of the reaction is ammonia adsorption. The type of acid sites, Brønsted or Lewis, that adsorb ammonia molecules is depended on type of the catalyst used.[68,137] E.g. Amblard *et al.*,[106] and Jabłońska *et al.*,[97] reported adsorption of ammonia in the form of NH_4^+ cations on Brønsted acid sites in the zeolite based catalysts.

Fourier transform infrared spectroscopy (FT-IR) conducted for different types of the catalytic materials, such as Ag/Al_2O_3, $Ru/CeZrO_2$, V_2O_5, V_2O_5-WO_3/TiO_2, Fe_2O_3/TiO_2,[138-141] led to the concussion that upon heating, adsorbed ammonia is activated by abstraction of hydrogen atoms to form -NH_2, -NH or -N. Such intermediates, depending on the availability of oxygen can be converted in various reaction pathways to produce N_2, NO and N_2O.

Zawadzki proposed the mechanism involving in the first step formation of imide species by reaction with atomic oxygen (equation 8).[142] In the next step imide species are subsequently oxidised by atomic oxygen to nitrosyl (equation 9) intermediate. N_2 and H_2O are formed in the reaction between nitrosyl and imide (equation 10). Other final products such as NO, N_2O and H_2O are formed as a result of the reactions involving intermediate compounds: HNO, NH, HNO_2 and O_2 (equations 11, 12a, 12b).

$$NH_3 + O \rightarrow NH + H_2O \qquad (8)$$

$$NH + O \rightarrow HNO \qquad (9)$$

$$HNO + NH \rightarrow N_2 + H_2O \qquad (10)$$

$$2\ HNO \rightarrow N_2O + H_2O \qquad (11)$$

$$NH + O_2 \rightarrow HNO_2 \qquad (12a)$$

$$HNO_2 \rightarrow NO + OH \qquad (12b)$$

As it can be seen, the formation of active atomic oxygen species is the crucial reaction step of this mechanism. Active atomic oxygen species (O) are produced by recombination of OH species (equation 13) and by O_2 dissociation (equation 14):

$$2\ OH \rightarrow H_2O + O \qquad (13)$$

$$O_2 \rightarrow 2\ O \qquad (14)$$

Imide mechanism was proposed for noble metals, such as Pt and Rh.[143,144] An example proving the imide mechanism proposed by Zawadzki are studies of Mieher and Ho for the platinum catalyst using electron energy loss spectroscopy (EELS).[145] These studies were performed as functions of both NH_3 coverage and annealing temperature for various NH_3 exposures on clean, atomic oxygen and molecular oxygen covered Pt(111) surfaces. OH, NH and NH_2 were identified by EELS as stable intermediate species. Consequently, NO and N_2 were formed by recombination of N and/or O atoms. Unfortunately, the formation of N_2O was not mentioned in this work. Moreover, DFT simulations were used to study the mechanism of ammonia oxidation over Pt(100),[146] Pt(111),[143] and Rh(111),[144] surfaces. The obtained results led to the conclusion that the reaction proceeds via an imide mechanism, in which NH_3 is progressively dehydrogenated by adsorbed O or OH species and the resulting N atoms are converted to the reaction products (N_2, NO, N_2O).

As it was mentioned above the reaction mechanism depends on reaction conditions. The other mechanism, called hydrazine (N_2H_4) mechanism, was proposed for the process performed under conditions of the limited O_2 concentration. In this case the only oxygen available was surface lattice oxygen (O^{2-}) of transition metal oxides.[137,140,147]

$$NH_3 + O \rightarrow NH_2 + OH \qquad (15)$$

$$NH_2 + NH_2 \rightarrow N_2H_4 \qquad (16)$$

$$N_2H_4 + O_2 \rightarrow N_2 + H_2O \qquad (17)$$

$$2\ N_2H_4 + 3\ O_2 \rightarrow 2\ N_2O + 4\ H_2O \qquad (18)$$

$$NH_2 + O_2 \rightarrow NO + H_2O \qquad (19)$$

In the first step surface amide species are formed by abstraction of hydrogen atom from adsorbed ammonia molecules by surface oxygen (equation 15). Recombination of surface amide species results in the formation of hydrazine-type (NH_2-NH_2) intermediate (equation 16) and then its subsequent oxidation by O_2 to N_2 (equation 17) and/or N_2O (equation 18). NO is formed by the reaction between surface amide and O_2 from gas phase (equation 19).

The formulation of the hydrazine mechanism was possible by an early study of Williamson *et al.* based on IR and EPR measurements.[148] It was suggested that surface amide (NH_2) species, formed by ammonia oxidation on Cu^{2+} sites, are key intermediates in ammonia oxidation to dinitrogen on the zeolite Cu-Y catalyst. Further studies on reaction mechanism over copper oxide supported on titania suggested hydrazine (N_2H_4) as an intermediate in ammonia oxidation.[149] FT-IR spectra of adsorbed ammonia on CuO/TiO_2 in the absence of oxygen, after treatment to 423 K, gave rise to adsorbed hydrazine and nitroxyl species. Additional studies for surface adsorbed hydrazine revealed the formation of N_2. Moreover, it was shown that N_2 was the main product together with small amounts of NO and N_2O appearing from about 520 K. Hydrazine mechanism over CuO/TiO_2, together with other supported transition metal oxides, such as V_2O_5, V_2O_5/TiO_2, V_2O_5-WO_3/TiO_2, Fe_2O_3/TiO_2, was proved further by Ramis *et al.*[140,141] It was shown that adsorbed ammonia was oxidised by surface lattice oxygen of metal oxide catalysts during thermal treatment, resulting in the formation of amide species. Further studies for alumina-supported Ni, Cu, Cr, Mn, Fe and Co showed that oxygen pre-treatment prior to ammonia adsorption led to the formation of active oxidized surface species active in ammonia oxidation.[68] NH_2, N_2H_4 and HNO were found as intermediates formed on the O_2-pretreated CuO/Al_2O_3 catalyst in the absence of O_2.

Another mechanism of the selective ammonia oxidation, called internal selective catalytic reduction (i-SCR) mechanism, consists of two steps. In the first step part of ammonia is oxidized to NO, according (equation 6), while in the second step NO is reduced by unreacted in the first step ammonia, according to the SCR reaction (equation 3). The main products are N_2 and H_2O. In this step also the formation of N_2O is possible (equation 20):

$$4\ NO + 4\ NH_3 + 3\ O_2 \rightarrow 4\ N_2O + 6\ H_2O \qquad (20)$$

The i-SCR mechanism was proposed for a large number of the catalytic systems, such as Pt, Pd and Rh wires,[150] Pt_{95}-Rh_5 alloy,[146,151] (Pt, Rh, Pd)/Al_2O_3, (Pt, Rh, Pd)-ZSM-5,[76] Ag,[152] Ag/Al_2O_3,[138] Ag/SiO_2,[80] Fe_2O_3, Cr_2O_3, CeO_2,[147] Fe_2O_3-Al_2O_3, Fe_2O_3-TiO_2, Fe_2O_3-ZrO_2, Fe_2O_3-SiO_2,[153] CuO/Al_2O_3,[114] Ni/Al_2O_3,[154] hydrotalcite originated mixed metal oxides Cu-Mg-Fe,[134] and (Pt, Rh, Pt)/Cu-Mg-Al,[98] Beta, H-ZSM-5, HY,[106] Fe-ZSM-5,[110] and Pd-Y,[97] or $H_3PW_{12}O_{40}$.[155]

Various experimental methods and strategies were applied for proving of the i-SCR mechanism. Examples are catalytic tests performed with different space velocities for hydrotalcite derived Mg-(Cu)-Fe mixed metal oxides,[134] and palladium modified Y zeolites.[97] It was shown that for the test performed with a relatively low space velocity, the contact time of reactants with catalyst surface was long enough for both reaction step - ammonia oxidation to NO and subsequent reduction of NO by unreacted ammonia. In contrast, for experiments performed with increased space velocity, the contact time was too short for effective reduction of NO by ammonia, and therefore, selectivity to NO increased, while selectivity to N_2 decreased. Also, the catalytic tests with changing W/F (weigh to flow) from 0.0075 to 0.075 $g \cdot s \cdot cm^{-3}$ over CuO/Al_2O_3 showed that the amount of NO detected in the product stream increased as the contact time decreased.[114] This behaviour is consistent with NO being an intermediate in the reaction leading to the formation of dinitrogen. Moreover, there is some reports suggesting that overoxidation of ammonia leads also to the formation of NO_2.[114] An example are FT-IR studies of ammonia adsorbed on Pd-Y zeolites, which revealed, in addition to the presence of NO, also small amounts of NO_2.[97] Similar results were also reported for Fe-exchanged zeolites.[108] On the other side, Olofsson *et al.* proposed the formation of NO_2 as intermediate product over Pt/Al_2O_3, CuO/Al_2O_3 and $Pt\text{-}CuO/Al_2O_3$.[156] It was supposed that NO_2 interacts with surface NH_x species with N_2 production.

Jabłońska *et al.* reported the studies of hydrotalcite derived Cu-Mg-Fe mixed metal oxides in the role of the catalysts for selective ammonia oxidation (SCO) and selective reduction of NO with ammonia (SCR).[158] Comparison of both SCO and SCR processes for the same Cu-Mg-Fe mixed metal oxide, revealed that the ammonia oxidation process started at about 550 K, whereas conversion of NO in the SCR process was noticed at temperature lower by about 100 K. Therefore, it was concluded that oxidation of NH_3 into NO (equation 6) is the rate-controlling step for the process performed in the presence of Cu-Mg-Fe mixed metal oxide.

In general, transition oxide species are less active in ammonia oxidation than noble metals. Consequently, dehydrogenation of chemisorbed ammonia is much slower, and therefore the significant population of NH_{3-x} species on their surfaces is expected.[156] Such species can react with NO to form N_2, and/or N_2O (equations 21 and 22):[122,138]

$$NH_x + NO \rightarrow N_2 + H_2O \qquad (21)$$

$$NH_x + NO \rightarrow N_2O + H_2O \qquad (22)$$

In particular, Burch and Southward suggested that over Pt-CuO/Al_2O_3 under fuel-rich conditions (0.1% O_2), ammonia was partially reduced over CuO to produce NH_x.[159] While, under lean condition (2.1% O_2), NH_3 was again oxidized to NO on Pt, but formed NO was reduced to N_2 by NH_x on CuO.

Moreover, there are some studies indicating that ammonia oxidation proceeds according to different pathways, depending on reaction temperature. In particular, Zhang and He suggested that the ammonia oxidation process in the presence of Ag/Al_2O_3 proceeds at temperature below 415 K according to the imide mechanism, while above this temperature according to the i-SCR mechanism.[138] On the other hand an appearance of hydrazine and nitroxyl species on the ammonia pre-adsorbed Pd-Y catalyst at 523 K suggests that the ammonia oxidation process is more complicated and followed different parallel routes.[97]

Concluding, various mechanisms of the selective ammonia oxidation were proposed. The validity of these mechanisms depends on type of the catalyst used as well as reaction conditions. Moreover, it was shown that also parallel conversion of ammonia according to various mechanisms may occur.

5. Concept of bi-functional for the selective ammonia oxidation

The studies focused on determination of the possible mechanisms of ammonia oxidation over various types of catalysts resulted not only in better understanding the chemical nature of this process on the molecular level but also were inspiration for designing new types of catalytic materials. An example is the concept of bi-functional catalyst, which is a result of i-SCR (internal selective catalytic reduction) mechanism recognition for many catalytic systems.[76,98,122] According to the i-SCR mechanism (see previous section and Fig. 5) in the first step part of ammonia present in a reaction mixture is oxidised to NO_x (NO or/and NO_2), while in the second step NO_x is reduced by NH_3 (unreacted in first reaction step).

Fig. 5

Thus, effective catalysts, operating according to the i-SCR mechanism, should contain (i) component catalytically active in ammonia oxidation to NO_x and (ii) component active in reduction of NO_x to N_2 by NH_3. Noble metals are the most important candidates to be components active in oxidation of ammonia to NO_x.[74,76,80] On the other hand there are a lot of catalytic systems, including V_2O_5-TiO_2, Fe- or Cu-modified zeolites, active in selective reduction of NO_x with ammonia.[12] A very important issue in bi-functional catalysts designing is the ratio of components active in both processes. When there is an excess of the component active in ammonia oxidation to NO_x the lower selectivity to dinitrogen in the overall ammonia oxidation process could be expected. On the other hand too low content of the component active in ammonia oxidation to NO_x should result in increased selectivity to N_2 but lower activity in the low-temperature range. Moreover, it should be noted that catalytic efficiency of the components active in both processes may change in different ways with the reaction temperature increase or decrease. Thus, the optimal ratio of both catalytically active components may be valid only for narrow temperature window. Other important issues are the form, in which catalytically active components are present in catalysts, possible interaction between catalytically active components as well as these components and support, guarantying high activity, selectivity to N_2 and stability of the catalytic systems.

Bi-functional catalysts, containing components active in ammonia oxidation to NO_x (CeO_2 or noble metals - Pt, Rh, Pd) and iron active in NO_x reduction to N_2 by ammonia deposited on

ZSM-5 were studied by Long and Yang.[18] It was reported that bi-functional catalysts, especially platinum containing, presented much better activity in the low-temperature range with relatively high selectivity to N_2 in comparison to Fe-ZSM-5 (Fig. 6). Moreover, it was shown that Pt/Fe-ZSM-5, which is one of the most promising catalyst reported in scientific literature, presented high stability in the presence of water vapour and SO_2. For this catalyst the ammonia conversion at 623 K decreased from 91 to about 76% after introduction of water vapour (2.5 vol.%) and SO_2 (500 ppm) in to reaction mixture. The NH_3 conversion was almost unchanged during next 3 h on-stream in the presence of water vapour and SO_2.[18] The inhibition effect of water vapour is possibly related to its competition with ammonia for these same adsorption sites.

Fig. 6.

Similar catalytic systems, based on Pt and Fe-particles deposited on ZSM-5, were tested in the selective ammonia oxidation to dinitrogen by Kim *et al.*[77] Iron (0.5 and 4 wt. %) and platinum (1.5 wt.%) were deposited on the zeolite surface by impregnation method using $FeCl_2$ and $Pt(NH_3)_4(NO_3)_2$ solutions, respectively. The presence of iron strongly influenced the characteristics of Pt particles in the Pt-Fe/ZSM-5 catalyst. It was reported that platinum particles were dispersed almost exclusively on the Fe oxide domains, and the size of Pt particles dramatically decreased as Fe-loading increased. The Pt- and Fe-doped zeolite catalysts were found to effectively operate in the low-temperature range. E.g. NH_3 conversion about 81% with 93% of N_2 selectivity was obtained in the presence of the Pt(1.5%)-Fe(0.5%)/ZSM-5 catalyst at 398 K. For Pt-Fe deposited of on Al_2O_3 and SiO_2 different Pt-Fe interaction and NH_3 oxidation activity from those of the Pt-Fe/ZSM-5 catalysts were found. In this case Pt particles were drifted out of FeO_x domain and the NH_3 oxidation activity was deteriorated. Thus, ZSM-5 was suggested to be the more suitable support for deposition of Pt-FeO_x species active in NH_3 oxidation.

Olofsson *et al.* reported much higher activity and dinitrogen selectivity of the bi-functional Pt-CuO/Al_2O_3 catalyst comparing to Pt/Al_2O_3 and CuO/Al_2O_3.[156] Authors suggested that the main reaction route over the Pt-CuO/Al_2O_3 catalyst to form dinitrogen proceeds via direct oxidation involving NH_x species and includes the reaction at the phase boundary between NH_x species adsorbed on CuO and oxygen adsorbed on Pt. An option is a spill-over of oxygen from Pt to CuO. Moreover, a second possible reaction pathway is reduction of NO_2 by adsorbed NH_x species.

Similar catalytic system, based on CuO deposed on Al_2O_3, was studied by Yang *et al.*[160] However, in this case silver was tested as component responsible for ammonia oxidation to NO_x. It was reported that mixing of Ag with Cu improved the NH_3 conversion activity of the Cu-based catalyst and the N_2 selectivity of the Ag-based catalyst.[160] The supported Cu(5 wt.%)-Ag(5 wt.%)/Al_2O_3 catalyst presented relatively low ammonia conversion temperature (<590 K) with high N_2 selectivity (>95%). Moreover, it was suggested that the low selectivity to dinitrogen found for Ag(5 wt.%)/Al_2O_3 is related to the presence of the crystallized Ag_2O phases. Doping of copper decreases crystallinity of Ag_2O.

Similar catalytic systems, based on alumina supported Cu-Ag, were studied by Gang *et al.*[161] The Ag/Al_2O_3, Cu/Al_2O_3 and Ag-Cu/Al_2O_3 catalysts with different Ag and Cu loadings were prepared by incipient wetness impregnation. Silver and copper were deposited on alumina using $AgNO_3$ and $Cu(NO_3)_2$ solutions. It was reported that the addition of copper to the Ag/Al_2O_3 catalysts, by co-incipient wetness impregnation, increased the selectivity to dinitrogen during the catalytic oxidation of ammonia without significant decrease in activity. An increase in N_2 selectivity from 80 to about 95% was observed at 100% ammonia conversion at the optimum Ag/Cu weight ratio (between 1:1 and 3:1) at 523 K. It was shown that the catalyst consists of copper oxide monolayer on alumina upon which silver particles are deposited. Thus, intimate contact between silver and copper on alumina-supported Ag-Cu catalysts could be responsible for excellent properties of these catalysts. The promotional effect of copper can be explained by a bi-functional mechanism, in which silver component mainly catalyses ammonia oxidation to NO (the first step of this reaction) and copper species catalyse the selective reduction of NO to nitrogen.

Chmielarz *et al.* reported interesting catalytic properties of bi-functional catalysts based on hydrotalcite derived mixed metal oxides doped with selected noble metals.[98] Platinum, palladium and rhodium played a role of components active in ammonia oxidation to NO_x, while Cu-Mg-Al and Fe-Mg-Al mixed metal oxides were components active in selective reduction of NO with ammonia to dinitrogen and water vapour. Cu-Mg-Al mixed metal oxide was found to be active catalyst of the selective ammonia oxidation at lower temperatures (complete NH_3 conversion with N_2 selectivity about 92% was reached at 673 K) than Fe-Mg-Al mixed metal oxide (complete NH_3 conversion with selectivity to N_2 about 90% was obtained at 773 K). Deposition of small amounts of noble metals increased low-temperature activity but also decreased dinitrogen selectivity (e.g. for Pt/Cu-Mg-Al complete NH_3 conversion with N_2 selectivity about 87% was obtained at 623 K).

Interesting concept of dual-layer catalytic converter for selective oxidation of ammonia was reported by Shrestha *et al.* [161]. The efficiency of ammonia oxidation on combined Fe-ZSM-5 and Pt/Al_2O_3 system in the form of dual-layer and mixed catalyst washcoated on a monolith was compared. Authors showed that the addition of the Fe-zeolite layer, active in selective reduction of NO_x by NH_3 to N_2, on top of the Pt/Al_2O_3 oxidation layer, active in oxidation of NH_3 to NO_x, shifts the product selectivity from N_2O and NO_x to N_2. Moreover, it was reported that N_2O and NO_x formed in the bottom layer of Pt crystallites are selectively reduced by the top Fe-ZSM-5 layer to N_2. A comparison between the dual layer and mixed catalysts at high space velocity showed higher NH_3 oxidation capability of the mixed catalyst due to the shorter diffusion length. On the other hand, for the low space velocity experiments, it was shown that the dual layer catalyst is more effective than the mixed catalyst at high temperature with respect to higher N_2 selectivity and lower selectivity towards NO_x and N_2O. On the other hand rather poor results were obtained for dual-layer Pt/Al_2O_3 and Cu-ZSM-5 based catalytic system.[163]

Similar studies were reported by Scheuer *et al.*, who compared efficiency of the automotive single layer Pt/Al_2O_3 catalyst and dual layer bifunctional, Pt/Al_2O_3 and Fe-zeolite, catalytic system for the selective ammonia oxidation.[74] Authors demonstrated that the dual layer catalyst shows reduced NO formation and improved selectivity to N_2. However, a lower overall NH_3 conversion was observed for the dual layer catalyst. Moreover, it was shown that numerical models can accurately predict the performance of such multilayer catalysts, and therefore, computer simulation can be used as useful tool for designing of such systems.

Caudle *et al.* patented bifunctional catalyst based on Pt(0.57 wt.%)/Al_2O_3 and Fe(1.1 wt.%)-BEA components active in ammonia oxidation to NO_x and NO_x reduction with ammonia, respectively.[164] Complete ammonia conversion in the presence of such bifunctional catalyst was achieved at temperatures about 500 K with rather poor selectivity to N_2 (<60%). Moreover, significant amount of N_2O were produced in the temperature range of 500-620 K.

Catalytic performance of the bi-functional catalysts in selective oxidation of ammonia is compared in Table 4. Analysis of these results shows that the catalytic systems consisting of platinum as component active in ammonia oxidation to NO_x and iron as component active in reduction of NO_x to N_2 by ammonia belong to most promising with respect to high activity in the low-temperature range as well as selectivity to dinitrogen. It should be noted that high activity for the Pt-Fe system was observed for various types of catalysts – calcined hydrotalcites[98], modified zeolites[18,77], supported catalysts based on Al_2O_3[77] and SiO_2[77] as well as dual layer catalytic system.[160]

6. Conclusions and perspectives

Selective catalytic oxidation of ammonia to dinitrogen is the most promising method for NH_3 conversion in oxygen containing waste gases. Although, a large number of various studies related to development of active, selective and stable catalysts for this process was reported in scientific literature, the problem is not fully solved. One of the main problems is development of the catalysts operating in a broad temperature range with the simultaneous high ammonia conversion and selectivity to dinitrogen. It is important in case of ammonia oxidation in gas stream of variable temperature (e.g. car exhaust gases). Moreover, it was shown that the majority of the studies have been carried out for model gas streams (typically containing ammonia and oxygen diluted in inert gas). On the other hand the studies performed in the presence of gas mixtures simulating real exhaust gases (containing apart from NH_3 and O_2 also hydrocarbons, CO_2, CO, H_2S etc.) showed that the result obtained for model gas mixtures cannot be in a simple way extrapolated for real flue gases. Thus, these additional components play a very important role in the overall efficiency of ammonia oxidation process and the future studies focused on development of commercial catalysts should be carried out with gas mixtures simulating compositions of real flue gases. Moreover, designing of such catalysts should include possible changes in composition of such gas mixture in the range typical for real flue gases. Another important issue is testing of the catalysts in the structured form (e.g. monolith, rings) to include effects that may occur in real installations for selective ammonia oxidation.

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Table 1. Selective oxidation of ammonia to dinitrogen – summary of the results for noble metal based catalysts.

Noble metal	Catalyst	NH_3 conversion [%]	Selectivity to N_2 [%]	Reaction conditions	Ref.
Pt	**Pt**(2.5 wt.%)-ZSM-5	100 (523 K)	41 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Pt(1.5 wt.%)-ZSM-5	98 (523 K)	57 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.06 g	78
	Pt(0.03 wt.%)/Al_2O_3	80 (523 K)	61 (523 K)	500 ppm NH_3, 5% O_2, GHSV – 66000 h^{-1}	162
	Pt(0.46 wt.%)/Al_2O_3	100 (523 K)	50 (523 K)	500 ppm NH_3, 5% O_2, GHSV – 66000 h^{-1}	162
	Pt(2.6 wt.%)/Al_2O_3	100 (523 K)	82 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Pt(1.0 wt.%)/Al_2O_3	34 (493 K)	48 (493 K)	500 ppm NH_3, 10% O_2, total flow 200 cm^3/min, catalyst – 0.2 g	138
	Pt(1.2 wt.%)/Al_2O_3 - reduced	100 (473 K)	75 (473 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	101
	Pt(0.05 wt.%)-MgO-Al_2O_3	98 (573 K)	48 (573 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	97
	Pt-Rh (3:1) binary system	58 (523 K)	40 (523 K)	800 ppm NH_3, 4% O_2, GHSV – 92000 h^{-1}	89
Pd	**Pd**(4.1 wt.%)-ZSM-5	94 (523 K)	75 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Pd(5.5 wt.%)-ZSM-5	80 (523 K)	73 (573 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g, GHSV – 230000 h^{-1}	96
	Pd(1.0 wt.%)-Y	87 (523 K)	97 (523 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g, GHSV – 19200 h^{-1}	97
	Pd(2.5 wt.%)-Y	100 (523 K)	95 (523 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g, GHSV – 19200 h^{-1}	97
	Pd(4.2 wt.%)/Al_2O_3	84 (523 K)	97 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Pd(1.2 wt.%)/Al_2O_3 - reduced	60 (523 K)	97 (523 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	101
	Pd(1.0 wt.%)/Al_2O_3	40 (413 K)	76 (413 K)	500 ppm NH_3, 10% O_2, total flow 200 cm^3/min, catalyst – 0.2 g	138
	Pd(0.09 wt.%)-MgO-Al_2O_3	90 (573 K)	58 (573 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	97
Rh	**Rh**(2.7 wt.%)-ZSM-5	9 (523 K)	95 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Rh(2.7 wt.%)/Al_2O_3	84 (523 K)	97 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Rh(1.2 wt.%)/Al_2O_3 - reduced	100 (473 K)	75 (473 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	101
	Rh(0.09 wt.%)-MgO-Al_2O_3	25 (623 K)	90 (573 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	97
Ir	**Ir**(1.2 wt.%)/Al_2O_3 - reduced	100 (473 K)	95 (473 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	101
Ru	**mesoporous RuO_2**	100 (523 K)	78 (523 K)	1000 ppm NH_3, 2% O_2, total flow 100 cm^3/min, catalyst – 0.08 g	122
Ag	**Ag powder**	100 (573 K)	72 (573 K)	1000 ppm NH_3, 10% O_2, total flow 50 cm^3/min, catalyst – 0.1 g	152
	Ag(10 wt.%)/Al_2O_3	98 (523 K)	96 (523 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	161
	Ag(10 wt.%)/Al_2O_3	100 (523 K)	69 (523 K)	1% NH_3, 10% O_2, total flow 400 cm^3/min, catalyst – 0.8 g	160
	Ag(10 wt.%)/Al_2O_3	90 (473 K)	49 (473 K)	500 ppm NH_3, 10% O_2, total flow 200 cm^3/min, catalyst – 0.2 g	138
	Ag(10 wt.%)/SiO_2	100 (573 K)	62 (573 K)	1000 ppm NH_3, 10% O_2, total flow 50 cm^3/min, catalyst – 0.1 g	80

Table 2. Selective oxidation of ammonia to dinitrogen – summary of the results for zeolite based catalysts.

Zeolite	Metal *deposition method*	NH_3 conversion [%]	Selectivity to N_2 [%]	Reaction conditions	Ref.
ZSM-5	**Fe**(3.6 wt.%), *$FeCl_3$ sublimation*	66 (523 K)	99 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	108
	Fe(2.5 wt.%), *$Fe(NO_3)_3$ impregnation*	25 (523 K)	89 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.06 g	109
	Fe(2.5 wt.%), *$FeCl_2$ impregnation*	40 (523 K)	99 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.06 g	109
	Fe(2.5 wt.%), *$FeSO_4$ impregnation*	27 (523 K)	96 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.06 g	109
	Fe(1.6 wt.%), *$FeCl_2$ ion-exchange*	28 (523 K)	99 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.06 g	109
	Fe(1.6 wt.%), *$FeCl_2$ ion-exchange*	63 (523 K)	92 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	96
	Fe(2.0 wt.%), *$Fe(NO_3)_3$ impregnation*	78 (623 K)	90 (623 K)	500 ppm NH_3, 2% O_2, total flow 200 cm^3/min, catalyst – 0.1 g	110
	Fe(0.5 wt.%), *$Fe(NO_3)_3$ impregnation*	10 (623 K)	72 (623 K)	500 ppm NH_3, 2% O_2, total flow 200 cm^3/min, catalyst – 0.1 g	110
	Fe(0.5 wt.%), *$FeCl_2$ ion-exchange*	25 (623 K)	76 (623 K)	500 ppm NH_3, 2% O_2, total flow 200 cm^3/min, catalyst – 0.1 g	110
	Cu(4.3 wt.%), *$Cu(MeCO_2)_2$ ion-exchange*	48 (523 K)	95 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	96
	Co(1.2 wt.%), *$Co(MeCO_2)_2$ ion-exchange*	58 (523 K)	73 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	96
	Co(3.8 wt.%), *ion-exchange*	26 (523 K)	77 (523 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	Mn(1.0 wt.%), *$Mn(MeCO_2)_2$ ion-exchange*	68 (523 K)	77 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	96
	Ni(0.9 wt.%), *$Ni(MeCO_2)_2$ ion-exchange*	39 (523 K)	69 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	96
Mordenite (MOR)	**Fe**, *$FeCl_3$ sublimation*	26 (523 K)	88 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	108
Ferrierite (FER)	**Fe**, *$FeCl_3$ sublimation*	18 (523 K)	95 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	108
Y	**Fe**, *$FeCl_3$ sublimation*	12 (523 K)	89 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	108
	Fe(2.0 wt.%), *$FeCl_2$ impregnation*	29 (623 K)	61 (623 K)	500 ppm NH_3, 2% O_2, total flow 200 cm^3/min, catalyst – 0.1 g	110
Beta	**Fe**, *$FeCl_3$ sublimation*	13 (523 K)	95 (523 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g	108
	Cu(6.6 wt.%), *$Cu(NO_3)_2$ ion-exchange*	100 (623 K)	96 (623 K)	0.54% NH_3, 8% O_2, total flow 200 cm^3/min, W/F – 0.015 g s cm^{-3}, catalyst – 0.025 g	111

Table 3. Selective oxidation of ammonia to dinitrogen – summary of the results for transition metal oxide based catalysts.

metal	Catalyst	NH_3 conversion [%]	Selectivity to N_2 [%]	Reaction conditions	Ref.
Cu	**CuO**(5 wt.%)/Al_2O_3, supported	75 (623 K)	96 (623 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	107
	CuO(10 wt.%)/Al_2O_3, supported	100 (623 K)	90 (623 K)	1.14% NH_3, 8.21% O_2, total flow 74.7 cm^3/min, catalyst – 0.2 g	107
	CuO(4.6 wt.%)/Al_2O_3, supported	77 (598 K)	92 (598 K)	0.54% NH_3, 8% O_2, total flow 20 cm^3/min, catalyst – 0.025 g	114
	CuO/Al_2O_3, supported	60 (523 K)	100 (523 K)	1000 ppm NH_3, 10% O_2, total flow 100 cm^3/min, catalyst – 0.2 g	113
	CuO(5 mol.%)-Mg-Al, calcined hydrotalcite	98 (623 K)	80 (623 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	130
	Cu(8 mol.%)-Mg-**Fe**(31 mol.%), calcined hydrotalcite	80 (623 K)	93 (623 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	134
	CuO(20 wt.%)/Al_2O_3-ZrO_2 supported	19 (473 K)	100 (473 K)	500 ppm NH_3, 5% O_2, total flow 200 cm^3/min, catalyst – 0.1 g	124
	CuO/carbon nono-tubes, supported	98 (448 K)	99 (448 K)	1000 ppm NH_3, 2% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	125
V	**V_2O_5**(5 wt.%)/TiO_2, supported	77 (623 K)	89 (623 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.1 g	76
	V_2O_5(2 wt.%)-CeO (10 wt.%)/TiO_2, supported	98 (548 K)	75(548 K)	200 ppm NH_3, 8% O_2, 6% moisture, total flow 500 cm^3/min, GHSV – 60000 h^{-1}	136
Co	**Co**(5 mol.%)-Mg-Al, calcined hydrotalcite	48 (623 K)	60 (623 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	130
Fe	**Fe**(4.6 mol.%)-Mg-Al, calcined hydrotalcite	22 (623 K)	88 (623 K)	0.5% NH_3, 2.5% O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
	Fe_2O_3(5 wt.%)-TiO_2, sol-gel method	65 (623 K)	78 (623 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.2 g	153
	Fe_2O_3(5 wt.%)-ZrO_2, sol-gel method	62 (623 K)	80 (623 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.2 g	153
	Fe_2O_3(5 wt.%)-Al_2O_3, sol-gel method	68 (623 K)	80 (623 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.2 g	153
	Fe_2O_3(5 wt.%)-SiO_2, sol-gel method	47 (623 K)	79 (623 K)	1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.2 g	153
Mn	**MnO_2 pure**	96 (473 K)	67 (473 K)	500 ppm NH_3, 3% O_2, total flow 1000 cm^3/min, catalyst – 2 g	144
	Mn_2O_3 pure	100 (473 K)	70 (473 K)	500 ppm NH_3, 3% O_2, total flow 1000 cm^3/min, catalyst – 2 g	144
	natural manganese ore	80 (473 K)	77 (473 K)	500 ppm NH_3, 3% O_2, total flow 1000 cm^3/min, catalyst – 2 g	144

Table 4. Selective oxidation of ammonia to dinitrogen – summary of the results for bi-functional catalysts (*Function 1*: Ammonia oxidation to NO_x, *Function 2*: SCR of NO_x with NH_3).

Function 1	Function 2	NH_3 conversion [%]	Selectivity to N_2 [%]	Reaction conditions	Ref.
Pt(0.2 wt. %)	**Cu**(5 wt.%)-Mg-Al calcined hydrotalcite	75 (573 K)	90 (573 K)	0.5 % NH_3, 2.5 % O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
Pt(0.2 wt. %)	**Fe**(5 wt.%)-Mg-Al calcined hydrotalcite	92 (573 K)	85 (573 K)	0.5 % NH_3, 2.5 % O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
Pt(1.5 wt.%)	**Fe**(0.5 wt.%)/ZSM-5, supported	95 (473 K)	82 (473 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, space velocity- 8333 cm^3/(g·min)	77
Pt(1.5 wt.%)	**Fe**(4 wt.%)/ZSM-5, supported	94 (473 K)	80 (473 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, space velocity- 8333 cm^3/(g·min)	77
Pt(0.5 wt.%)	**Fe**(1.5 wt.%)-ZSM-5, supported	100 (523 K)	88 (523 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, catalyst – 0.1 g	18
Pt(1.5 wt.%)	**Fe_2O_3**(0.5 wt.%) /Al_2O_3, supported	73 (473 K)	85 (473 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, space velocity - 8333 cm^3/(g·min)	77
Pt(1.5 wt.%)	**Fe_2O_3**(0.5 wt.%)/SiO_2, supported	88 (473 K)	75 (473 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, space velocity - 8333 cm^3/(g·min)	77
Pt(1 wt.%)	**CuO**(20 wt.%)/Al_2O_3, supported	42 (473 K)	82 (473 K)	700 ppm NH_3, 8% O_2, total flow 1000 cm^3/min, space velocity - 3000 cm^3/(g·min)	157
Pt(4 wt.%)	**CuO**(20 wt.%)/Al_2O_3, supported	59 (473 K)	81 (473 K)	700 ppm NH_3, 8% O_2, total flow 1000 cm^3/min, space velocity - 3000 cm^3/(g·min)	157
Pt(10 wt.%)/Al_2O_3	**Fe**(1.5 wt.%)-ZSM-5 dual-layer	99 (498 K)	63 (498 K)	500 ppm NH_3, 5% O_2, GHSV- 66000 h^{-1}	162
Rh(0.2 wt. %)	**Cu**(5 wt.%)-Mg-Al calcined hydrotalcite	40 (573 K)	95 (573 K)	0.5 % NH_3, 2.5 % O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
Rh(0.5 wt.%)	**Fe**(1.5 wt.%)-ZSM-5, supported	92 (573 K)	90 (573 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, catalyst – 0.1 g	18
Pd(0.2 wt. %)	**Cu**(5 wt.%)-Mg-Al calcined hydrotalcite	85 (573 K)	88 (573 K)	0.5 % NH_3, 2.5 % O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
Pd(0.2 wt. %)	**Fe**(5 wt.%)-Mg-Al calcined hydrotalcite	84 (573 K)	84 (573 K)	0.5 % NH_3, 2.5 % O_2, total flow 40 cm^3/min, catalyst – 0.1 g	98
Pd(0.5 wt.%)	**Fe**(1.5 wt.%)-ZSM-5, supported	56 (573 K)	92 (573 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, catalyst – 0.1 g	18
Ru(20 wt. %)	**CuO**(20 wt. %)/ZrO_2, supported	55 (473 K)	95 (473 K)	400 ppm NH_3, 5% O_2, 6% H_2O, total flow 200 cm^3/min, catalyst – 0.1 g	124
Ru(20 wt. %)	**CuO**(20 wt. %)/ZrO_2-Al_2O_3, supported	100 (473 K)	95 (473 K)	400 ppm NH_3, 5% O_2, 6% H_2O, total flow 200 cm^3/min, catalyst – 0.1 g	124
RuO_2	**CuO**(10 wt.%) supported	99 (473 K)	95 (473 K)	1000 ppm NH_3, 4% O_2, total flow 100 cm^3/min, catalyst – 0.08 g	124
CeO_2(40 wt.%)	**CuO**(60 wt.%), co-precipitated	99 (673 K)	86 (673 K)	1000 ppm NH_3, 5% O_2, space velocity- 1533 cm^3/(g·min)	117
CeO_2(10 wt.%)	**V_2O_5**(2 wt.%)/TiO_2, co-impregnated	98 (548 K)	77 (548 K)	200 ppm NH_3, 8% O_2, 6% H_2O, total flow 500 cm^3/min, GHSV- 60000 h^{-1}	136
CeO_2(0.1 wt.%)	**Fe**(1.5 wt.%)-ZSM-5, supported	51 (673 K)	96 (673 K)	1000 ppm NH_3, 2 % O_2, total flow 500 cm^3/min, catalyst – 0.1 g	18
CeO_2	**CuO**(10 wt.%), supported on CeO_2	46 (473 K)	99 (473 K)	1000 ppm NH_3, 10% O_2, total flow 100, cm^3/min, GHSV- 40000 h^{-1}	120
Ag(5 wt.%)	**CuO** (5 wt.%)/Al_2O_3, supported	70 (473 K)	97 (473 K)	1% NH_3, 10% O_2, total flow 400, cm^3/min, catalyst – 0.1 g	160
Ag(10 wt.%)	**CuO** (10 wt.%)/Al_2O_3, supported	68 (473 K)	77 (473 K)	1% NH_3, 10% O_2, total flow 400, cm^3/min, catalyst – 0.1 g	160
Ag(7.5 wt.%)	**CuO**(2.5 wt.%)/Al_2O_3, supported	90 (473 K)	91 (473 K)	1000 ppm NH_3, 10% O_2, total flow 50 cm^3/min, catalyst – 0.1 g	161

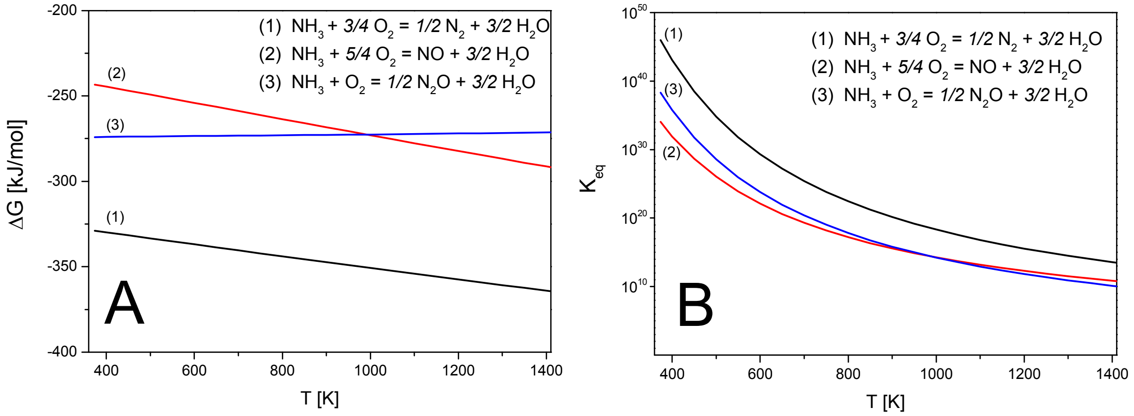

Fig. 1. Temperature dependence of Gibbs free energy - ΔG (A) and equilibrium constant - K_{eq} (B) for reactions of ammonia oxidation

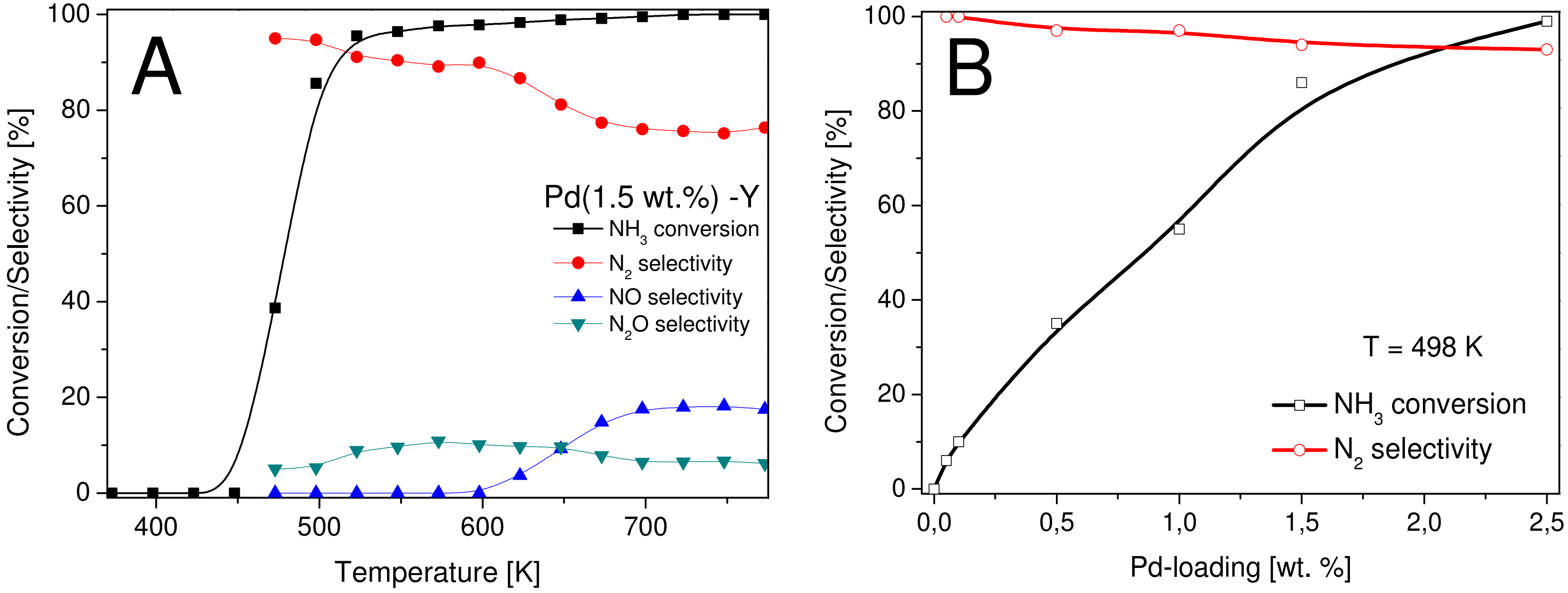

Fig. 2. Results of ammonia oxidation in the presence of Y zeolite doped with 1.5 wt. % of palladium (A) and NH$_3$ conversion and selectivity towards N$_2$ vs palladium loading in Y zeolite (B)[97]. Conditions: 0.5% NH$_3$, 2.5% O$_2$, total flow 40 cm^3/min, catalyst – 0.1 g, GHSV – 19200 h^{-1}

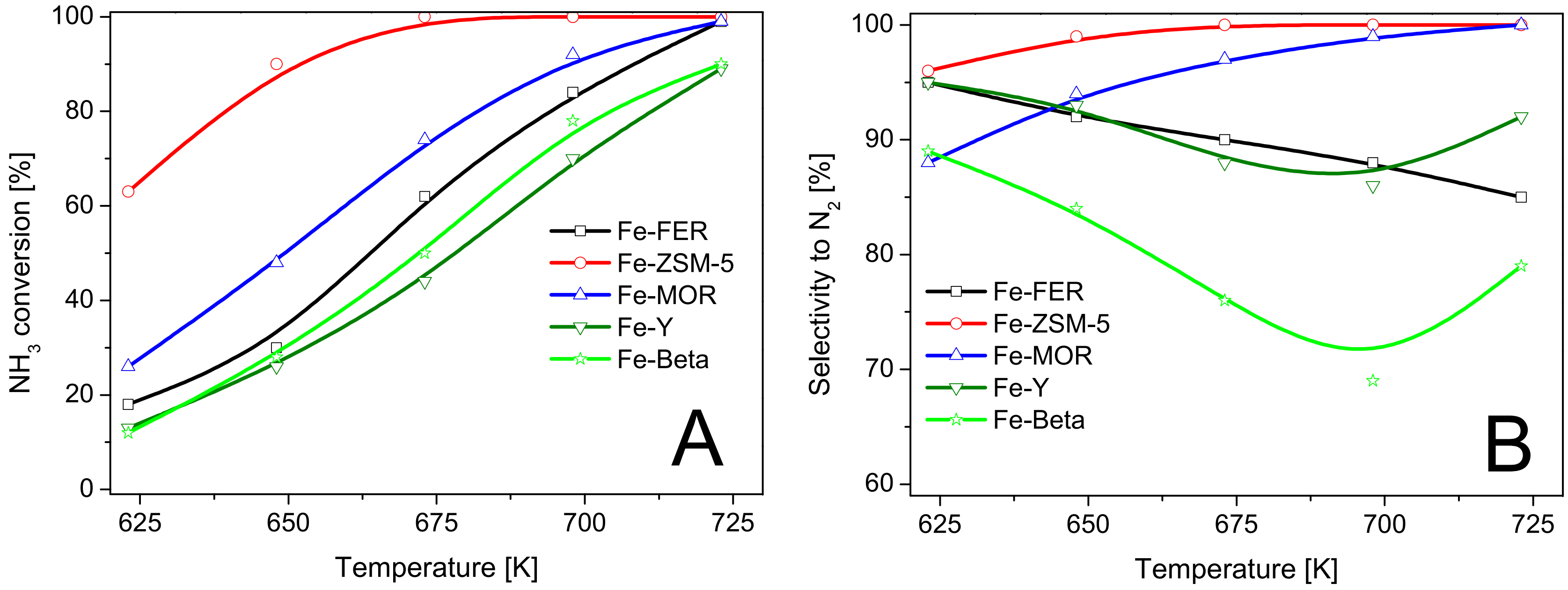

Fig. 3. Results of ammonia oxidation in the presence of various zeolites modified with iron by sublimation of $FeCl_3$: ammonia conversion (A) and selectivity towards dinitrogen (B).[108] Conditions: 1000 ppm NH_3, 2% O_2, total flow 500 cm^3/min, catalyst – 0.1 g.

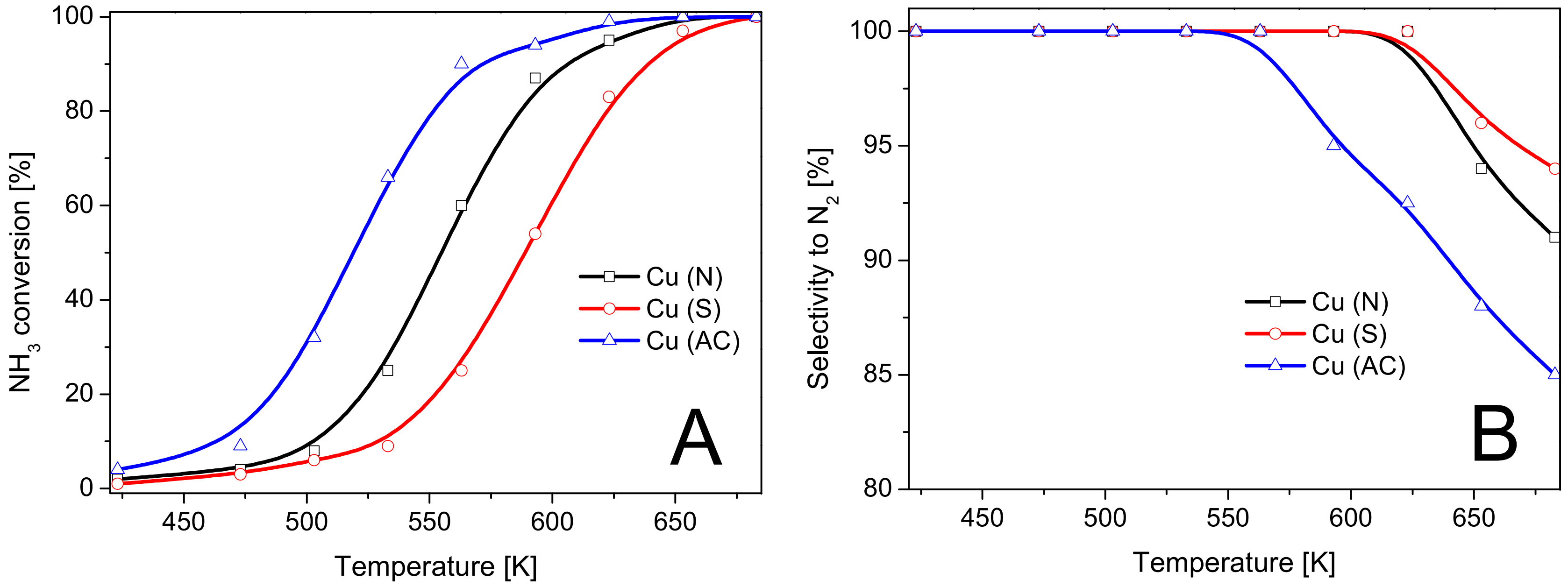

Fig. 4. NH_3 conversion (A) and N_2 selectivity (B) over CuO/Al_2O_3 catalysts prepared with different precursors: $Cu(NO_3)_2$ - Cu(N), $CuSO_4$ – Cu(S) and $(CH_3COO)_2Cu$ - Cu(AC).[113] Reaction conditions: NH_3 (1000 ppm), O_2 (10 vol.%), total flow rate - 100 cm^3/min; catalyst weight - 0.2 g.

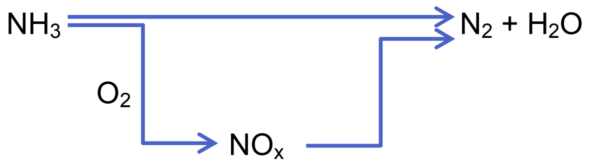

Fig. 5. Schematic presentation of the i-SCR mechanism

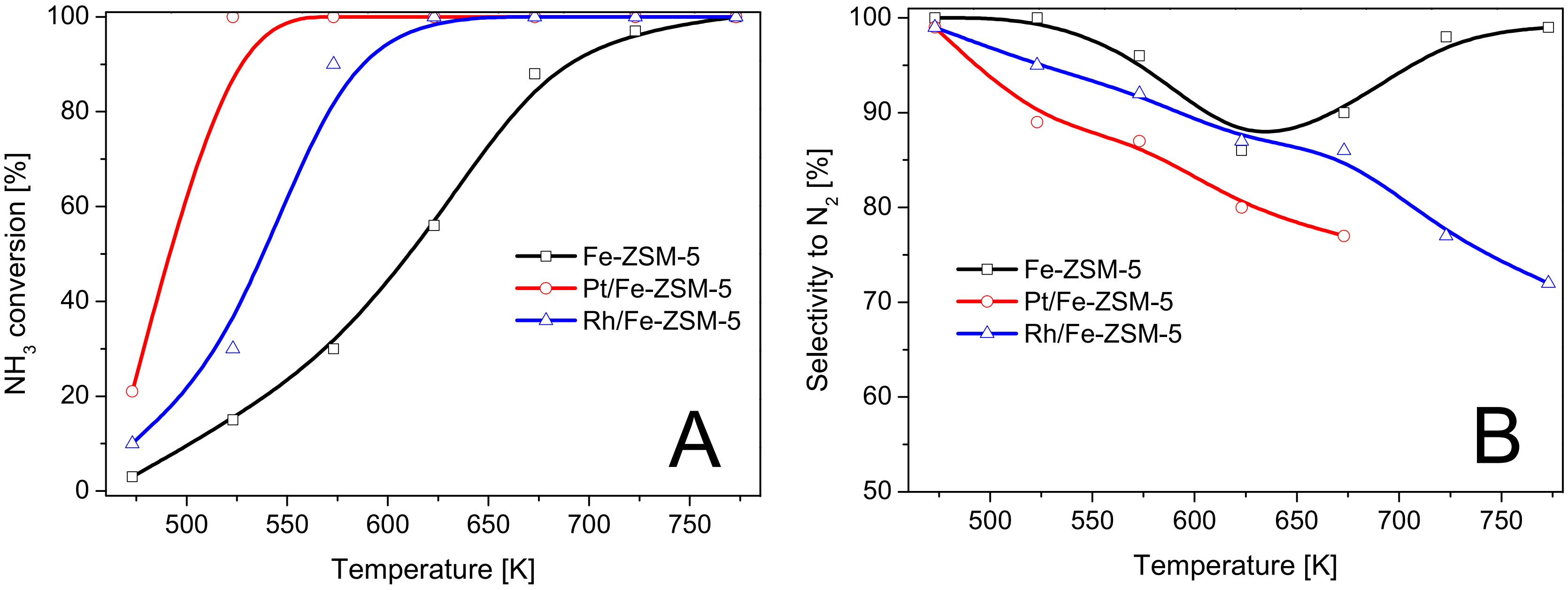

Fig. 6. NH_3 conversion (A) and N_2 selectivity (B) over Fe-ZSM-5 catalysts and its modifications with platinum (Pt/Fe-ZSM-5) and rhodium (Rh/Fe-ZSM-5).[18] Conditions: NH_3 (1000 ppm), O_2 (2 vol.%), total flow rate - 500 cm^3/min; catalyst weight - 0.1 g.