The application of modified layered double hydroxides in selective catalytic reduction of nitrogen oxides by ammonia (NH₃-SCR)

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Selective catalytic reduction with ammonia (NH₃-SCR) is very efficient DeNOx technique. According to some problems with the commercial catalyst, novel one should be prepared. Hydrotalcites are potential precursors of the new catalysts of NH₃-SCR. In this paper, several attempts to apply these materials in NH₃-SCR are presented.

Keywords: Yerba, antioxidant activity, infusions, minerals

INTRODUCTION

Among recent years a serious problem of excessive emission of nitrogen oxides (NOₓ) is observed. The presence of NOₓ in the atmosphere has many dangerous consequences, including the formation of acid rains and photochemical smog or depletion of ozone layer. Moreover, nitrogen oxides are hazardous for human health and aggravate the quality of the environment. Therefore, the implementation of official regulations according to NOₓ emission was required. One of the most important examples is EU directive 2010/75/EU that restrictively limits the permitted amount of NOₓ present in flue gases emitted from stationary and mobile sources⁴⁻⁵. The most efficient technology of NOₓ abatement is the selective catalytic reduction (SCR), mainly by ammonia. However, other reducers like hydrocarbons can be also used. Currently, the majority of industrial DeNOₓ systems exploit this method⁶⁻⁹. Generally, the technology is based on the reaction of nitrogen oxides with the reducing agent that is injected into the stream of flue gas. The desired products are molecular nitrogen and water vapour. The interaction between the reactants takes place on the surface of the catalyst that plays the essential role in the whole process. Additionally, depending on the nature and properties of the catalyst, the reaction can occur according to the mechanism of Langmuir-Hinshelwood (L-H) or Eley-Rideal (E-A). The first is based on simultaneous adsorption of NH₃ and NOₓ on the catalyst surface and their consequent interaction. The second assumes that only ammonia is adsorbed on the catalyst surface and NOₓ are reduced during their flow through the catalyst saturated with NH₃⁵. In Fig. 1. the simplified scheme of the NH₃-SCR reaction is presented.

At the typical conditions (300–400°C) the process is followed by the reaction (1)⁶

\[
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (1)
\]

In comparison to the other DeNOₓ techniques, NH₃-SCR is the most effective, mainly due to the application of the catalyst that increases the selectivity of the reaction and therefore, reduces the amount of by-products. The most frequently used catalyst is alumina- or titania-supported V₂O₅-WO₃ or V₂O₅-MoO₃ in a monolithic form⁹. However, the commercial catalyst has several drawbacks that limit its application and meeting the NOₓ emission standards. One of the most important obstacles is the narrow temperature window of the catalyst. The solution might be placing the catalyst at the tail end, but in that case additional heating of the flue gas is required. On the other hand, placing the SCR installation upstream of electrostatic precipitator results in deactivation by the alkali metals and other contaminations present in the flue gas⁵.⁶⁻¹¹. According to these problems, there is an increasing interest in the development of a novel, efficient catalyst.

Layered double hydroxides (LDHs), known also as hydrotalcite-like compounds (HTLcs) have been intensively investigated as potential catalysts and of many processes, including selective catalytic reduction of NOₓ¹²⁻¹⁵. The layer structure of the natural hydrotalcite is closed to brucite, Mg(OH)₂, in which a part of Mg²⁺ cations are replaced by Al³⁺. Electro-neutrality of the structure is provided by interlayer carbonate anions¹⁶. What is more, hydrotalcite-like compounds possess anion-exchange properties and there is a wide range of organic and inorganic anions that can be introduced into the interlayer space. For instance, intercalation of polyoxometallates anionic metal complexes permits incorporation of at least one catalytically active component¹⁷,¹⁸. Due to direct synthesis of LDHs, and their unique features, e.g. ion-exchange properties and easy modulation of chemical composition, the materials can be successively applied in heterogeneous catalysis. Upon thermal decomposition, LDHs are transformed into mixed metal oxides. The active sites exhibit very high dispersion on the whole surface of the obtained material. Therefore the selectivity of a catalytic reaction can be significantly increased¹⁸. According to the above, in this paper the...
structural features of LDHs, examples of incorporated interlayer anions and possibilities of their application as NH3-SCR catalysts are discussed.

**STRUCTURE OF LAYERED DOUBLE HYDROXIDES (LDHS)**

Layered double hydroxides are the group of materials that refer to “non-silicate oxides and hydroxides” with similar physicochemical properties to cationic clay minerals. Due to the variety of chemical composition, layer structure and ion-exchange properties of LDHs, the materials are often called as “clay mineral-like materials”. However, in contrast to the layer silicate-based cationic clays, LDHs possess anion-exchange properties. Hence they are defined as anionic clays.16, 17, 19

The representative of LDHs is natural hydrotalcite. The material exhibits rhombohedral crystalline system with a three-layer repeat (3R)15. Its chemical formula, Mg$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O is the base for synthetic LDHs which have the following general notation (2):16

$$[\text{M}^{II}_{x} \cdot \text{M}^{III}_{1-x} (\text{OH})_2]^{x+} \cdot \text{A}^{z-} \cdot n\text{H}_2\text{O} \quad (2)$$

where M$^{II}$ and M$^{III}$ are di- and tri-valent cations, A – interlayered anions and x – molar ratio of cations M$^{II}$ and M$^{III}$ (commonly x oscillates around 0.15 and 0.34)18.

As it was already mentioned, the structure of LDHs derives from brucite – Mg(OH)$_2$, which comprises a close packing of OH ions with octahedral sites on every two layers occupied by Mg$^{2+}$. In LDHs a fraction of Mg$^{2+}$ ions is substituted by an ion Al$^{3+}$. The exchange generates the excessive positive charge of the layers. Its compensation is provided by the introduction of interlayer anions A$^-$. Apart from the anions, the interlayer space is occupied by water molecules. In Fig. 2, the idealized structure of LDHs is presented17, 21.

**SYNTHESIS OF LAYERED DOUBLE HYDROXIDES (LDHS)**

Synthesis of the LDHs on both laboratory and industrial scale is easy and inexpensive. However, to obtain a pure LDHs phase, some specific precautions must be taken. The most significant concerns pH control and avoidance of the contact with atmospheric CO$_2$ that can cause precipitation of impurities and contamination with CO$_3^{2-}$ ions21. The most common route to prepare LDHs is co-precipitation at variable or constant pH. Pure and chemically homogeneous materials are obtained upon synthesis at constant pH. The influence of co-precipitation pH on the chemical, textural and structural properties of LDHs was confirmed in several works24,28. Practically, co-precipitation is based on adding a base solution to a solution containing a mixture of salts M$^{II}$ and M$^{III}$. While the pH is kept constant, NaOH, KOH or NH$_3$ are simultaneously added24. Although this LDHs preparation route is relatively simple and the obtained materials are repetitive, sometimes it is limited by competitive precipitation of metal salts (e.g. oxometalates)17.

Another method for the synthesis of LDHs is sol-gel route that involves the hydrolysis of metal alkoxides. The method is more expensive than co-precipitation, however it allows to obtain materials with enhanced specific surface area and higher thermal stability28. What is more, heating to the certain temperature (usually between 350–450°C) results in the formation of mixed metal oxides29,31. Interestingly, mixed metal oxides obtained upon thermal decomposition have a unique ability to retain the layer structure while they are exposed to aqueous solution. This specific property is commonly called as “memory effect”.32.

There are also post-synthesis treatments that can be applied to “as-prepared” samples. These modifications are applied mainly due to the control of textural and structural parameters. For instance, microwaves used during the synthesis increase the porosity and specific surface area of the materials, while ultrasound radiation or hydrothermal reactions at high temperature improve their crystallinity.

**CATION-EXCHANGE PROPERTIES OF LDHS**

There is a wide range of cations that can be introduced into the brucite-like layers of LDHs. The only requirement of the exchange is that the radii of octahedral coordination is close to Mg$^{II}$ or Al$^{III}$. Therefore, Mg$^{2+}$ and Al$^{3+}$ can be replaced by divalent (e.g. Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Zn$^{2+}$) and trivalent (e.g. Ga$^{3+}$, Fe$^{3+}$, Cr$^{3+}$, V$^{3+}$, Ru$^{3+}$, Rh$^{3+}$) cations, respectively.30, 22. Another crucial factor is to maintain the appropriate molar ratio of divalent and trivalent metals, in order to avoid the deformation of the octahedral structure. Additionally, some tetravalent cations such as Ti$^{4+}$, Zr$^{4+}$ or Sn$^{4+}$ can be incorporated into brucite-like layer and form multi-metal cations with di- and trivalent metals. Table 1 shows the most common cations that replace Mg$^{2+}$ and Al$^{3+}$ in the brucite structure16, 20.
When pH decreases, the nuclearity is increased. Polymerization degree of oxovanadates in dependence on pH for a 0.1 M aqueous vanadate solution is as it follows:

- **Decavanadate** (pH = 1–3)
  - $V_{10}O_{26}(OH)_2^{4–}$
  - $V_{10}O_{27}(OH)_5^{–}$
  - $V_{10}O_{26}^{6–}$

- **Metavanadate** (pH = 4–6)
  - $V_3(OH)_3$, $VO_2(OH)$, $V_3O_9^{3–}$
  - $V_4O_{12}^{4–}$

- **Pyrovanadate** (pH = 8–11)
  - $VO_3(OH)_2^{–}$
  - $HV_2O_7^{3–}$
  - $V_2O_7^{4–}$

- **Vanadate** (pH > 12)
  - $VO_4^{2–}$

What is interesting, in case of pyrovanadate anions ($V_2O_7^{4–}$ and $HV_2O_7^{3–}$) which consist of two $[VO_4]$ tetrahedra that share a vertex, two different arrangements in the interlayer space are possible. On one hand, V-V edge can be placed in a perpendicular position to the brucite-like layers and the basal spacing calculated from the size of $V_2O_7^{4–}$ is 12.6 Å. On the other hand, the anions can take the parallel position with the calculated basal spacing of 9.8 Å. The scheme of the pyrovanadate anions positions in the interlayer space are presented in Fig. 3.

### ANION-EXCHANGE PROPERTIES OF LDHS

The interlayer spaces of the LDHs can be intercalated with the wide range of inorganic or organic ions. The examples of anions which can be introduced into LDHs structure are presented in Table 2. The anionic species present in the interlayer region can be mediated by colonic forces between the positively charged layers and negatively charged anions or by hydrogen bonding between hydroxyl groups of the anions and water molecules.

The anion-exchange capacity (AEC) is dependent on the x (Eq. 2), while intercalation of the particular anion is related to the affinity of the anions in aqueous solution. For the interlayer region, this affinity is associated with the anions charge density and their size. More stable hydrotalcites are obtained while anionic charge increases, which is the result of stronger interaction between the positively charged hydroxide layer and the particulate anion.

Anion exchange is used in order to extend the chemical composition of LDHs. In some cases these materials can contain at least three different catalytically active metals which can spectacularly enhance their catalytic properties.

### Table 2. The list of anions that can be introduced into LDHs interlayer space

| Inorganic anions | Organic anions |
|------------------|----------------|
| Common inorganic ions (e.g. Cl–, CO32–, NO3–) | Carboxylates, dicarboxylates, alkylsulfates, metalorganic complex |
| Heteropoly acids (HPA) | Dyes |
| Polyoxometallatetates (POMs) | Metalloporphyrins |
| Polyoxometallatetates of transition metals | |
| Complex anions | |

### LDHs intercalated with metal-containing anions

LDHs incorporated with metal-containing anions are especially interesting for catalytic applications. Some metals, such as molybdenum or vanadium cannot replace Mg2+ in the brucite layer, adequately due to their large ionic radius. These metals are very active components of the commercial SCR catalyst, thus their introduction into the structure of LDHs could potentially make the materials suitable for the process. It turns out that the metals can be successfully introduced into the LDHs interlayers as anionic species. There are some examples of materials which were already described in the literature, especially for vanadate and molybdate ions.

### Vanadate anions

The widest group of metal-containing anions that can be incorporated into the interlayer space of LDHs are oxovanadates. It was reported, that the polymerization degree of vanadium-containing anions strongly depends on pH maintained during the intercalation procedure.

When pH decreases, the nuclearity is increased. Polymerization degree of oxovanadates in dependence on pH for a 0.1 M aqueous vanadate solution is as it follows:

- **Decavanadate** (pH = 1–3)
  - $V_{10}O_{26}(OH)_2^{4–}$, $V_{10}O_{27}(OH)_5^{–}$, $V_{10}O_{26}^{6–}$

- **Metavanadate** (pH = 4–6)
  - $V_3(OH)_3$, $VO_2(OH)$, $V_3O_9^{3–}$, $V_4O_{12}^{4–}$

- **Pyrovanadate** (pH = 8–11)
  - $VO_3(OH)_2^{–}$, $HV_2O_7^{3–}$, $V_2O_7^{4–}$

- **Vanadate** (pH > 12)
  - $VO_4^{2–}$

What is interesting, in case of pyrovanadate anions ($V_2O_7^{4–}$ and $HV_2O_7^{3–}$) which consist of two $[VO_4]$ tetrahedra that share a vertex, two different arrangements in the interlayer space are possible. On one hand, V-V edge can be placed in a perpendicular position to the brucite-like layers and the basal spacing calculated from the size of $V_2O_7^{4–}$ is 12.6 Å. On the other hand, the anions can take the parallel position with the calculated basal spacing of 9.8 Å. The scheme of the pyrovanadate anions positions in the interlayer space are presented in Fig. 3.

### Figure 3. Possible orientations of $V_2O_7^{4–}$ in LDHs – perpendicular (A) and parallel (B) (based on:18, 47)

Palmer et al. took the interesting attempt to describe the manner of inclusion of the anions into interlayer LDHs space. The authors indicated that these species can be intercalated or adsorbed into/onto hydrotalcite structures, in dependence on the Mg/Al ratio. The materials described in the research were obtained by the co-precipitation method. The mixed metal solution of Mg2+ and Al3+ of the appropriate Mg/Al ratio that results in formation of hydrotalcite structure was added dropwise to the mixture of NaOH, Na2CO3 and...
**Molybdate anions**

Except the vanadate anions, there are also several studies concerned on incorporation of molybdate anions into the interlayer space of LDHs\(^{44, 45}\). Molybdenum, as one of the components of the commercial SCR catalyst provides high stability of the system and some amount of active sites. Therefore, it is predicted that molybdate anions may have a promoting influence as the components of LDHs applied for NO\(_x\) removal via selective catalytic reduction. Ciocan et al.\(^{44}\) reported an facile method to prepare Mo-containing LDHs catalysts by ion exchange. In order to intensify the process and to obtain ordered structure of the materials, the exchange was performed during aging under hydrothermal conditions. For comparative purposes, the material was also prepared via ion exchange without applying hydrothermal treatment. SEM analysis performed on the prepared samples proved that both materials are consisted of pellets or agglomerates. However, the application of hydrothermal conditions during the synthesis resulted in better crystallinity of the sample.

Molybdate anionic species can be introduced into interlamellar space in the various forms. In order to study the nature of interlayer anions, the Mo-containing LDHs were examined by Raman spectroscopy. The study indicated the presence of the characteristic peaks assigned to the lattice vibrations of the Al-O-Al and Al-O-Mg (brucite octahedral layers) at 557 cm\(^{-1}\), for parent material and nitrate vibrations at 1050 and 709 cm\(^{-1}\). However, after incorporation of molybdate anions these peaks disappeared completely. Therefore, it can be concluded that under the hydrothermal conditions, nearly all of the nitrate anions from the starting material were successfully exchanged. The most important frequencies that belong to the three types of anions: MoO\(_4^{2-}\), MoO\(_2\)\(\text{V}^2\) and MoO\(_2\)\(\text{V}^2\) are in the domain 890–950 cm\(^{-1}\). The results are in full agreement with the similar study carried out by Dobrea et al.\(^{45}\) who examined the dependence of the nature of molybdate anions on the loading of these species. Additionally, both authors proved that heptamolybdate anions were the most dominant species. The Raman spectra obtained for materials prepared with various Mo loading indicated that the more Mo was introduced into the interlayer space, the more complex is the spectra and octahedrally coordinated polymolybdate species (Mo\(_2\)O\(_7\)\(\text{V}^2\) and Mo\(_2\)O\(_{24}\)\(\text{V}^2\)) are formed.

**MODIFIED LDHS AS CATALYSTS OF SELECTIVE CATALYTIC REDUCTION OF NO\(_x\) WITH AMMONIA**

Many researchers proved that layered double hydroxides, including hydrotalcite-originated mixed metal oxides are promising materials that can be used in selective catalytic reduction with ammonia\(^{12, 14, 15}\).

Carja et al.\(^{46}\) carried out NH\(_3\)-SCR catalytic tests over mixed oxides derived from pillared oxovanadates. In order to increase the catalytic performance of the materials, the selected samples were ion-exchanged with copper species. LDHs were prepared using co-precipitation, with a careful control of pH. In all cases, the aqueous solutions of Mg and Al or Mg, Al and Cu cations were dropwise added to the NaVO\(_x\)/NaOH mixture at the desired pH (8.5–9.5). The gelatinous suspension were heated at certain temperature for several hours. The certain pH applied during the synthesis resulted in the predomination of V\(_2\)O\(_7\)\(^2\) and HV\(_2\)O\(_7\)\(^2\) in the obtained mixture. The basal spacing between the layers of LDHs was determined by X-ray diffraction. It was 9.18 Å and 8.97 Å for the samples unmodified and modified with copper, respectively and the thickness of brucite layer was 4.8 Å. Therefore, the interlayer spacing that is occupied by vanadate ions equals 4.38 Å and 4.27 Å for samples without and with Cu, respectively. It indicates, that oxovanadate anions are incorporated into interlayer space in “lying down” position and V-V axis in two [VO\(_4\)] tetrahedra are parallel to the layers. Analysis of the chemical composition proved that enrichment in vanadium occurs for the samples that contain copper. Therefore, the presence of transition metal increase the efficiency of pillaring with oxovanadates. Additionally, the presence of oxovanadates as interlayer anions was proved by Fourier transform infrared spectroscopy (FT-IR) analysis. Catalytic tests carried out over the oxovanadate-pillared LDHs and the same materials modified with Cu demonstrated approximately equivalent NO conversion for both materials. However, for the samples promoted with Cu, the maximum conversion of NO was reached at lower temperature (350°C). Additionally, that case, only negligible formation of N\(_2\)O (about 10–20 ppm) was observed. On the other hand, above 400°C copper-containing catalyst exhibited a tendency to catalyse undesired reaction of ammonia oxidation. High catalytic activity of vanadium containing catalysts was explained by the relation of SCR activity with the surface acidity caused by the V\(^{5+}\)-OH sites. In view of the above, the further research over V- and Cu-containing LDHs needs to focus on their coexistence in appropriate amount, so that both catalytic activity and selectivity are enhanced.

Montanari et al.\(^{46}\) studied the influence of the content of the transition metal in Cu-Mg-Al-O\(_x\) synthesized via co-precipitation, followed by calcination of hydrotalcite-like precursors at 650°C. The loading of copper oxide was calculated to reach between 4.0–12.5 wt%. The reference
sample was represented by Mg-Al-Oₓ impregnated with 10 wt% of copper oxide. Comparing the nature of copper species in both cases, impregnation method resulted in the formation of crystalline CuO, while for the materials prepared by co-precipitation CuO segregation did not occur. Catalytic tests carried out over the materials indicated that in case of 12.5 wt% loading of copper oxide, NO was completely reduced at 350°C and decrease of the copper oxide results in the lower catalytic activity. However, it was observed that the catalytic performance was significantly higher in the whole temperature range (150–500°C) for the catalyst obtained by impregnation. The results were in full agreement with H₂-TPR analysis of the prepared materials. The catalysts impregnated with Cu²⁺ showed lower reduction temperature of about 200°C, while hydrotalcite-derived mixed metal oxides were reduced in the temperature between 240 and 300°C. Therefore, significantly higher catalytic performance of CuO-containing materials is the result of the lower reduction temperature.

Carja et al. (2009) presented alternative attempt to use hydrotalcite-like compounds as NH₃-SCR catalysts. Calcined iron-substituted LDHs Mg-Al-Fe-O were modified with aqueous solutions of iron and cerium sulphates, in order to deposit Fe₂O₃ and CeO₂ on the hydrotalcite-like support. Subsequently, the samples were calcined at 550°C. Catalytic tests indicated that the catalysts containing CeO₂ showed considerably higher activity below 250°C, while above this temperature, samples doped with Fe₂O₃ exhibited higher conversion of NO. The effect might be caused by the low thermal resistance of CeO₂ as a promoter of NH₃-SCR in the high temperature range.

Xu et al. prepared CoMnAl-CO₃ and CoAl-MnO₂ LDHs via ion-exchange and hexamethylenetetramine (HMT) hydrolysis. Mixed metal oxides Co-Mn-Al and MnO₂-Co were formed upon calcination at 500°C. The obtained materials were tested as catalysts of NH₃-SCR. It was found that the samples obtained by ion-exchange show significantly higher catalytic activity. MnO₂-Co-Al exhibited 90% of NO conversion and 95% selectivity to N₂ in the temperature range of 90–270°C. The same results were obtained for Co-Mn-Al that were obtained at about 150–240°C. Brauner-Emmet-Teller (BET) surface area analysis of the materials indicated higher specific surface area of MnO₂-Co-Al (156.8 m²/g) in comparison to Co-Mn-Al (85.3 m²/g). Additionally, MnO₂-Co-Al exhibited more narrow pore size distribution (3–7 nm) than the other material (3–20 nm). Hence, the adsorption of the reagents on the internal surface of MnO₂-Co-Al was facilitated. H₂-TPR study showed that all of the reduction peaks detected for MnO₂-Co-Al shifted to lower temperature regions of about 250–600°C, in contrast to Co-Mn-Al that was reduced at about 370–650°C. NO-TPD analysis carried out over the catalysts revealed one large desorption peak for MnO₂-Co-Al at 158°C indicating the presence of monodentate nitrate species. In contrast, several peaks below 200°C, at 255°C and at 305°C were detected for Co-Mn-Al. According to the authors, the signals are assigned to the decomposition of monodentate, bridging and bidentate nitrate species, respectively. It was reported that monodentate nitrates have a positive influence on the catalytic activity in NH₃-SCR. Therefore it was concluded that one of the reasons of the better catalytic performance of MnO₂-Mn-Al was the facilitated adsorption of these species on the surface of the catalyst.

**CONCLUSIONS**

Layered double hydroxides are the class of materials with a strong potential as catalysts for the reduction of nitrogen oxides from the industrial sources. Wide variety of the chemical compositions of LDHs was tested to develop active, selective and stable catalyst of NH₃-SCR. Excellent structural properties of the materials make them an attractive precursors for catalysts and catalysts supports. The number of studies showed that especially inclusion of transition metals in various forms into the LDHs and their transformation into mixed metal oxides results in high catalytic activity. However, one of the main problems that still needs to be resolved is broad operating temperature window of these materials. Moreover, LDHs should be also tested using gas mixtures that mimic real composition of exhaust gases. Therefore, further studies under real conditions and tailoring LDHs-based catalysts active in the wide temperature range still remains a challenge.

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**LITERATURE CITED**

1. The European Parliament and the Council of the European Union. (2010). Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). Official Journal of the European Union 17.12.2010.
2. Samojeden, B. & Grzybek, T. (2016). The influence of the promotion of N-modified activated carbon with iron on NO removal by NH₃-SCR (Selective catalytic reduction). *Energ.* 116, 1484–1491. DOI: 10.1016/j.energy.2016.04.059.
3. Gao, F., Tang, X., Yi, H., Zhao, S., Li, C., Li, J., Shi Y. & Meng, X. (2017). A Review on Selective Catalytic Reduction of NOₓ by NH₃ over Mn–Based Catalysts at Low Temperatures: Catalysts, Mechanisms, Kinetics and DFT Calculations. *Catalysts, 7(7)*, 199. DOI: 10.3390/catal7070199.
4. Samojeden, B. & Grzybek, T. (2017). The influence of nitrogen groups introduced onto activated carbons by high- or low-temperature NH₃ treatment on SO₂ sorption capacity. *Adsorp. Sci. Technol. 35(5–6), 572–581*. DOI: 10.1177/0263617417702153.
5. Motak, M., Kuterasiński, L., Da Costa, P. & Samojeden, B. (2015). Catalytic activity of layered aluminosilicates for VOC oxidation in the presence of NO: *Comptes Rendus Chim.* 18(10), 1106–1113. DOI: 10.1016/j.crci.2015.05.005.
6. Carja, G. & Delahay, G. (2004). Mesoporous mixed oxides derived from pillared oxovanadates layered double hydroxides as new catalysts for the selective catalytic reduction of NO by NH₃. *Appl. Catal. B. Environ.* 47(1), 59–66. DOI: 10.1016/j.apcata.2003.07.004.
7. Cheng, M., Jiang, B., Yao, S., Han, J., Zhao, S., Tang, X., Zhang, J. & Wang, T. (2018). Mechanism of NH₃ Selective Catalytic Reduction Reaction for NO Removal from Diesel Engine Exhaust and Hydrothermal Stability of Cu-Mn/Zelite Catalyst. *J. Phys. Chem.* 122(1), 455–464. DOI: 10.1021/acs.jpcc.7b09339.
8. Koebel, M., Elsenere, M. & Kleemann, M. (2000). Urea-SCR: a promising technique to reduce NOx emissions from...
automotive diesel engines. Catal. Today. 59(3-4), 335-345. DOI: 10.1016/S0920-8561(00)00299-6.

9. Grzybek, T. (2007). Layered clays as SCR deNOx catalysts. Catal. Today. 119(1-4), 125-132. DOI: 10.1016/j.cattod.2006.08.006.

10. Peng, Y., Li, J., Si, W., Luo, J., Wang, Y., Fu, J., Li, X., Crittenden, J. & Hao, J. (2015). Deactivation and regeneration of a commercial SCR catalyst: Comparison with alkali metals and arsenates. Appl. Catal. B Environ. 168-169, 195-202. DOI: 10.1016/j.apcatb.2014.12.005.

11. Chang, H., Shi, C., Li, M., Zhang, T., Wang, C., Jiang, L., Wang, X. (2018). The effect of cations (NH4+, Na+, K+, and Ca2+) on chemical deactivation of commercial SCR catalyst by bromine. Chinese J. Catal. 39(4), 710-717. DOI: 10.1016/S1872-2067(18)30111-6.

12. Basag, S., Kocooł, K., Piwowarska, Z., Rutkowska, M., Baran, R. & Chmielarz, L. (2017). Activating effect of cerium in hydrotalcite derived Cu-Mg-Al catalysts for selective oxidation of ammonia and the selective reduction of NO with ammonia. React. Kinet. Mech. Catal. 121(1), 225-240. DOI: 10.1007/s11141-017-1141-y.

13. Wu, X., Feng, Y., Du, Y., Liu, X., Zou, C. & Li, Z. (2019). Enhancing DeNOx performance of CoMnAl mixed metal oxides in low-temperature NH3-SCR by optimizing layered double hydroxides (LDHs) precursor template. Appl. Surf. Sci. 467-468, 802-810. DOI: 10.1016/j.apsusc.2018.10.191.

14. Jabłońska, M., Nothdurft, K., Nocuński, M., Girman, V. & Palkovits, R. (2017). Redox-performance correlations in Ag-Cu-Mg-Al, Ce-Cu-Mg-Al, and Ga-Cu-Mg-Al hydrotalcite derived mixed metal oxides. Appl. Catal. B Environ. 207, 385-396. DOI: 10.1016/j.apcatb.2017.01.079.

15. Chmielarz, L., Jabłońska, M., Strumińska, A., Piwowarska, Z., Wegrzyn, A., Witkowski, S. & Michalik, M. (2013). Selective catalytic oxidation of ammonia to nitrogen over Mg-Al, Cu-Mg-Al and Fe-Mg-Al mixed metal oxides doped with noble metals. Appl. Catal. B Environ. 130-131, 152-162. DOI: 10.1016/j.apcatb.2012.11.004.

16. Xu, Z.P., Zhang, J., Adebajo, M.O., Zhang, H. & Zhou, C. (2011). Catalytic applications of layered double hydroxides and derivatives. Appl. Clay Sci. 53(2), 139-150. DOI: 10.1039/C4CSC0160E.

17. Forano, C., Costantino, U., Prévot, V. & Guicho, C.T. (2013). Layered Double Hydroxides (LDH). In F. Bergaya and G. Lagaly (Eds.), Handbook of clay science based on the reconstruction method of layered double hydroxides (LDHs) by chemical precipitation and hydrothermal method. Mater. Chem. Phys. 121(1-2), 223-229. DOI: 10.1016/j.matchemphys.2010.01.026.

18. Ghosal, P.S., Gupta, A.K. & Ayoob, S. (2015). Effect of formation pH, molar ratio and calcination temperature on the synthesis of anionic clay based adsorbent targeting de-fluoridation. Appl. Clay Sci. 116-117, 120-128. DOI: 10.1016/j.clay.2015.08.026.

19. Comelli, N.A., Ruiz, M.L., Aparicio, M.S.L., Merino, N.A., Cecilia, J.A., Rodríguez-Castellón, E., Lick, I.D. & Ponzi, M.I. (2018). Influence of the synthetic conditions on the composition, morphology of CuMgAl hydrotalcites and their use as catalytic precursor in diesel soot combustion reactions. Appl. Catal. B Environ. 157, 148-157. DOI: 10.1016/j.apcatb.2018.02.039.

20. Ramos-Ramírez, E., Ortega, N.L.G., Soto, C.A.C., Gutiérrez, M.T.O. (2009). Adsorption isotherm studies of chromium (VI) from aqueous solutions using sol-gel hydrotalcite-like compounds. J. Hazard. 172(2–3), 1527-1531. DOI: 10.1016/j.jhazmat.2009.08.023.

21. Jabłońska, M., Arán, M.A., Beale, A.M., Delahay, S., Petitto, C., Nocuń, M. & Palkovits, R. (2019). Understanding the origins of N2O decomposition activity in Mn(Fe)CoAlOx hydrotalcite derived mixed metal oxides. Appl. Catal. B Environ. 243, 66-75. DOI: 10.1016/j.apcatb.2018.10.010.

22. Wang, Z., Li, Q., Wang, L. & Shangguan, W. (2012). Simultaneous catalytic removal of NOx and soot particulates over CuMgAl hydrotalcites derived mixed metal oxides. Appl. Clay Sci. 55, 125-130. DOI: 10.1016/j.clay.2011.11.003.

23. Mascolo, G. & Mascolo, M.C. (2015). On the synthesis of layered double hydroxides (LDHs) by reconstruction method based on the “memory effect”. Micropor. Mesopor. Mater. 214, 34-36. DOI: 10.1016/j.micromeso.2015.03.024.

24. Zhi, P. & Guo, Q.L. (2005). Hydrothermal synthesis of layered double hydroxides (LDHs) from mixed MgO and Al2O3: LDH formation mechanism. Chem. Mater. 17(5), 1055-1062. DOI: 10.1021/cm048085g.

25. Genty, E., Brunet, J., Poupin, C., Casale, S., Capelle, S., Massiani, P., Siffter, S. & Cousin, R. (2015). Co-Al Mixed Oxides Prepared via LDH Route Using Microwaves or Ultrasound: Application for Catalytic Toluene Total Oxidation. Catalyst. 5(2), 851-867. DOI: 10.3390/catal5020851.

26. Vacari, A. (1998). Preparation and catalytic properties of cationic and anionic clays. Catal. Today. 41(1–3), 53–71. DOI: 10.1016/S0920-5861(98)00038-8.

27. Palmer, S.J., Soisonard, A. & Frost, R.L. (2009). Determination of the mechanism(s) for the inclusion of arsenate, vanadate, or molybdate ions into hydrotalcites with variable cationic ratio. J. Colloid Interface Sci. 329(2), 404-409. DOI: 10.1016/j.jcis.2008.09.065.

28. Palomeque, J., Figueiras, F. & Gelbard, G. (2006). Epoxidation with hydrotalcite-intercalated organotungstic complexes. Appl. Catal. A Gen. 300(2), 100–108. DOI: 10.1016/j.apcata.2005.10.037.
39. Liu, K., Xu, Y., Yao, Z., Miras, H.N. & Song, Y.F. (2016). Polyoxometalate-Intercalated Layered Double Hydroxides as Efficient and Recyclable Bifunctional Catalysts for Cascade Reactions. ChemCatChem. 8(5), 929–937. DOI: 10.1002/cctc.201501365.

40. Chen, F., Wu, X., Bu, R. & Yang, F. (2017). Co – Fe hydrotalcites for efficient removal of dye pollutants via synergistic adsorption and degradation. RSC Advances. 7, 41945–41954. DOI: 10.1039/C7RA07417D.

41. Stepniowski, W.J., Norek, M., Michalska-Domańska, M., Bombalska, A., Nowak-Stepniowska, A., Kwaśny, M. & Bojar, Z. (2012). Fabrication of anodic aluminum oxide with incorporated chromate ions. Appl. Surf. Sci. 259, 324–330. DOI: 10.1016/j.apsusc.2012.07.043.

42. Zhou, W., Tian, P., Sun, F., He, M. & Chen, Q. (2016). Highly efficient transformation of alcohol to carbonyl compounds under a hybrid bifunctional catalyst originated from metalloporphyrins and hydrotalcite. J. Catal. 335, 105–116. DOI: 10.1016/j.jcat.2015.11.017.

43. Conterosito, E., Palin, L., Antonioli, D. & Viterbo, D. (2015). Structural Characterisation of Complex Layered Double Hydroxides and TGA-GC-MS Study on Thermal Response and Carbonate Contamination in Nitrate- and Organic-Exchanged Hydrotalcites. Chem.; Eur. J. 21, 14975–14986. DOI: 10.1002/chem.201500450.

44. Ciocan, C.E., Dumitriu, E., Cacciaguerra, T, Fajula, F. & Hulea, V. (2012). New approach for synthesis of Mo-containing LDH based catalysts. Catal. Today. 198(1), 239–245. DOI: 10.1016/j.cattod.2012.04.071.

45. Dobrea, I.D., Ciocan, C.E., Dumitriu, E., Popa, M.I., Peti, E. & Hulea, V. (2015). Raman spectroscopy - Useful tool for studying the catalysts derived from Mo and V-oxyanion-intercalated layered double hydroxides. Appl. Clay Sci. 104, 205–210. DOI: 10.1016/j.clay.2014.11.034.

46. Montanari, B., Vaccari, A., Gazzano, M., Kaßner, P., Papp, H., Pasel, J., Dziembaj, R., Makowski, W. & Lojewski, T. (1997). Characterization and activity of novel copper-containing catalysts for selective catalytic reduction of NO with NH₃. Appl. Catal. B Environ. 13, 205–217. DOI: 10.1016/S0926-3373(96)00106-3.

47. Twu, J. & Dutta, K. (1990). Decavanadate Ion-Pillared Hydrotalcite: Spectroscopic Studies of the Thermal Decomposition Process. J. Catal. 110, 502–510. DOI: 10.1016/0021-9517(90)90196-Q.

48. Jabłońska, M. & Palkovits, R. (2015). Nitrogen oxide removal over hydrotalcite-derived mixed metal oxides. Catal. Sci. Technol. 6(1), 49–72. DOI: 10.1039/c5cy00646e.

49. Carja, G., Dranca, S., Husanu, E. & Volf, I. (2009). Iron Containing Anionic Clays Supported With Iron Andcerium Oxides As Catalyst Precursors for NOx Reduction. Environ. Eng. Manag. J. 8(3), 553–557. DOI: 10.30638/eemj.2009.076.

50. Wu, X., Feng, Y., Du, Y., Liu, X., Zou, C. & Li, Z. (2019). Enhancing DeNOx performance of CoMnAl mixed metal oxides in low-temperature NH₃-SCR by optimizing layered double hydroxides (LDHs) precursor template. Appl. Surf. Sci. 467–468, 802–810. DOI: 10.1016/j.apsusc.2018.10.191.