

Review

Modified Layered Silicas as Catalysts for Conversion of Nitrogen Pollutants in Flue Gases—A Review

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Abstract: This paper is focused on the recent achievements in the studies of modified layered zeolites and cationic layered clay minerals. These materials are very promising catalysts in green chemistry processes, such as selective catalytic reduction of NO_x with ammonia (NH_3 -SCR) and selective catalytic oxidation of ammonia to dinitrogen (NH_3 -SCO). Special attention is paid to the roles of the micro- and mesoporous structures of the catalytic materials, the type and location of deposited transition metals, as well as surface acidity in the design of effective catalysts for the NH_3 -SCR and NH_3 -SCO processes. The majority of the presented analysis is based on the authors' research.

Keywords: layered clay minerals; layered zeolites; selective catalytic reduction of NO_x with ammonia; selective catalytic oxidation of ammonia



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1. Introduction

Cationic layered minerals, especially those belonging to the group of phyllosilicates, still have great potential in catalytic applications. This is not surprising, considering the various ways in which they can be modified, resulting in materials with properties tailored for specific catalytic applications. Acid treatment of such layered minerals may cause the partial leaching of clay layer components and delamination of the layer ordering [1]. Thus, such treatment with mineral acids opens the interlayer spaces for catalysis and modifies the chemical composition of the clay layers. More advanced methods of clay mineral modification are based on intercalation with inorganic, thermally stable pillars via ion exchange method and surfactant-directed method [2]. Deposition of pillars permanently opens the interlayer spaces of clays, therefore resulting in porous materials with a relatively high specific surface area. Considering that clay minerals modified in this way are still characterized by ion exchange properties and surface acidity, it is not surprising that they are very interesting materials [3,4].

Layered zeolites are another very interesting group of materials with great potential for catalytic applications [5]. Similarly to layered clay minerals, such zeolites can be intercalated with silica pillars via surfactant-directed method, resulting in materials with a bimodal micro- and mesoporous structure. Micropores are channels in the zeolite layers, while spaces between intercalated layers are mesopores. Another effective method for obtaining materials with such bimodal porous structures is delamination of the layered zeolite. This kind of modification causes opening of the interlayer space via separation and chaotic orientation of the zeolite layers. Of course, in the case of delaminated zeolites, the sizes of mesopores are less uniform compared to pillared zeolites. Zeolites with a bimodal porous structure were reported to be catalytically active in various processes, especially in conversion of bulkier molecules [6]. However, the beneficial effects of the bimodal porous structure of zeolites for the conversion of smaller molecules (e.g., NH_3 -SCR [7]) were also presented. This effect is possibly related to the more effective internal diffusion of reactants, and therefore their improved overall reaction efficiency.

The selective catalytic reduction of nitrogen oxides with ammonia (NH₃-SCR) is the most important approach used for the conversion of nitrogen oxides (NO_x represents both NO and NO₂) to dinitrogen. This approach is used for NO_x conversion in flue gases emitted by stationary sources, such as electric power stations and industrial boilers. Recently, a modified version of this approach, called Blue Tech, was adapted for NO_x conversion in exhaust gases from diesel engines. Ammonia, due to its toxic and corrosive properties and problems related to its handling and transportation, was replaced by urea solution in this technology. Urea solution is hydrolyzed on-board to NH₃ and CO₂ upstream of the NH₃-SCR converter. NH₃-SCR technologies used for both stationary and mobile NO_x emission sources are characterized by their highly efficient reduction of nitrogen oxides to nitrogen. However, there is still a risk that ammonia is not completely used in the NH₃-SCR converter and may be emitted to the atmosphere. To avoid the risk of ammonia leaking downstream of the NH₃-SCR converter, ammonia present in exhaust gases should be selectively oxidized to nitrogen and water vapor. This process should be conducted at the same temperature as the exhaust gases and should be selective to nitrogen. The efficiency of this process, called selective catalytic oxidation of ammonia (NH₃-SCO or AMO_x), should be strictly controlled using suitable catalysts [8]. Modified layered clays and layered zeolites were reported to be very promising catalysts of NH₃-SCR and NH₃-SCO [7,9,10]. This is not surprising, considering the presence of acid sites in both cationic clay minerals and layered zeolites, which are necessary for ammonia chemisorption and catalytic activation for NH₃-SCR and NH₃-SCO processes [8]. Moreover, zeolites and clay minerals exhibit ion exchange properties that are important for deposition of the catalytically active metals in highly dispersed forms, which is important in the case of the studied processes. On the other hand, the open interlayers of the delaminated or pillared structures of layered zeolites and clay minerals are important to the increased rate of internal diffusion of the reactants, which improves the overall rates of the studied reactions.

The advances in the studies of layered silica-based catalysts for selective NO_x reduction with ammonia and selective ammonia oxidation to nitrogen are presented and discussed in this paper.

1.1. Cationic Layered Clay Minerals and Their Modifications

Cationic layered clay minerals have been intensively studied as precursors for the synthesis of catalysts for several decades [3,4,11–15]. The interest from scientists and engineers is related to the great variety of clay minerals with different layered structures and containing various intralayer and interlayer chemical elements. Moreover, relatively simple methods can be applied for their modification, resulting in materials tailored for the specific catalytic processes. Another important motivation for the application of these materials in different areas, including catalysis, is their low cost and relatively easy accessibility in nature.

Montmorillonite is one of the most common cationic layered clays. The model structure of montmorillonite, which is possibly the most intensively studied cationic clay mineral, is presented in Figure 1. The structure of the layers in this mineral is classified as 2:1 (octahedral alumina sublayer located between two silica sublayers) and as dioctahedral clay (two-thirds of octahedral positions are occupied by Al³⁺ cations and one-third are vacancies). In montmorillonite, a part of trivalent Al³⁺ cations in octahedral sheets is replaced by divalent Mg²⁺ ions, resulting in a negative charging of the montmorillonite layers. The negative charge of the clay layers is compensated by common cations, typically Na⁺, K⁺, or Mg²⁺, which together with water molecules are located in the interlayer spaces of clay mineral. Such interlayer cations can be relatively easily exchanged for other cations, which delivers an opportunity to modify these materials.

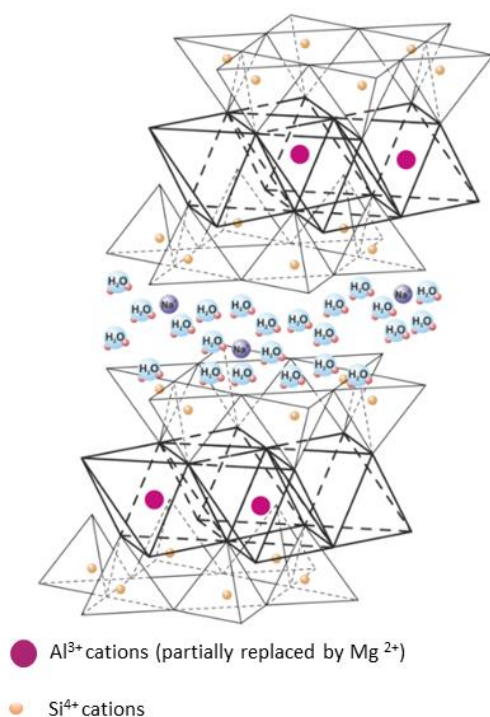


Figure 1. Model structure of montmorillonite. Reprinted with permission from ref. [2]. Copyright 2018 Elsevier.

1.2. Pillared Interlayered Clays (PILCs)

One of the most important methods for the modification of cationic layered clays is their interaction with inorganic pillars via ion exchange [16,17]. This method is based on the exchange of the interlayer cations compensating for the negative charge of the clay layers for significantly larger metal polyoxocations [16]. During the subsequent calcination, metal polyoxocations are converted into thermally stable metal oxide pillars. The concept of the intercalation of layered clays with aluminum polyoxocations via the ion exchange method is presented in Figure 2. Apart from aluminum oligocations, other polyoxocations such as zirconium [18,19] and titanium [20] have been successfully used as precursors of the interlayer pillars. The ion exchange process precedes swelling of the clay samples in water, resulting in accommodation of water molecules in the interlayer spaces of the clay, therefore extending the interlayer distance. Large metal polyoxocations can be easily accommodated into such extended interlayer spaces via ion exchange mechanisms. Such interlayer metal polyoxocations under calcination conditions are converted to thermally stable metal oxide pillars, resulting in permanently opened interlayer spaces. The clays modified via this method, called pillared interlayered clays (PILCs), are characterized by relatively high surface areas, typically in the range of 150–350 m² g^{−1}, a developed microporous structure with a slit-like pore geometry, as well as ion exchange properties and surface acidity. The ion exchange features are very important for the further catalytic functionalization of modified clays with catalytically active metal cations. The acid sites in PILCs are located on the clay layers and on the pillar surfaces. Thus, through the selection of clay minerals and pillaring agents, the surface acidity of such pillared materials can be tailored for the specific needs of the catalytic reaction, e.g., cracking of hydrocarbons [16] or synthesis of ethers from alcohols [21]. PILCs obtained by montmorillonite intercalation are characterized by the limited thermal stability of the pillared structure, which is stable to about 400–450 °C. Above this temperature, the shrinking of the interlayer distance is observed, with the final collapse of the pillared structure. Thus, montmorillonite-based PILC catalysts can be used only for low- and medium-temperature processes. More thermally stable PILCs can be obtained through intercalation of vermiculites [22] or phlogopites [23] with alumina pillars, however due to the high energy involved in the stabilization of interlayer cations in their

minerals, the pillaring procedures are more complex and intercalation is less effective. More detailed descriptions of the clay intercalation procedures and their applications in various catalytic reactions were presented in review papers [2,16].

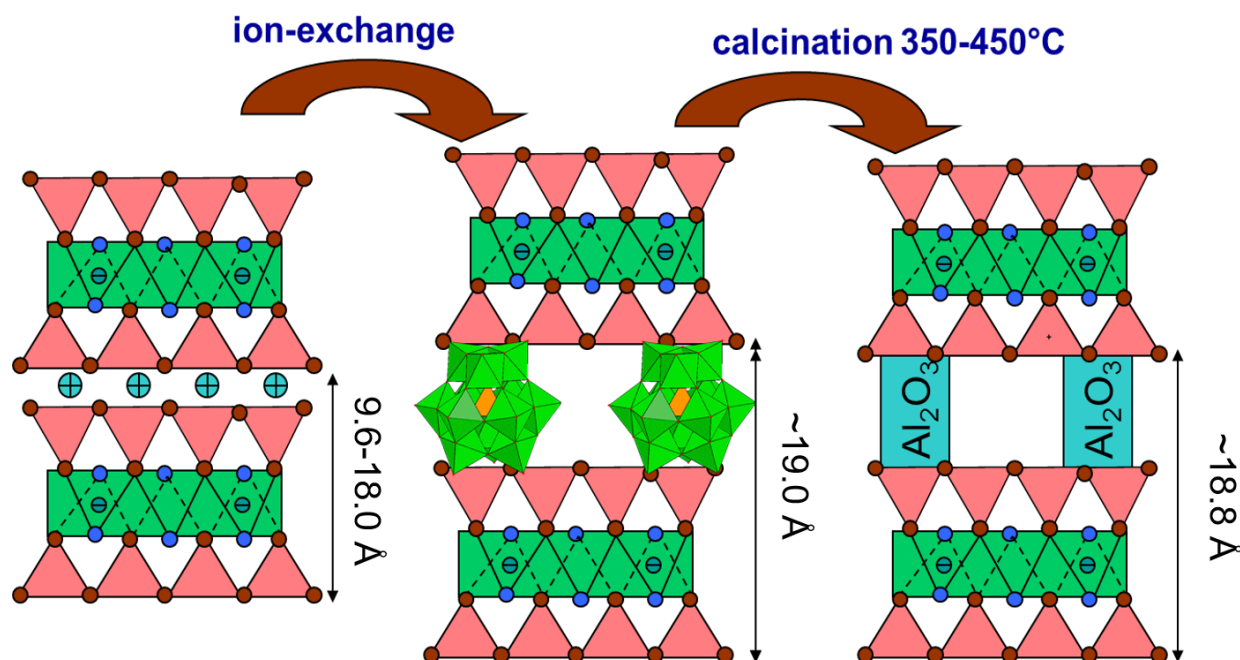


Figure 2. Intercalation of cationic layered clay minerals with alumina pillars. Aluminum Kegging polyoxocations, $[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$, were used as precursors of Al_2O_3 pillars. Reprinted with permission from ref. [2]. Copyright 2018 Elsevier.

1.3. Porous Clay Heterostructures (PCHs)

The development of ordered mesoporous silica materials in 1992 by scientists from the Mobil Oil Corporation was one of the most spectacular achievements in the field of nanomaterials science and engineering in the last few decades [24]. The concept of these materials synthesis is based on the organization of alkylammonium surfactants in solution with the formation of micellar structures, followed by silica condensation around such micellar species. Under calcination conditions, ordered mesoporous silica shows a relatively high specific surface area and pore volume [25,26]. In 1995, three years after development of ordered mesoporous silica materials, a similar procedure was used for the intercalation of clay minerals [27]. The concept for the synthesis of these materials, called porous clay heterostructures (PCHs), is presented in Figure 3. In the first step, cationic alkylammonium surfactants are introduced into interlayer spaces of swollen layered clay minerals via the ion exchange method. Additionally, neutral alkylamine co-surfactants are deposited into interlayer spaces of the clay. Surfactants and co-surfactants are organized into micellar structures in the interlayer spaces. In the next step, a silica source, such as tetraethyl orthosilicate (TEOS), is introduced into the reaction mixture. TEOS is hydrolyzed via water present in the interlayer spaces of the clay and condensed around organic templates with the formation of silica pillars. Finally, organic templates are removed from the pore system of PCHs via calcination or extraction with suitable solvents. Apart from pure silica, multicomponent pillars, such as silica–titania [14,28], silica–alumina [14], and silica–zirconia [29], have also been intercalated into the interlayer spaces of layered clays. Moreover, the successful intercalation of various clay minerals, such as rectorite, fluorohectorite, magadiite, and vermiculite, via surfactant-directed method has been reported [27,30]. PCHs are characterized by high specific surface areas of up to $1000 \text{ m}^2 \text{ g}^{-1}$, uniform porous structures with pore diameters characteristic of small mesopores, ion exchange properties, and surface acidity. Ion exchange properties are

important for the deposition of catalytically active metal cations in highly dispersed forms. Both ion exchange properties and surface acidity are dependent on the clay minerals used for PCHs synthesis, as well as additional components incorporated into silica pillars. Moreover, the pillared structure of PCHs is significantly more thermally stable than pillared structures of PILCs. It was reported that no changes in the pillared structure of PCHs was observed under thermal treatment at 600 °C, and only a small decrease in their textural parameters was identified after calcination at 850 °C [13]. Thus, in contrast to PILCs, the catalysts based on PCHs can also be used in high-temperature processes. More detailed information about porous clay heterostructures, including their synthesis and catalytic applications, can be found in review papers [2,11].

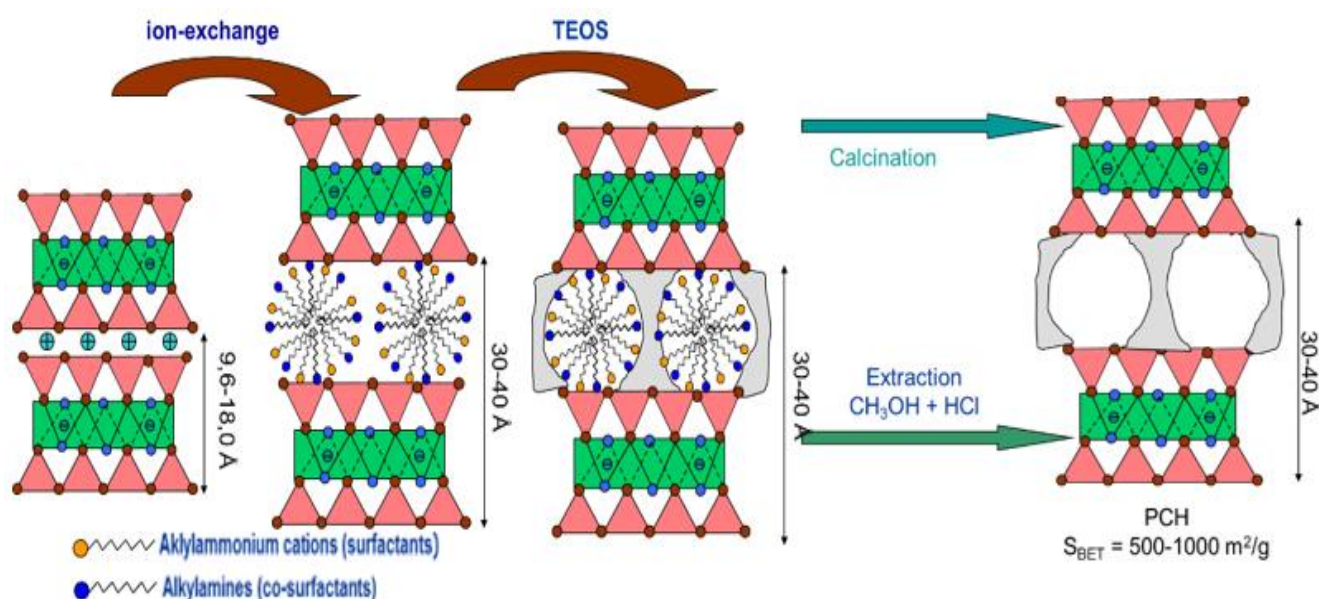


Figure 3. Synthesis of PCH materials. Tetraethyl orthosilicate (TEOS) was used as a precursor of interlayered silica pillars. Reprinted with permission from ref. [2]. Copyright 2018 Elsevier.

2. Layered Zeolites and Their Modifications

Zeolites are well-known group of crystalline solids with well-defined framework structures containing micropores of molecular dimensions. Zeolites can accommodate exchangeable extra-framework cations compensating for the negative charge of the zeolite framework. The zeolite framework is composed of corner-sharing TO_4 tetrahedra, with T standing for tetrahedrally coordinated framework atoms, such as Si and Al or other heteroatoms [31,32]. The negative charging of the zeolite framework results from the presence of Al^{3+} or other cations with valency values lower than 4+ incorporated into its structure. Extra-framework cations, compensating for the negative charge of the zeolite framework, can be relatively easily exchanged for other cations, and therefore this property may be used for the introduction of catalytically active metal cations into zeolites. Moreover, due to the presence of aluminum or some other cations, e.g., Fe^{3+} [33] or Ti^{4+} [34], zeolites are characterized by the presence of acid sites. Thus, considering their uniform porous structure with pore sizes similar to the sizes of small molecules, the surface acidity, ion exchange properties, as well as the relatively high thermal and hydrothermal stability of zeolites make them very promising materials for catalytic applications [5]. Therefore, it is not surprising that zeolites are commercially used as catalysts of hydrocarbon conversions in petroleum and chemical industries [35–37]. Moreover, zeolites have been intensively studied as promising catalysts or catalytic supports for many other applications [38,39].

Traditionally, zeolites have been defined as covalently bonded continuous three-dimensional (3D) frameworks [40,41]. Most zeolites are synthesized using the solvothermal method, and a great variety of zeolitic structures can be obtained using different reaction

conditions and reactants, including various structure-directing agents [5]. The formation of the zeolite structure may be preceded directly by 3D growth or by the formation of 2D sheets of the zeolite precursor in the initial step, with the condensation of such sheets resulting in the 3D zeolite structure in the next step [5]. Formation of such “intermediate” 2D zeolite precursor opens new options for the synthesis of zeolitic materials with open microporous and mesoporous structures [42–45]. Layered zeolites are synthetic materials, and therefore their structures and other properties can be fully designed. An example of the possible transformation of 2D zeolite precursors is shown in Figure 4.

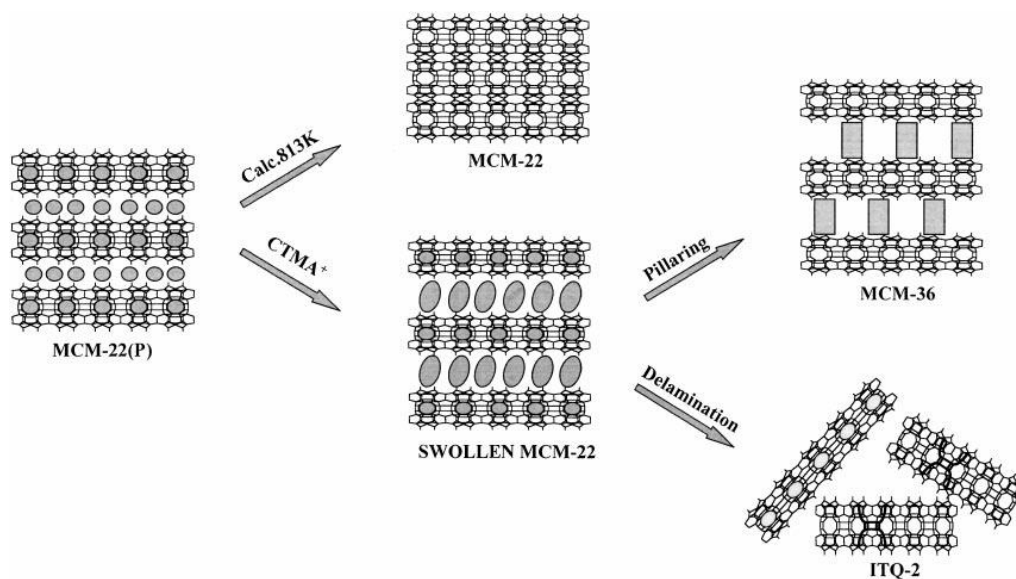


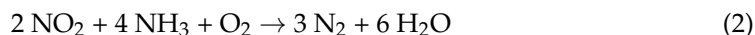
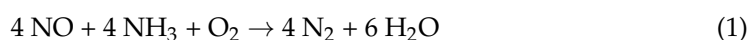
Figure 4. Schematic representation of various derivatives from the MCM-22 precursor. Reprinted with permission from ref. [43]. Copyright 1999 Elsevier.

As mentioned, 2D zeolite precursors, e.g., MCM-22(P), can be calcined, resulting in condensation of the zeolite layers and formation of a 3D microporous zeolite structure, e.g., MCM-22. To open the interlayer spaces, the zeolite precursor must be swollen with cationic alkyl ammonium surfactants, then a silica source, such as TEOS, must be introduced to form interlayer pillars. After calcination, resulting in organic matter removal from the pore system, a zeolitic material with bimodal porosity can be produced. Micropores are located within the zeolite layers, while the spaces between layers separated by silica pillars are mesoporous in size. An alternative synthesis method for micro- and mesoporous zeolitic materials is based on sonication of a swollen zeolite precursor, which results in so-called delaminated structures. In this case, the zeolite layers are chaotically oriented and spaces between the layers stacked in a non-parallel manner are of meso- or even mesoporous size. Both silica-intercalated or delaminated layered zeolites are characterized by relatively high thermal and hydrothermal stability and exhibit ion exchange and acidic properties, which depend on the zeolite later composition. Thus, the modified layered zeolites have great potential in catalytic applications.

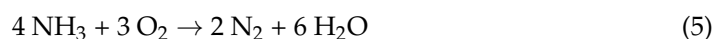
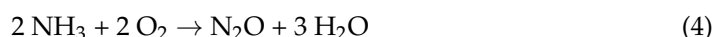
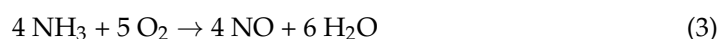
3. Selective Catalytic Reduction of NO_x with Ammonia (NH₃-SCR)

The selective catalytic reduction of NO_x with ammonia (NH₃-SCR) is a mature and relatively well-optimized process. It was patented in the United States by the Engelhard Corporation in 1957 [46]. Over the following years, the optimization of NH₃-SCR technology was continued, mainly in Japan and the United States, resulting in less expensive and more durable catalytic systems. The first large-scale NH₃-SCR installation was imple-

mented by the IHI Corporation in 1978 [47]. The process of NO_x reduction with ammonia can be described by Equations (1) and (2):



The NH₃-SCR technology is typically used in electric power stations and industrial and municipal solid-waste boilers. More recently, this technology was adapted for NO_x conversion in flue gases emitted by diesel engines, such as those in large ships, diesel locomotives, gas turbines, and even automobiles. Commercial catalysts for NH₃-SCR implemented in stationary sources of NO_x emissions are based on V₂O₅-WO₃-TiO₂ and V₂O₅-MoO₃-TiO₂ metal oxide systems. Such catalysts effectively operate in the temperature range of 300–400 °C, with a relatively high selectivity to nitrogen, which is a desired reaction product. At temperatures below 300 °C, the efficiency of NO_x conversion is not satisfactory, while at temperatures above 400 °C, the side reactions of direct ammonia oxidation (Equations (3)–(5)) may decrease the efficiency of the NH₃-SCR process:



One of the main problems related to the commercial NH₃-SCR catalysts is their operation occurring over a relatively narrow temperature range; therefore, studies focusing on the development of catalysts for low- and high-temperature NO_x conversion have been conducted. Another problem is related to the relatively high volatility of vanadium oxide, as well as WO₃ and MoO₃ [48], resulting in serious environmental problems. An important issue in the field of the catalytic NO_x conversion is the development of catalysts for the low-temperature NH₃-SCR process. Among others, copper and manganese have been reported as promising components of such catalytic systems. Moreover, an important motivation for such studies is the relatively high costs of the commercial catalysts; therefore, cheaper catalytic systems with catalytic efficiency similar to commercial levels or even higher are still needed.

3.1. Catalysts Based on Modified Layered Clay Minerals

3.1.1. Pillared Interlayered Clays—PILCs

Possibly the majority of the studies in the literature on modified clay minerals as catalysts of the NH₃-SCR process have been performed on cationic layered minerals intercalated with titania pillars and additionally doped with vanadium [49–55]. The motivation for such studies has been the desire to imitate real commercial V₂O₅-TiO₂-based catalysts. However, clay-based catalysts are characterized by significantly larger specific surface area and porosity, and therefore better accessibility of the catalytically active sites. Long and Yang [49] compared catalytic activity levels in NH₃-SCR of V₂O₅-TiO₂ and V₂O₅-WO₃-TiO₂ metal oxide systems with TiO₂-intercalated bentonite additionally doped with V₂O₅ (V₂O₅/TiO₂-PILC) or both V₂O₅ and WO₃ (V₂O₅-WO₃/TiO₂-PILC). The comparison of the metal-oxide-based catalysts and modified clay minerals with this same content of V₂O₅ (4.4 wt%) and WO₃ (8.8 wt%) resulted in very interesting conclusions (Figure 5). In the temperature range of 350–375 °C, the activity of both series of catalysts is very similar, however at temperatures in the range of 400–450 °C, the catalysts based on modified clay minerals presented much higher efficiency in the NO conversion to N₂. This effect was due to intensive ammonia oxidation observed in the presence of V₂O₅-TiO₂ and V₂O₅-WO₃-TiO₂ catalysts. Thus, in the case of the V₂O₅/TiO₂-PILC and V₂O₅-WO₃/TiO₂-PILC catalysts, the temperature window for effective catalytic operation is shifted to higher temperatures compared to V₂O₅-TiO₂ and V₂O₅-WO₃-TiO₂ metal oxide catalysts. The problem is the limited thermal stability of the pillared structures of clay minerals, and

therefore their possible destruction, resulting in deactivation of these types of catalysts at elevated temperatures [56].

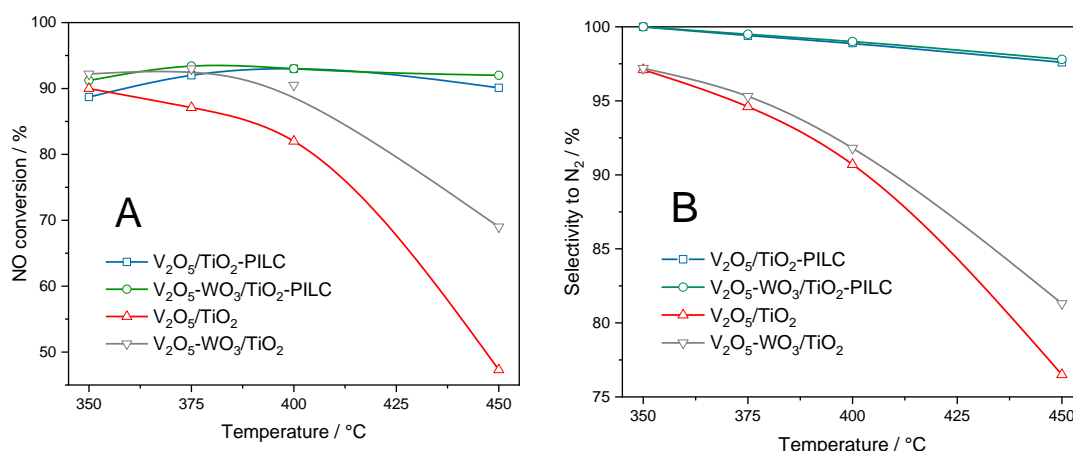


Figure 5. Results for NH₃-SCR tests over V₂O₅/TiO₂-PILC and V₂O₅-WO₃/TiO₂-PILC catalysts (A) and V₂O₅-TiO₂ and V₂O₅-WO₃-TiO₂ metal oxides as reference catalysts (B). Reaction conditions: 0.3 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, He = balance, total flow rate = 500 mL min^{−1}, and GHSV = 75,000 h^{−1}. Based on the results presented in [49] with permission from ref. [49]. Copyright 2000 Elsevier.

Arfaoui et al. [50] compared the catalytic activity of V₂O₅/TiO₂-PILCs obtained from different precursors of Ti pillars in the NH₃-SCR process. TiCl₄, as well as titanium alkoxides Ti(OCH₃)₄ and Ti(OC₂H₅)₄, were used as pillaring agents for montmorillonite intercalation. TiCl₄ was hydrolyzed under controlled pH conditions, resulting in Ti-oligocations, while titanium alkoxides underwent hydrolysis and condensation with the formation of similar oligocations. It was shown that Ti-PILCs synthesized using titanium alkoxides were characterized by higher specific surface area and porosity compared to the clay samples modified with TiCl₄. Additionally, the Ti-PILCs obtained using Ti(OCH₃)₄ and Ti(OC₂H₅)₄ as titanium pillars precursors, demonstrated higher catalytic activity after vanadium deposition in the NH₃-SCR process.

Flue gases emitted by coal-fired power plants and industrial boilers typically contain significant sulfur oxides (SO₂ and SO₃), which may result in deactivation of catalysts. The commercial V₂O₅-TiO₂-based catalysts are known to be resistant to SO_x poisoning. Moreover, as was previously reported, the lifetime of such catalysts can be prolonged by their sulfation with SO₂ or H₂SO₄ [51,52]. Commercial NH₃-SCR catalysts containing about 0.5–1% of sulfur, mainly in the form of surface sulfates, were reported to be still active, and were additionally characterized by decreased activity in the side process of the oxidation of ammonia to NO_x. It was suggested that the surface sulfate species inhibit oxidation of NH₃ to NO_x, therefore increasing the efficiency of the NH₃-SCR process at higher temperature [53]. Similar studies on sulfonated V₂O₅/TiO₂-PILC and V₂O₅-WO₃/TiO₂-PILC have shown their resistance to sulfur poisoning [54]. It was reported that sulfonation of V₂O₅ is significantly more important for the catalysts' activation than sulfonation of WO₃ [54]. Moreover, it was reported that introduction of vanadium to sulfated, titanium-pillared clay influenced the reduction behavior of the sulfate [53]. It was supposed that sulfate species interact much more strongly with vanadium than with the titanium-pillared clay surface. The high performances in the NH₃-SCR reaction of V₂O₅/TiO₂-PILC was due to the structural combination between acid and redox sites. The presence of sulfate species, which exhibit Brönsted-type acidity, in proximity with the vanadia sites on sulfated, titanium-pillared clay possibly results in a promoting effect on NH₃-SCR activity [53]. Thus, similarly to the commercial NH₃-SCR catalysts, titanium-pillared clays modified with vanadia were also found to be resistant to deactivation by SO_x. Moreover, it was shown that sulfonation of the Ti-PILC support prior to the vanadia

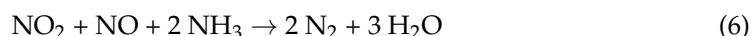
deposition resulted in activation of these catalytic systems. Boudali et al. [55] reported an activation effect resulting from the sulfonation of Ti-PILCs prior to the deposition of vanadia on the efficiency of the NH_3 -SCR process. It was suggested that sulfonation of Ti-PILCs results in generation of additional acid sites for ammonia chemisorption and activation. On the other hand, it was reported that the catalytic activity of the sulfonated catalysts increased but their selectivity to nitrogen decreased. Thus, it could be supposed that part of the ammonia chemisorbed on sulfonated $\text{V}_2\text{O}_5/\text{Ti-PILCs}$ is not properly activated to the NH_3 -SCR reaction, and at higher temperature is oxidized by oxygen present in the reaction mixture.

A very important scientific problem is related to the nature of vanadium species deposited on Ti-PILCs and their catalytic activity in the NH_3 -SCR reaction. One study was conducted by Chae et al. [57], who deposited different amounts of vanadium on Ti-PILCs, analyzed the structure and aggregation of the deposited vanadium species, and compared their catalytic activity in NH_3 -SCR. Moreover, the preferable formation of various vanadium species was compared for various supports, such as Ti-PILCs, TiO_2 , Al_2O_3 , and SiO_2 , with similar coverage of vanadia. It was shown that for Ti-PILCs, deposition of small amounts of vanadium resulted mainly in the formation of surface-isolated vanadium species. An increase in vanadium loading up to the monolayer coverage of Ti-PILCs enhanced the formation of the polymerized vanadium species, while further increases in vanadium loading resulted in the formation of the microcrystalline V_2O_5 particles. It was reported that polymerized vanadium species are more catalytically active in the NH_3 -SCR reaction compared to isolated vanadium species and V_2O_5 microcrystallinities. Moreover, it was shown that the formation of polyvanadates is more favorable on Ti-PILC than on TiO_2 , Al_2O_3 , or SiO_2 with similar coverage of vanadia on the catalyst's surface.

As already mentioned, the relatively high volatility of vanadia is one of the motivations for development of new catalytic systems for the NH_3 -SCR process. Very promising results were reported for Ti-PILCs modified with iron [58–60]. Long and Yang [58] studied Ti-PILCs obtained by intercalation of montmorillonite with Ti oligocations, which under calcination conditions were transformed into TiO_2 pillars. Deposition of iron into Ti-PILCs resulted in active and selective catalysts of the NH_3 -SCR process. It was shown that such Fe/Ti-PILCs catalysts, in contrast to commercial $\text{V}_2\text{O}_5\text{--TiO}_2$ -based catalysts, effectively operated up to temperatures as high as 450 °C. This effect was explained by the significantly lower catalytic activity of the Fe/Ti-PILCs catalysts in the side process of ammonia oxidation compared to the catalysts based on the $\text{V}_2\text{O}_5\text{--TiO}_2$ metal oxide system. Moreover, additional activation of the Fe/Ti-PILCs catalysts was observed after simultaneous introduction of SO_2 and water vapor into the reaction mixture. This interesting effect was explained by the formation of additional strong acid sites. As shown by IR and XPS experiments, SO_2 was partially oxidized to SO_3 by O_2 on the surface and sulfate species was formed under reaction conditions. Such sulfate species play a role in strong acid sites of Brönsted and Lewis types, however when a water molecule is bonded to the Lewis acid sites, these become Brönsted acid sites. The sulfonation of Fe/Ti-PILCs and Ti-PILCs resulted in much higher increases in acid site concentrations for the Fe/Ti-PILCs catalysts, indicating that the sulfate species are formed mainly by the interactions of SO_2 with monomeric iron ions or aggregated iron species. However, in this case, the role of iron as a catalyst of SO_2 -to- SO_3 oxidation cannot be excluded. Long et al. [59] verified the activity of Fe/Ti-PILCs in the process of ammonia oxidation as a side reaction of NH_3 -SCR. It was shown that ammonia oxidation at temperatures above 350 °C is significantly limited after sulfonation of the Fe/Ti-PILC catalysts. The authors postulated that ammonia in the gas phases is much more easily oxidized compared to ammonia bound to the acid sites of the catalysts. Sulfonation of Fe/Ti-PILC results in the generation of additional acid sites for ammonia chemisorption, and therefore decreased ammonia contribution in the gas phase. Thus, NH_3 oxidation to NO_x was inhibited and the NH_3 -SCR efficiency at higher temperatures was enhanced. Sulfonation of the Fe/Ti-PILC catalysts also improved their selectivity to nitrogen in the process of ammonia oxidation, especially at temperatures above 400 °C. Thus, similarly to

V₂O₅-Ti-PILCs, Fe/Ti-PILCs also showed very good catalytic performance in the presence of a gas mixture containing SO₂, which is a typical component of flue gases emitted from coal power plants and other sources. Moreover, in contrast to the commercial V₂O₅-TiO₂-based catalysts, modified PILCs also effectively operated at temperatures above 400 °C.

The mechanism of the NH₃-SCR process over Fe/Ti-PILCs was studied by Long and Yang [60], who reported their catalytic activity in NO-to-NO₂ oxidation. NO₂ is necessary for so-called “fast SCR”, being one of the possible pathways for low-temperature NO_x reduction with ammonia:



Comparison of the results for NO-to-NO₂ oxidation by oxygen present in the reaction mixture for Ti-PILCs and Fe/Ti-PILCs showed that this reaction is possible mainly due to the presence of iron. The activity of iron species in NO-to-NO₂ oxidation has been recently reported for other catalytic systems [61,62]. It was shown that under reaction conditions, ammonia is chemisorbed on Brönsted and Lewis acid sites in the form of NH₄⁺ cations and coordinated NH₃ species, respectively [60]. NO_x adspecies were found on the catalysts surface under reaction conditions. Both these forms of chemisorbed ammonia are active in NO_x conversion, however the reaction with NO₂ is much faster than with NO. On the other side, it was also reported that sulfonation of the Fe/Ti-PILC catalyst decreased its efficiency in NO-to-NO₂ oxidation [59]. Chmielarz et al. [28] studied Ti-PILCs obtained from montmorillonite and modified with iron, which were deposited mainly in the form of small iron oxide aggregates. Similarly to the study by Long and Yang [60], it was reported that ammonia chemisorbed on the catalyst's surface, possibly on iron cations and iron oxide aggregates, is activated to NH₃-SCR reaction. NO_x surface species were not detected under reaction conditions [28]. Moreover, it seems that small iron oxide aggregates are less active in the side reaction of direct ammonia oxidation compared to monomeric iron cations, and therefore catalysts containing such iron species are more effective in the high-temperature NH₃-SCR process [28]. For the Fe/Ti-PILC catalyst containing small, aggregated iron oxide species, the NO conversion was at the level of about 88%, with selectivity to N₂ of about 93% at 550 °C [28].

The catalytic performance of Fe/Ti-PILCs can be improved by deposition of the additional components. Cheng et al. [63] verified the catalytic activity of a series of Ti-PILCs doped with iron and chromium. The Ti-PILC samples modified only with iron or chromium, as well as those modified with both these components with different ratios, were prepared and tested. It was shown that the Ti-PILC samples doped simultaneously with iron and chromium presented the highest catalytic activity in the NH₃-SCR process. The Fe-Cr/Ti-PILC catalyst with a Fe/Cr ratio of 3:1 presented better catalytic activity than commercial V₂O₅/TiO₂ catalysts under the same reaction conditions. Moreover, the Fe-Cr/Ti-PILC catalyst was less active in the undesired reaction of SO₂-to-SO₃ oxidation by about 75–80% compared to the commercial catalysts based on the V₂O₅/TiO₂ oxide system. The higher contribution of Brönsted acidity than the Lewis acidity on the surface under reaction conditions was observed. Moreover, a direct correlation between the NH₃-SCR activity and the Brönsted acidity among pillared clays with different Fe/Cr ratios was proven.

As already mentioned, the efficiency of the low-temperature NH₃-SCR process can be significantly influenced by the presence of both NO and NO₂ in the reaction mixture, which is necessary for the fast SCR reaction (Equation (6)). Thus, increasing the activity of the catalysts in NO-to-NO₂ oxidation should result in more effective NH₃-SCR catalysts. Long and Yang [64] reported that the introduction of small amounts (≤2 wt%) of cerium, praseodymium, or terbium oxides significantly improved the activity of Fe/Ti-PILC catalysts in NO-to-NO₂ oxidation, and therefore also activated them in the low-temperature NH₃-SCR process. The most significant activation effect was observed after introduction of CeO₂. However, an increase in CeO₂ loading to 5 wt% resulted in the catalyst's deactivation due to formation of the cubic CeO₂ phase, which is less effective in NO-to-NO₂

oxidation than dispersed cerium oxide species. The commercial NH_3 -SCR catalysts based on vanadia–titania were reported to be only slightly active in NO-to- NO_2 oxidation and after addition of CeO_2 , in contrast to Ce–Fe/Ti-PILCs catalysts [64].

In general, deposition of iron into alumina-pillared clays (Al-PILCs) resulted in less active catalysts compared to Fe/Ti-PILCs. Chmielarz et al. [65,66] studied Fe/Al-PILCs based on acid-treated phlogopite and vermiculite. Intercalation of these types of clay minerals was reported to result in more thermally stable pillared structures compared to the montmorillonite-based PILCs [22,23]. However, due to the very strong stabilization of interlayer cations in such clays, it is necessary to extract some of the aluminum cations from the clay layers to decrease the stabilization energy of the interlayer cations and make possible their exchange for aluminum oligocations. Thus, prior to the intercalation, such clays must be treated with mineral acids to extract some of the aluminum cations from clay layers. Therefore, the intercalation process in this case is much more complicated and less effective, especially in the case of phlogopite [65,66]. Iron was introduced into Al-PILCs using the ion exchange method. The Fe/Al-PILCs catalysts based on phlogopites presented activity only at higher temperatures. However, above 400 °C, intensive ammonia oxidation decreased the efficiency of the NH_3 -SCR process [65]. The catalysts based on alumina-intercalated vermiculite were more active, especially at lower temperatures, however in this case intensive ammonia oxidation above 400 °C also significantly decreased the efficiency of the NH_3 -SCR process [66]. On the other hand, Ziemniński et al. [67] studied montmorillonite intercalated with mixed iron–alumina pillars (Fe–Al-PILCs) as NH_3 -SCR catalysts. In this case, the NO conversion started above 200 °C and the level of 90% was obtained at about 350 °C. The drawback of the reaction conducted in the presence of these catalysts was the relatively high production of N_2O , which is the main side product of the NH_3 -SCR process.

Chmielarz et al. [19,20] reported promising catalytic activity for zirconium-intercalated montmorillonite doped with manganese and carbon aggregates in low-temperature NH_3 -SCR. In this case, the NO conversion started at about 150 °C and the level of about 95%, with selectivity to N_2 above 94%, which was obtained at 365 °C. Moreover, these catalysts presented a relatively good stability in the reaction tests conducted in the presence of water vapor and SO_2 [68]. Very promising results for low-temperature NH_3 -SCR were reported by Shen et al. [69] for Mn– CeO_x /Zr-delaminated montmorillonite. Manganese and cerium were deposited into Zr-PILCs by impregnation method, and therefore there was a significant contribution of manganese in the form of MnO_2 crystallites in the samples. In the presence of the most active Mn– CeO_x /Zr-PILC catalysts, the NO conversion above 90% was obtained at temperatures below 200 °C. Moreover, it was shown that the catalytic activity of Mn– CeO_x /Zr-PILCs is higher than Mn– CeO_x /Ti-PILCs and Mn– CeO_x /Fe-PILCs in the delaminated forms. On the other hand, the effect of the significant catalytic deactivation of Mn– CeO_x /Zr-PILCs in NH_3 -SCR by deposition of alkali metals was shown [69]. Shen et al. [70] intercalated bentonite simultaneously with zirconium and cerium, and therefore ceria was incorporated directly into zirconia pillars. Manganese was deposited into Ce–Zr-PILCs by impregnation method, and under calcination conditions formed MnO_2 , Mn_2O_3 , and Mn_3O_4 crystallites. It was shown that the optimal loading of manganese, resulting in the most active catalysts, is 12–18 wt%. The NO conversion in the presence of these catalysts started below 100 °C and reached the level of 95% at 200 °C. At temperatures above 250 °C, a small decrease in the NH_3 -SCR efficiency due to the side process of direct ammonia oxidation was observed. The Mn/Ce–Zr-PILC catalysts presented very good stability in the wet reaction mixture (8 vol % of water vapor), as well as in catalytic runs conducted with a relatively high space velocity ($\text{GHSV} = 50,000 \text{ h}^{-1}$) [70]. Thus, zirconia-intercalated clays modified with manganese deposited in the form of aggregates or small crystallites are very promising catalysts for the low-temperature NH_3 -SCR process. The low-temperature activity can be improved by deposition of cerium, which probably intensifies NO-to- NO_2 oxidation [64].

Very promising results for low-temperature NH_3 -SCR were reported by Chmielarz et al. [20] for titania-intercalated montmorillonite doped with copper via the ion exchange method (Cu/Ti-PILCs). For the most active catalysts of this series, the NO conversion was above 80%, with selectivity to N_2 of 98–99% at 200 °C. The efficiency of the NH_3 -SCR process decreased above 400 °C due to the side reaction of direct ammonia oxidation by oxygen present in the reaction mixture. Moreover, the NO conversion only slightly decreased (by less than 2%) for the reaction conducted in the wet reaction mixture. The catalysts obtained via intercalation of montmorillonite with pillars containing both titanium and copper (Cu-Ti-PILCs), as well as alumina-pillared montmorillonite doped with copper via the ion exchange method (Cu/Al-PILCs), were less active in the NH_3 -SCR process [20]. Thus, it seems that copper deposited on titania pillars is more effectively activated than copper deposited on the clay surface or alumina pillars. In the case of pillars simultaneously containing aluminum and copper, part of transition ion metal is located inside of the pillars, and therefore is not accessible for the catalytic process. A comparison of the catalytic performance of Cu/Ti-PILCs and Cu/Zr-PILCs showed a significantly higher activity of the clay intercalated with titania [12]. Moreover, comparison studies of NO and NH_3 chemisorption on Cu/Al-PILCs, Cu/Ti-PILCs, and Cu/Zr-PILCs showed that both these reactants could be chemisorbed on the studied samples [12]. The largest amount of NO was chemisorbed on Cu/Ti-PILCs. Additionally, for this sample the most intensive NO-to-nitrate oxidation was detected. Such activity in NO oxidation may also high indicate efficiency in NO-to- NO_2 oxidation, and therefore possible conversion of part NO_x at lower temperatures according to the fast SCR pathway.

In summary, catalysts based on pillared interlayered clays (PILCs) were reported to be effective in the NH_3 -SCR process, both in high and low temperature ranges. Considering the limited thermal stability of the pillared structures of PILCs, the studies focused on development of low-temperature catalysts based on such pillared clays seems to be the most effective. The results obtained for Zr-PILCs modified with manganese aggregates and crystallites, as well as Cu-Ti-PILCs, are very promising and may indicate further directions of research focused on development catalysts for the low-temperature NH_3 -SCR process.

3.1.2. Porous Clay Heterostructures-PCHs

As already mentioned, porous clay heterostructures (PCHs) obtained via intercalation of cationic layered clay minerals with silica pillars are characterized by their high surface area, relatively uniform porous structure [27], and stable pillared structure (at least to 600–700 °C [13,15]). Thus, these materials, in contrast to PILCs, can also be used at higher temperatures. PCHs are characterized by the presence of surface acid sites associated with the separated clay layers. Additional acid sites can be generated by incorporation of additional elements, such as aluminum or titanium, into silica pillars [13–15,71,72]. Thus, through the selection of suitable clay minerals, as well as the composition of interlayer pillars, the surface acidity of PCHs can be tailored for the specific needs of the catalytic process. Moreover, the ion exchange properties of PCHs, which depend mainly on the clay minerals used for their synthesis, favor the introduction of catalytically active metal species in highly dispersed forms. These very promising properties of PCHs have sparked great interest in these materials as potential catalysts for various processes, including selective catalytic reduction of NO with ammonia (NH_3 -SCR) [13,15,30] and selective catalytic oxidation of ammonia (NH_3 -SCO) [67]. Chmielarz et al. [72] reported promising results for the NH_3 -SCR process for PCHs obtained from synthetic saponite intercalated with silica pillars and modified with copper and iron via the ion exchange method. There is a risk of hydrogen ions migrating from the surface of the saponite layers into vacancies in octahedral sublayers, resulting in decreasing ion exchange potential. To avoid this effect, the freshly calcined PCH samples were treated in the flow of gaseous ammonia. This treatment results in conversion of protons into ammonium cations ($\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+$), which are too large to be accommodated in vacancies in octahedral sublayers of saponite. The treatment of PCH supports resulted in significantly increased loading of copper, however did not

influence the loading of iron. The copper-modified PCH operated at significantly lower temperatures in NH_3 -SCR (with the maximum NO conversion occurring at about 350 °C) than iron-doped PCH, which presented maximum NO conversion at about 450 °C. For the series of catalysts containing copper and iron, the selectivity to nitrogen was above 92% up to 500 °C [72]. Moreover, these catalysts were found to be resistant to poisoning by water vapor and SO_2 . The catalysts modified with iron seem to be promising for the high-temperature NH_3 -SCR process. Comparison studies of the catalytic performance of PCHs obtained from various clay minerals, including montmorillonite, saponite, and vermiculite, were reported by Chmielarz et al. [30]. It was shown that the PCH sample obtained from vermiculite presented much better catalytic activity in NH_3 -SCR than other PCHs. This interesting effect was explained by the significantly larger contribution of iron, which is a natural component of vermiculite and is known to be catalytically active in NH_3 -SCR [73]. After deposition of copper and iron via ion exchange method into the PCH materials, their very significant catalytic activation in NH_3 -SCR was observed. In a group of catalysts doped with iron, the best results were obtained for saponite based PCH. In this case, the NO conversion above the level of 90% with selectivity to nitrogen above 95% was measured in the range of 350–500 °C [30]. Similarly, in a group of the PCH samples modified with copper, the best catalytic results were reported for silica-intercalated saponite. However, in this case, the temperature range of the effective NO conversion was narrower than for the iron-modified catalyst. The NO conversion above the level of 90% with selectivity to nitrogen above 93% was obtained in the range of 400–500 °C [30]. All of the studied PCH catalysts-based on different clay minerals and modified with copper or iron-were reported to be resistant to poisoning by SO_2 and water vapor, which may indicate that this is a general property of the PCH-based catalysts. Additionally, these studies [30] indicate very promising properties of iron-modified PCHs as catalysts for the high-temperature NH_3 -SCR process. Very promising catalytic results in the NH_3 -SCR process were reported for montmorillonite-based PCH intercalated with silica–titania pillars [13,15]. It was shown that titanium is present mainly in highly dispersed forms, such as monomeric cations or small polymeric chains incorporated into amorphous silica pillars, which play a role as additional acid sites for ammonia chemisorption. Aggregation of such dispersed titanium species was significantly limited to temperatures as high as 850 °C [13,15]. Such PCHs intercalated with silica–titania pillars presented only limited catalytic activity in NO reduction by ammonia, indicating that ammonia molecules chemisorbed on such Ti sites are not effectively activated for the NH_3 -SCR process (Figure 6). Deposition of copper and iron via ion exchange method resulted in significant catalytic activation of such PCH materials. It should be noted that the presence of titanium in silica pillars in both series of the Cu- and Fe-modified catalysts significantly activated them in the NH_3 -SCR process (Figure 6, compare Cu-PCH and Fe-PCH intercalated with silica pillars with the analogous samples intercalated with silica–titania pillars). It seems that ammonia chemisorbed on Ti sites, which is released at higher temperatures, is a reservoir of the reducing agent for the high-temperature NH_3 -SCR process. High selectivity to nitrogen may indicate the effective protection of ammonia molecules chemisorbed on Ti sites against the side reaction of their direct oxidation. Cu-modified PCHs intercalated with silica–titania pillars and PILCs pillared with TiO_2 and doped with copper showed very significant differences in the temperature windows of their effective operation (Figure 6A). For the PILC-Cu catalyst, NO conversion above the level of 80% was observed in the range of 250–400 °C, while for the most active catalysts of PCH series, PCH-7.5Ti–Cu and PCH-15Ti–Cu, this was shown in the range of 350–550 °C. Such significant differences are possibly related to the different interactions of copper species with TiO_2 aggregates present in PILC-Cu and highly dispersed titanium species incorporated into the silica pillars of the PCH-based catalysts [15,28]. As reported by Chmielarz et al. [28], differently aggregated Ti species result in various types of acid sites. TiO_2 aggregates, being interlayer pillars in PILCs, are characterized by the presence of mainly Lewis-type acidity, while titania species dispersed in amorphous silica pillars of PCHs generate both Lewis- and Brønsted-type acidity. There

is a significant contribution of strong acid sites of Lewis type in such PCHs, which are possibly able to protect chemisorbed ammonia molecules against oxidation, and therefore extend their effective operation to the high-temperature NH_3 -SCR process [15].

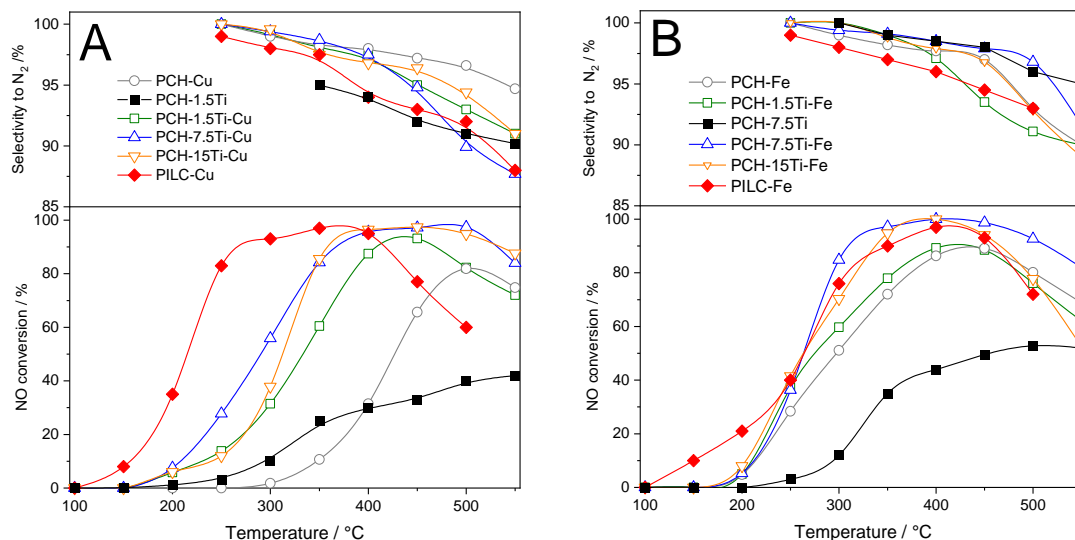


Figure 6. Results of catalytic tests for the PCH samples intercalated with titania–silica pillars (Ti molar contents in pillars were 0, 1.5, 7.5, and 15%) modified with copper (A) and iron (B). For comparison, results for Ti-PILCs modified with copper and iron are presented. Reaction conditions: 0.1 g catalyst, $[\text{NO}] = [\text{NH}_3] = 2500$ ppm, $[\text{O}_2] = 2.5\%$, He = balance, total flow rate = 40 mL min^{-1} , and GHSV = $12,500 \text{ h}^{-1}$. Based on the results presented in [15] with permission from ref. [43]. Copyright 2009 Elsevier.

In the series of iron-modified catalysts based both on PCHs and PILCs, the temperature windows for effective catalytic operation are in very similar temperature ranges (Figure 6B). However, the most active catalysts of the PCH series—PCH-7.5Ti-Fe—is more effective in the NH_3 -SCR process compared to PILC-Fe. Moreover, the NO conversion in the PCH-based catalysts is less affected by the side reaction of direct ammonia oxidation, and therefore the decrease in the NH_3 -SCR efficiency in the high-temperature range is less significant than for PILC-Fe (Figure 6B).

Another very important advantage of the silica–titania-intercalated PCHs modified with copper and iron is their catalytic stability in the reaction mixtures containing SO_2 and water vapor. Both SO_2 and water vapor are typical components of flue gases, which can result in catalyst deactivation [15]. Thus, titania–silica-intercalated PCHs, especially those doped with iron, seem to be very promising for the formulation of high-temperature NH_3 -SCR catalysts. In this case, there is no risk of the collapse of the pillared structure under reaction conditions because of the much higher stability of the PCH structure compared to PILCs.

3.2. Catalysts Based on Layered Zeolites

There is a relatively broad group of layered zeolites with different porous structures that can be tailored for specific applications [5,43,44]. The ion exchange and acidic properties of aluminum–silicon zeolites are dependent on the Si/Al ratio, while inter-layer spaces in such materials can be opened via their intercalation or delamination. Zeolitic materials modified by these methods are characterized by their bimodal micro- and mesoporous structure, and have been reported to be very promising in various catalytic applications [5,6,9,43,44], including the selective catalytic reduction of NO_x with ammonia [7,61,74–77].

Rutkowska et al. [74] reported high catalytic activity of intercalated (MCM-36) and delaminated (ITQ-2) layered zeolites modified with iron and copper via ion exchange method.

Both zeolites were obtained by swelling of MCM-22 precursors with an aqueous solution of a mixture containing hexadecyltrimethylammonium bromide and hexadecyltrimethylammonium hydroxide, as well as tetrapropylammonium bromide and hydroxide. Swollen MCM-22 precursor, containing surfactant molecules in the interlayer spaces, was intercalated with silica pillars using TEOS as the silica source. Calcination of the modified MCM-22 precursor resulted in silica-intercalated MCM-36. On the other hand, sonication of MCM-22 precursor in an ultrasound bath followed by its calcination resulted in a delaminated structure of ITQ-2 [74]. The intended Si/Al molar ratio in the zeolite layers was 15. The ion exchange method, used for the introduction of iron and copper into the zeolitic samples, resulted mainly in monomeric cations of these metals, however the content of deposited iron (0.9–1.0 wt%) was significantly lower than for copper (4.6–7.6 wt%). Layered zeolites modified with copper presented very promising catalytic properties in the NH_3 -SCR process. The NO conversion above the level of 90% was obtained in the range of 200–550 °C for MCM-22 (microporous) and MCM-36 (silica pillared) zeolites modified with copper. For Cu-ITQ-2, the NO conversion above 90% was obtained in the range of 200–500 °C. In this case, the side process of direct ammonia oxidation decreased the efficiency of the NH_3 -SCR process at higher temperatures [74]. On the other hand, the Cu-ITQ-2 catalyst was found to be resistant to the presence of water vapor in the reaction mixture. Iron-modified layered zeolites are significantly less effective NH_3 -SCR catalysts. For the Fe-MCM-22 catalyst, the NO conversion level above 90% was obtained in the range of 300–550 °C, while for Fe-ITQ-2 this was in the range of 350–500 °C. Due to the significantly lower loading of iron than copper in the zeolitic samples, it cannot be stated unequivocally that copper is more catalytically effective in the NH_3 -SCR process than iron. However, it should be noted that copper-modified MCM-22, MCM-36, and ITQ-2 effectively operated in much broader temperature ranges compared to commercial NH_3 -SCR catalysts based on the V_2O_5 - TiO_2 metal oxide system (300–400 °C). Thus, the results of the catalytic studies obtained for such modified layered zeolites are very promising.

Chen et al. [75] analyzed the influence of the method used for iron deposition into MCM-22 on the catalytic performance in NH_3 -SCR. The first catalyst was obtained via one-pot (OP) hydrothermal route using a mixture of silica sol, sodium meta-aluminate, and iron nitrate, also containing hexamethyleneimine, sodium hydroxide, and deionized water. The other catalysts were obtained via post-synthesis modifications with iron precursor (iron nitrate), namely incipient wetness impregnation (IM), mechanical mixing (MM), and solid-state ion exchange (SSIE). Interestingly, in the samples obtained via OP method, a significantly higher contribution of iron in the form of highly dispersed species, mainly monomeric cations, was found compared to the catalysts obtained via IM, MM, and SSIE, which contained larger amounts of iron in the form of aggregated iron oxide species (as confirmed by XRD and UV-Vis DRS analyses). Moreover, it was shown that the reduction of Fe^{3+} to Fe^{2+} in OP-Fe-MCM-22 occurred at temperatures lower than for other zeolitic catalysts. It is possible that this was due to the better catalytic activity of OP-Fe-MCM-22, especially in the low-temperature range, than for the catalysts modified with iron via IM, MM, and SSIE methods. The catalysts doped with iron using post-synthesis methods presented very similar profiles for the NO conversion, with a significant decrease in the NH_3 -SCR efficiency at temperatures above 400 °C due to the side process of direct ammonia oxidation [75]. These interesting studies clearly show that the form and aggregation of iron species deposited into zeolites are very important for their activation in the NH_3 -SCR process.

Jankowska et al. [61] studied MCM-22 and its silica–titania-pillared form, MCM-36, modified with iron via ion exchange method, in the role of NH_3 -SCR catalyst. It was shown that incorporation of titanium species into silica pillars generated additional acid sites and resulted in significant activation of the catalysts. For the most active catalysts of this series (Fe-Ti-MCM-36), NO conversion above the level of 90% was obtained in the range of 350–500 °C, while for the silica-intercalated zeolite (Fe-MCM-36), this was in the range of 400–500 °C. Thus, incorporation of titanium into silica pillars catalytically activated zeolites

at lower temperatures. This was explained by slightly higher activity of such silica–titania-intercalated zeolites modified with iron in the process of NO-to-NO₂ oxidation [61], which is needed for fast SCR (Equation (6)). It was reported that the activating role of titanium could be related to the bounding of NO₂ molecules to the surface $\equiv\text{Ti}-\text{O}-$ groups, resulting in reactive surface nitrates [76]. Moreover, it was postulated that such nitrate species can relatively easily react with ammonia molecules. During such reactions, the monomeric Ti⁴⁺ cations are reduced to Ti³⁺, which possibly play a role in active sites in the NH₃-SCR reaction [76,77]. Moreover, Liu et al. [78,79] postulated that the formation of Ti–O–Fe species in iron titanate catalysts for NH₃-SCR improved the redox properties of iron, and therefore improved its activity in NO-to-NO₂ oxidation.

MCM-22 zeolites modified with copper were reported to be very effective catalysts of low-temperature NH₃-SCR [80]. A series of catalysts were prepared via deposition of various amounts of copper on MCM-22 (Si/Al = 15) through incipient wetness impregnation. For the samples with the lower copper loading, mainly monomeric copper cations were deposited, while a higher contribution of aggregated copper oxide species was detected for the catalysts with the higher loadings of this metal (verified by XRD, UV-Vis DRS, and H₂-TPR). It was reported that the NO conversion obtained in the presence of the catalysts with higher copper loading and with a significant contribution of aggregated copper oxide species was above the level of 90% in the range of about 200–350 °C. In the case of the catalyst with the lowest copper loading, deposited mainly in the form of monomeric copper cations, the conversion above the level of 90% was obtained in the range of about 250–400 °C. These results may indicate that aggregated copper oxide species are more catalytically active in low-temperature NH₃-SCR and more active in the side process of direct ammonia oxidation than monomeric copper cations. The low-temperature activity of aggregated copper oxide species in NH₃-SCR is possibly attributed to their better reducibility compared to monomeric copper cations. This hypothesis was proved by the improved low-temperature activity of the catalyst with the lowest copper loading after hydrothermal ageing, which probably resulted in aggregation of copper species.

Świąć et al. [7,34] reported very interesting catalytic properties of ferrites (FER) and their delaminated and intercalated forms, which were modified with copper via ion exchange method. The studies were focused on the determination of the role of the porous structure and Si/Al framework ratio in their catalytic performance in the NH₃-SCR process [7]. It was shown that in the case of ferrierites (FER), copper is deposited mainly in the form of aggregated copper oxide species and is located on the outer surface of the zeolitic grains. It is probably related to the relatively small 10MR (member ring) channels in ferrierite with diameters of about 0.53–0.55 nm, which limits internal diffusion of copper aqua complexes during the ion exchange procedure. Therefore, copper is deposited mainly on the outer surface of the zeolite grains and during subsequent calcination is aggregated to larger metal oxide species. The opening of the interlayer space of ferrierite precursors via delamination or interaction of the zeolite layers yields ITQ-6 and ITQ-36, respectively. Deposition of copper into such zeolitic materials with a bimodal microporous and mesoporous structure resulted in highly depressed species, mainly monomeric copper cations, as proven in UV-vis DRS and H₂-TPR studies [7]. An increase in the Si/Al ratio in the zeolitic samples resulted in decreased surface concentrations of acid sites, as well as decreased loading of copper deposited via ion exchange method. This was exactly what was expected, considering the role of framework aluminum cations in the formation of acid sites and generation of ion exchange properties.

The microporous ferrierites modified with copper in the form of aggregated metal oxide species effectively operated in the high-temperature range, while conversion above the level of 90% for the more active catalyst of this series was achieved in the range of 325–425 °C (Figure 7). At higher temperatures, the side reaction of ammonia oxidation decreased the efficiency of the NH₃-SCR process. For the delaminated zeolite, ITQ-6, containing copper in highly dispersed form, the NO conversion above the level of 90% was achieved in the range of 275–425 °C (Figure 7), while for the silica-intercalated zeolite,

ITQ-36, which was also doped with highly dispersed copper species, this was achieved in the range of 300–425 °C [7]. Thus, the results were slightly different from those obtained for MCM-22 and its delaminated and intercalated forms modified with copper [80], which effectively operated in a broader temperature range compared to the catalysts of ITQ-6 and ITQ-36 series modified with copper [7]. This could be related to the differences in the porous structures of the zeolite materials, especially zeolite layers, however possibly the surface acidity of the zeolitic samples, related to the Si/Al ratio, is a more important factor. In the case of copper-modified intercalated (MCM-36) and delaminated (ITQ-2) layered zeolites, as studied by Rutkowska et al. [74], with the Si/Al molar ratio of zeolitic layers of about 15, their effective catalytic operation was observed across a much broader range than for copper-modified ITQ-6 and ITQ-36 with the much higher Si/Al ratios (30 and 50, respectively) [7]. The main difference was observed in the high-temperature NH_3 -SCR process, where the side reaction of direct ammonia oxidation was significantly less intensive for the samples with lower Si/Al ratios, and thus with higher concentrations of acid sites.

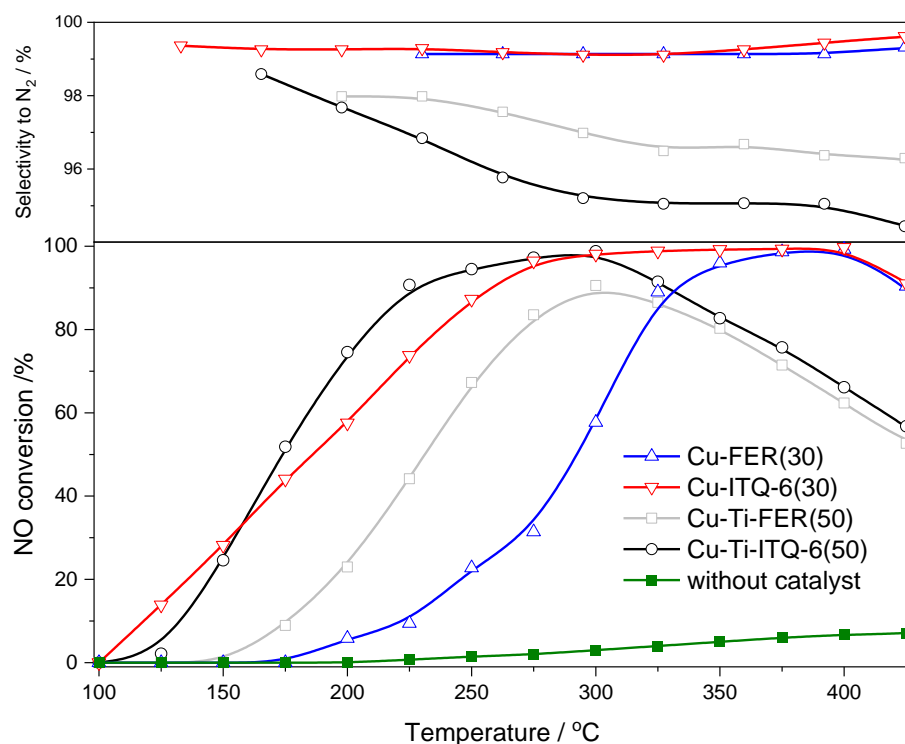


Figure 7. Results of NH_3 -SCR catalytic tests for aluminum–silicon (FER) and titanium–silicon (Ti-FER) ferrierites and their delaminated forms, ITQ-6 and Ti-ITQ-6, respectively, modified with copper via ion exchange method. Reaction conditions: 0.1 g catalyst, $[\text{NO}] = [\text{NH}_3] = 2500$ ppm, $[\text{O}_2] = 2.5\%$, He = balance, total flow rate = 40 mL min^{-1} , and GHSV = $12,500 \text{ h}^{-1}$. Values in brackets are intended molar Si/Al or Si/Ti ratios in the zeolite framework. Based on the results presented in [7,34] with permission from ref. [34]. Copyright 2021 The Royal Society of Chemistry.

A similar effect was also observed for the samples of ITQ-6 and ITQ-36 series modified with copper. The samples with higher contents of framework alumina were less active in the side process of direct ammonia oxidation, and therefore more effective in high-temperature NH_3 -SCR process compared to the zeolitic catalysts with the lower content of framework aluminum [7]. It is possible that the surface acid alumina sites protect chemisorbed ammonia molecules against direct oxidation, and therefore extend the high-temperature activity of the studied catalysts in the NH_3 -SCR process. Another important issue is the activation of the catalysts for the low-temperature NH_3 -SCR process. As was already mentioned, one of the most important mechanisms of this low-temperature

process, called fast SCR, is based on the partial oxidation of NO-to-NO₂ and then the reduction of such nitrogen oxide mixtures by ammonia (Equation (6)). Thus, catalysts for low-temperature NH₃-SCR should also be active in NO-to-NO₂ oxidation.

Świąś et al. [7] reported results for studies on copper-modified FER, ITQ-6, and ITQ-36 zeolites. It was shown that copper species in these zeolites are catalytically active in NO-to-NO₂ oxidation, however the form and aggregation of copper species are very important. The FER zeolite with a significant contribution of copper deposited in the form of copper oxide aggregates was significantly less active in this reaction compared to ITQ-6 and ITQ-36 zeolites containing mainly highly dispersed copper species (monomeric copper cations). Thus, it could be supposed that highly dispersed copper species are more catalytically active in NO-to-NO₂ oxidation compared to aggregates of copper oxide. The strict correlation between the activity of the catalysts in NO-to-NO₂ oxidation and their activity in low-temperature NH₃-SCR was shown, proving the very important role of the fast SCR mechanism in nitrogen oxide reduction with ammonia [7].

Very interesting results were obtained for titanium–silicon ferrierites (Ti-FER) and their delaminated forms (Ti-ITQ-6) doped with copper via ion exchange method [76]. Similarly to aluminum–silicon ferrierites [7], deposition of copper, due to the limited internal diffusion of copper aqua complexes in small pores of Ti-FER, resulted mainly in aggregated metal oxide species located on the external surface of the zeolite grains. For the open delaminated structure of Ti-ITQ-6, copper was introduced mainly in the form of highly dispersed species, with a significant contribution of monomeric copper cations. The form and aggregation of deposited copper species, similarly to silicon–aluminum zeolites [7], strongly influenced the temperature range of the effective operation of the catalysts. For the most active Ti-ITQ-6-based catalysts, the NO conversion above the level of 90% was achieved in the range of 225–325 °C, while for the most active catalyst based on Ti-FER, this was in the range of 300–325 °C (Figure 7). Thus, as already postulated, in this case the highly dispersed copper species seem to be very important for the low-temperature NH₃-SCR process [81]. It should be noted that the copper-modified catalysts of the Ti-ITQ-6 series effectively operated at lower temperatures [76] than catalysts based on aluminum–silicon ITQ-6 [7], and therefore seem to be very promising as catalysts for the low-temperature NH₃-SCR process. On the other hand, the side reaction of direct ammonia in the presence of copper-modified titanium–silicon zeolites started at temperatures significantly lower than in the cases of the copper doped aluminum–silicon zeolites [7,34]. The titanium–silicon zeolites, as shown by NH₃-TPD analyses, are characterized by weaker acid sites than analogues of aluminum–silicon zeolites. Thus, the acid sites in Ti-FER and Ti-ITQ-6 are possibly not strong enough to chemisorb ammonia molecules and protect them against direct oxidation by oxygen present in the reaction mixture. Thus, the conclusions from these studies [34] are in line with the results obtained for the aluminum–silicon zeolites [7].

Layered zeolites modified with copper or iron belong to the group of very promising NH₃-SCR catalysts. By controlling the loading and form of deposited metals, as well as the surface acidity of the zeolites, the specific properties of such catalysts can be tailored for low- or high-temperature NH₃-SCR processes. On the other hand, it was shown that the open porous structures of delaminated and intercalated zeolites facilitate the possibility of metal introduction in highly dispersed forms.

4. Selective Catalytic Oxidation of Ammonia (NH₃-SCO)

The oxidation of ammonia, which is a side reaction of the NH₃-SCR process, is considered an important reaction for the elimination of ammonia in various industrial waste gases [8]. In this case, the high selectivity of the ammonia-to-nitrogen conversion (Equation (5)) and the lack of activity in ammonia oxidation to nitrogen oxides (Equations (3) and (4)) are very important factors. Another important issue is the adjustment of the temperature window of the effective catalyst operation to the temperature of waste gas to avoid additional heating or cooling. In recent decades, the application of selective catalytic ammonia oxidation (NH₃-SCO, AMOx) to nitrogen has been considered to support NH₃-

SCR converters in electric power stations, as well as exhaust systems in diesel cars [8]. To avoid the unreacted ammonia leaking from the NH_3 -SCR converter, its residues in the gas stream are selectively oxidized into nitrogen over NH_3 -SCO catalysts located downstream of the NH_3 -SCR converter. Of course, there are different needs for the catalysts operating in flue gas cleaning systems in power plants and those operating in exhaust gas systems in diesel cars, related mainly to the different temperatures and compositions of such flue gases. Thus, effective catalysts for the selective oxidation ammonia to nitrogen, tailored to the parameters of real flue gases emitted by power stations and diesel engines, are still needed. Among the various catalytic systems, modified layered clay minerals and zeolites have been studied as catalysts of the NH_3 -SCO process [71,82–84].

The porous clay heterostructure (PCH) obtained through intercalation of synthetic saponite with silica pillars was used as the catalytic support for the preparation of the NH_3 -SCO catalysts [67]. Copper and iron were deposited into the PCH support via ion exchange method in the form of highly dispersed species, namely monomeric cations and small oligomeric metal oxide aggregates. The copper-containing catalysts, especially those with higher copper loading, operated at lower temperatures—complete NH_3 oxidation was achieved at about 400 °C. Iron-modified PCHs effectively operated at significantly higher temperatures. In this case, complete ammonia oxidation was achieved at about 550 °C. Importantly, the selectivity to nitrogen, both in the series of copper- and iron-modified PCHs, was very high and did not drop below 90% in the studied temperature range of 150–550 °C. Thus, such clay-based catalysts, depending on the catalytically active metal being deposited, effectively operated at lower and higher temperatures. The high selectivity to nitrogen, especially at higher temperatures, is a very important advantage of this group of the catalysts.

Zeolites modified with transition metals have been reported to be active and selective catalysts of NH_3 -SCO [8,82,83]. Wang et al. [83] compared the catalytic activity of copper-modified zeolites with different framework structures. Copper introduced into zeolites via impregnation method was deposited both in the form of highly dispersed copper species as well as larger copper oxide aggregates. The porous structure of the zeolites influenced the contributions of the different aggregated copper species. For the zeolites with narrow micropores, a larger contribution of aggregated copper oxide species was detected in comparison to the samples with larger micropores. This effect can be explained by the limited internal diffusion rate of copper aqua complexes in narrow pores of zeolites during their impregnation process. All of the studied zeolites were characterized by their similar molar Si/Al ratios in the range of 10 to 15 [83]. The catalysts based on MCM-49 and ferrierite (FER), obtained from layered precursors, presented very good activity in the NH_3 -SCO process. The complete conversion of ammonia in the presence of Cu/MCM-49 was achieved at temperature 400 °C, while in the case of Cu/FER this was achieved at 450 °C. In the group of the studied zeolites, the best results were obtained for Cu/ZSM-5 (100% NH_3 oxidation at 300 °C). The selectivity to nitrogen for these catalysts was above 90% up to 550 °C. The differences in activity of copper-modified zeolites were explained mainly by the various contributions of highly dispersed and aggregated copper species. It was postulated that highly dispersed copper species, such as monomeric cations, are more catalytically active in ammonia oxidation compared to aggregated copper oxide species [83,84]. On the other side, a higher contribution of such aggregated copper oxide species was found in zeolites with smaller pores, such as FER and ITQ-49 with 10 MR channels [78]. As already mentioned, the diffusion rate of copper aqua complexes in such channels is limited, and moreover plugging of such narrow channels is more likely than larger pores. Świąś et al. [7] studied ferrierites (FER) with intended molar Si/Al ratios of 30 and 50, as well as their delaminated (ITQ-6) and silica-intercalated (ITQ-36) forms modified with copper via ion exchange method, as catalysts of the NH_3 -SCO process. Similarly to previously reported studies [83,84], in this case significant amounts of copper were deposited in the form of aggregated copper oxide species on the external surfaces of microporous ferrierite grains [7]. In the opened interlayer structures of ITQ-6 and ITQ-36,

copper was deposited mainly in the form of monomeric copper cations [7]. The form of copper species in the zeolitic catalysts strongly influenced their activity in terms of ammonia oxidation. The samples containing mainly highly dispersed forms of this metal were more catalytically active than catalysts with a significant contribution of aggregated copper oxide species (Figure 7). Thus, these results prove the hypothesis regarding the higher catalytic activity of dispersed copper species than copper oxide aggregates in ammonia oxidation postulated by Wang et al. [83] and Zhang et al. [84]. Very significant differences in catalytic activity were observed for the zeolitic catalysts with the different Si/Al ratios [7]. In the case of Cu-ITQ-6 and Cu-ITQ-36 the catalysts with the higher Si/Al molar ratio (intended value-50) operated at temperatures significantly lower than the catalysts with the lower Si/Al molar ratio (intended value-30). Thus, it seems that acid sites, resulting from the presence of aluminum cations in the zeolite framework, are not beneficial for low-temperature ammonia oxidation. It is possible that some of the ammonia molecules are chemisorbed on the acid sites generated by framework aluminum cations, which are properly activated for the reaction with oxygen. On the other hand, ammonia bound to the surface copper species by the accommodation of free electron pairs of ammonia into unoccupied d-orbitals of copper (donor–acceptor binding of Lewis-type acid sites) is much more effectively activated in the oxidation reaction. Thus, it seems that there is competition in terms of ammonia chemisorption on catalytically active copper species and catalytically inactive framework aluminum acid sites. Of course, the higher contributions of such catalytically inactive acid sites may result in decreased efficiency of ammonia oxidation at lower temperatures. The selectivity to nitrogen, independently of the copper species aggregation, was above the level of 97% up to 500 °C. On the other hand, for catalysts with the higher Si/Al ratio in the zeolite framework, the selectivity to nitrogen was stable to the level of 95% up to 400 °C, but significantly decreased at higher temperatures [7].

In the next stage, titanium–silicon ferrierites (Ti-FER) and their delaminated forms (Ti-ITQ-6) modified with copper by ion exchange were tested as potential catalysts of the NH_3 -SCO process [9]. These catalysts, which were based on titanium–silicon zeolites, were compared with the analogous zeolitic aluminum–silicon-based catalysts. The intended molar Si/Al and Si/Ti ratios were 50. It was shown that the presence of aluminum or titanium in the zeolite framework influenced the form and aggregation of deposited copper species. In the case of Ti-zeolites, a significant contribution of aggregated copper species was identified, in contrast to Al-zeolites with higher contribution of the highly dispersed forms of copper [9]. This is not surprising, considering the dominant role of the ion exchange mechanism of copper deposition in Al-zeolites, as well as the much more complex mechanisms involved for Ti-zeolites. It was postulated [32] that part of the framework $\equiv\text{Si}-\text{O}-\text{Ti}\equiv$ bridges can be hydrolyzed under treatment with an aqueous solution of copper salt with the formation of weakly acidic $\equiv\text{Si}-\text{OH}$ and $\equiv\text{Ti}-\text{OH}$ groups, which are potential ion exchange sites. Moreover, it was suggested that copper can be attached to the $\equiv\text{Si}-\text{O}-\text{Ti}\equiv$ bridges as a surface complex [32]. In these cases, copper is attached to the zeolite framework by weaker forces compared to the Coulombic interactions of the negatively charged aluminum–silicon zeolite framework with copper cations. Therefore, aggregation of such copper species under calcination conditions is much easier for Ti-zeolites than Al-zeolites. The study by Świąć et al. [9] showed the better activity of the copper-modified layered titanium–silicon zeolites at lower temperatures compared to catalysts based on Al-zeolites (Figure 7). This effect was more evident for the Cu–Ti-FER and Cu–Al-FER catalysts than for their delaminated analogous counterparts (Figure 7). As already discussed, the more aggregated copper oxide species, which are present mainly in Ti-zeolites, should be less active in the low-temperature NH_3 -SCO than dispersed copper species, which are dominant in Al-zeolites. On the other hand, the acid sites in Ti-zeolites are much weaker than in Al-zeolites (as shown by NH_3 -TPD). Thus, in the case of Ti-zeolites, the higher contribution of ammonia chemisorbed on copper species, which can activate such ammonia species for oxidation, was expected. The results of the catalytic studies clearly show that in

such cases the surface acidity of the catalysts is more important for catalytic activity than the aggregation of copper species. Another factor showing the very important role of the surface acidity is the significant decrease in the selectivity to nitrogen at higher temperatures (above 400 °C) observed for the catalysts based on Ti-zeolites. Considering that ammonia oxidation proceeds according to the internal SCR mechanism (i-SCR) [8], which includes oxidation of part of NH_3 to NO in the first step (Equation (5)) and reduction of NO with residual ammonia resulting in nitrogen and water vapor in the second step (NH_3 -SCR, Equation (3)), a lack of such available ammonia at higher temperatures should result in increased selectivity to NO. As shown by NH_3 -TPD analysis, this strongly chemisorbed ammonia was not observed for Ti-zeolites, and therefore the selectivity to nitrogen at higher temperatures decreased [9]. In contrast, Al-zeolites contain much stronger acid sites, which can stabilize chemisorbed ammonia molecules at higher temperatures. These chemisorbed ammonia molecules are their reservoir for the reduction of NO to N_2 and H_2O at higher temperatures (the second step of the i-SCR mechanism). This is a possible explanation for the high selectivity to N_2 in the case of the catalysts based on Al-zeolites in the high temperature range and the much poorer selectivity to nitrogen in the presence of the titanium–silicon-based catalysts. The studies were extended for the copper-modified Ti-ITQ-6 delaminated zeolites with the different intended Si/Ti ratios of 25, 50, and 100 [34]. It was shown that catalytic activity slightly increased with an increase of the Si/Ti ratio in the zeolitic catalysts, indicating again that the surface acidity of the zeolite framework is not beneficial for the low-temperature ammonia oxidation. Similarly to the previously presented studies on copper-modified layered Ti-zeolites [9], in this case the selectivity to nitrogen decreased due to the formation of nitrogen oxides above 400 °C [76].

Jankowska et al. [61] reported on the studies of layered MCM-36 zeolite intercalated with silica–titania pillars and modified with iron via ion exchange method as catalysts for NH_3 -SCO. Incorporation of titanium into silica pillars significantly increased the surface concentrations of acid sites in the zeolitic samples. Iron species introduced onto the zeolites was present in both highly dispersed form, mainly as monomeric cations, as well as aggregated iron oxide species. This distribution of the different forms of iron was possibly related to Coulombic interactions of iron cations with the negatively charged zeolite framework, resulting in highly dispersed and stable iron species. On the other hand, much weaker interactions occurred with titanium species located in silica pillars, resulting in aggregated iron oxide species forming under calcination conditions. Such silica–titania-intercalated zeolites doped with iron presented activity only in the high temperature range. Moreover, the catalysts with the higher titanium content were slightly less active than the catalysts based on zeolite intercalated with pure silica [61]. The main reason for the activity only occurring at high temperature was possibly related to the redox properties of iron species, which require much higher temperatures for their reduction compared to copper species [34,61].

Layered zeolites have been intensively studied as catalysts of the NH_3 -SCO process. The main focus of these studies has been delaminated zeolites modified with copper (Figure 8). It was shown that such catalysts can effectively operate at relatively low temperatures, however the design of such catalysts requires very precise control of the type and aggregation of deposited copper species. Regarding the catalysts for the low-temperature NH_3 -SCO process, copper in the form of highly dispersed species, preferably monomeric copper cations, is necessary. Moreover, the high surface acidity of the zeolite framework is not beneficial for the low-temperature NH_3 -SCO process, possibly due to competitive adsorption of ammonia on catalytically active copper sites and catalytically inactive framework Al acid sites. On the other hand, such framework acid sites improve the selectivity of ammonia oxidation to nitrogen at higher temperatures [34].

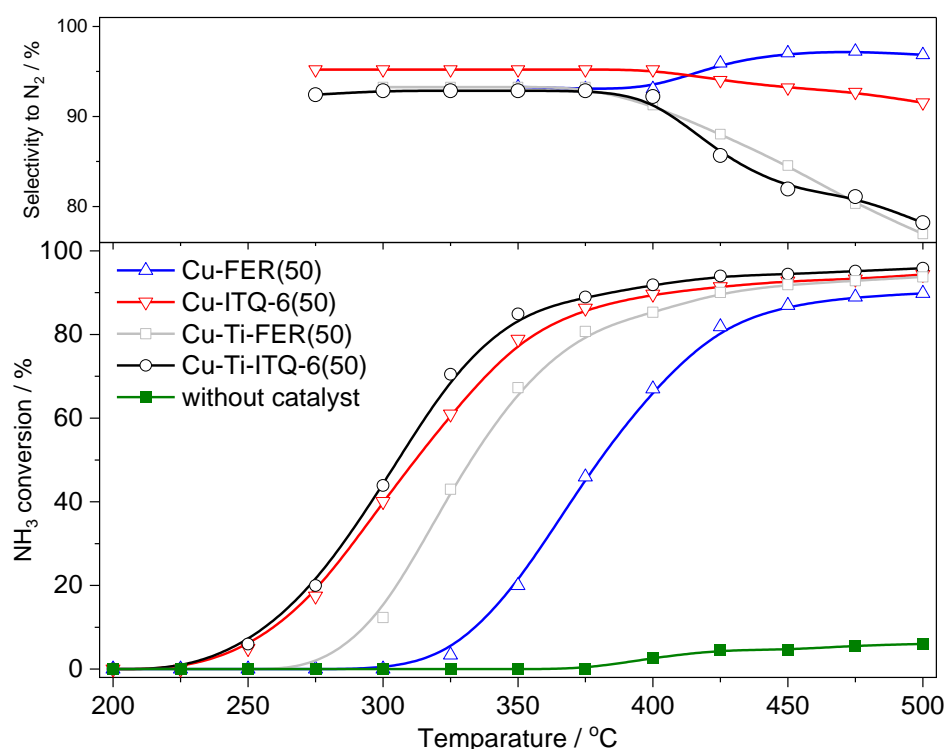


Figure 8. Results of NH_3 -SCO catalytic tests for aluminum–silicon (FER) and titanium–silicon (Ti-FER) ferrierites and their delaminated forms, ITQ-6 and Ti-ITQ-6, respectively, modified with copper by ion exchange method. Reaction conditions: 0.1 g catalyst, $[\text{NH}_3] = 5000$ ppm, $[\text{O}_2] = 2.5\%$, He = balance, total flow rate = 40 mL min^{-1} , and GHSV = $12,500 \text{ h}^{-1}$. Values in brackets are intended molar Si/Al or Si/Ti ratios in the zeolite framework. Based on the results presented in [9,34] with permission from ref. [34]. Copyright 2021 The Royal Society of Chemistry.

5. Conclusions and Predictions

Clay minerals are still very promising materials for the preparation of catalysts, including the NH_3 -SCR and NH_3 -SCO processes. As shown previously, PILCs are characterized by limited thermal and hydrothermal stability, and therefore their applications are limited only to low- and medium-temperature catalytic processes. On the other hand, one of the main requirements in the field of environmental catalysis is the development of effective catalysts for the low-temperature NH_3 -SCR process, operating at temperatures lower than 250°C . The pillared structure of the PILC-based catalysts is stable under these conditions, and therefore this group of materials seems to be very promising for the preparation of the low-temperature NH_3 -SCR catalysts. Future studies should be focused on the development of effective methods for the deposition of catalytically active components in a fully controlled manner, resulting in their desired form and aggregation and tailored for the needs of the low-temperature NH_3 -SCR process. Another important issue is the need to scale up the pillaring process, which will result in high-quality pillared structures for PILCs.

The catalytic applications of PCH materials, due to their thermally stable pillared structure, is not limited to low- and medium-temperature processes. Moreover, their specific surface area and porosity are significantly larger compared to PILCs. On the other hand, deposition of silica pillars into interlayer spaces of clay minerals, resulting in PCHs, decreases their surface acidity and ion exchange properties. Their surface acidity can be improved via incorporation of acid sites, in turn generating elements (e.g., aluminum or titanium) into silica pillars. Regarding the deposition of catalytically active metals in controlled form and during aggregation, in addition to from ion exchange, other innovative methods could be used. An example could be the modified template ion exchange (TIE) method used for the deposition of aluminum into PCHs reported by Chmielarz et al. [21]. It was shown that the TIE method resulted in greater loading of deposited aluminum species,

and to some extent allowed control of their form and aggregation. Another important problem, which also studied by the authors of this report, is the scaling up of the synthesis of PCHs, as well as development of synthesis methods with less expensive chemicals and with increased reproducibility of the final product.

Layered zeolites are some of the most promising materials, having great catalytic potential. The structures of both the zeolite layers and layers orientation can be designed and tailored for specific applications. The design of the porous zeolite structure is very important, allowing for fast diffusion of reactants. This is possible due to the relatively fast internal diffusion in interlayer mesopores and slower diffusion rate in the micropores of the zeolite layers, where Knudsen-type diffusion occurs. The tailoring of both types of porosity in such materials is important for the high effectivity of the catalyst's operation. Moreover, the porous character of the zeolitic samples is important for the effective deposition of catalytically active metals in highly dispersed forms, especially for zeolites with narrow micropores (e.g., ferrierite). Another very important issue is the role of the acidity of the zeolite framework in low- and high-temperature NH_3 -SCR processes. A positive role of such framework acid sites is postulated for the high-temperature NH_3 -SCR process, while such acid sites are not required for the low-temperature reaction.

The synthesis of the delaminated and intercalated zeolites should be optimized. One of the main problems is related to the strongly basic conditions of the swelling of the layered zeolite precursors prior to their intercalation or delamination, which may result in partial destruction of the layer's structure. Thus, studies focused on the modification of the pillaring and delamination procedures are necessary. Additionally, the scaling up of the synthesis procedure for layered zeolites, including the use of low-cost chemicals and reproducible procedures, should be an important issue in future studies. Layered zeolites offer interesting properties for the preparation of multifunctional catalysts, e.g., for the deposition of catalytically active components in the form of monomeric cations into the ion exchange positions of the zeolite layers. The second catalytic component, in the form of aggregated metal oxide species, could be deposited in the interlayer spaces of zeolites. In such cases, the catalytic functions could be separated. This concept seems to be interesting in terms of designing bifunctional NH_3 -SCO catalysts that are active in the oxidation of ammonia to NO and reduction of NO by residual ammonia to nitrogen (i-SCR mechanism).

The great potential of the modified cationic layered clay minerals, namely PILCs and PCHs, has still not been fully realized. Titania-intercalated PILCs are very promising for the preparation of low-temperature NH_3 -SCR catalysts, which is one of the main goals in this field. On the other hand, the stable pillared structure of PCHs, together with the other already discussed advantages of this group of materials, makes them very interesting catalytic supports for the high-temperature NH_3 -SCR process, as well as for NH_3 -SCO reactions. Even more promising are the layered zeolites, which are synthetic materials, meaning their properties can be tailored for the specific needs of the catalytic reactions.

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