

## Hydrotalcite-like materials containing manganese – a short review

Magdalena Jabłońska, Lucjan Chmielarz, Agnieszka Węgrzyn

Uniwersytet Jagielloński, Ingardena 3, 30-060 Krakow

email: jablonska\_magdalena@interia.eu

### Abstract

Numerous hydrotalcite-like or their derivatives have been reported as catalysts for a wide variety of chemical processes including selective reduction of nitrogen oxides with ammonia (SCR, DeNO<sub>x</sub>) or NO<sub>x</sub> storage/reduction process, selective ammonia oxidation to nitrogen and water vapour (SCO), N<sub>2</sub>O decomposition (DeN<sub>2</sub>O) and total oxidation for volatile organic compounds (VOCs). Among them manganese-containing hydrotalcite-like materials and their derivatives seems to possess high activity. This paper gives an overview of Mn-containing catalysts, including the catalyst development and their possible applications. The use of mixed metal oxides obtained from synthetic hydrotalcite-like materials mainly in the role of catalysts for the total VOCs decomposition has been reviewed. Achieved results clearly show that tested materials are candidates for potential application in real catalytic processes.

### 1. Hydrotalcite-like materials

Layered double hydroxides called also hydrotalcite-like compounds (HTs), are a group of naturally occurring anionic clays [1, 2]. The structure of these materials can be visualized by starting from a brucite network, (Mg(OH)<sub>2</sub>) [3]. In particular, the structure of HTs is created by replacing a fraction of M<sup>2+</sup> in the brucite lattice by M<sup>3+</sup>, conferring a positive layer charge. This charge is electrically balanced by the incorporation of anions and water molecules into the interlayer region. Naturally occurring hydrotalcite, Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O, has been taken as a reference name for many other isomorphous materials such as pyroaurite Mg<sub>6</sub>Fe<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4.5H<sub>2</sub>O, stichtite Mg<sub>6</sub>Cr<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O). Synthetic hydrotalcite-like materials, presented in Fig. 1., are described with the universal formula: [M<sup>II</sup><sub>1-x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>n+</sup>A<sup>n-</sup><sub>x/n</sub> · zH<sub>2</sub>O, where M<sup>II</sup> is a divalent cation (e.g. Mg<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> etc.), M<sup>III</sup> is a trivalent cation (e.g. Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> etc.), A<sup>n-</sup> can be organic or inorganic anion (e.g. CO<sub>3</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> etc.) [4, 5], x can generally have values between 0.2 < x < 0.4 and z is normally 4-5. The stabilization of a broad spectrum of M<sup>II</sup> and M<sup>III</sup> cations in different atomic compositions with varying interlayer anions in the hydrotalcite-like network allows the tailoring of desired properties in these materials [3]. A great number of hydrotalcite-like compounds with wide range of M<sup>II</sup>-M<sup>III</sup> or M<sup>I</sup>-M<sup>III</sup> cation pairs and different anions in the interlayer space and their physicochemical properties has been reported [1]. Direct synthesis of hydrotalcite-like materials can be conducted by various methods including coprecipitation, urea hydrolysis method, ion exchange method, hydrothermal method as well as less popular methods [1, 6].

Thermal decomposition of hydrotalcite-like materials at adequate temperatures, results in homogeneously dispersed mixed oxides of metals, exhibiting high surface area (>200 m<sup>2</sup>/g) and good thermal stability that is usually required for heterogeneous catalysts [7, 8].

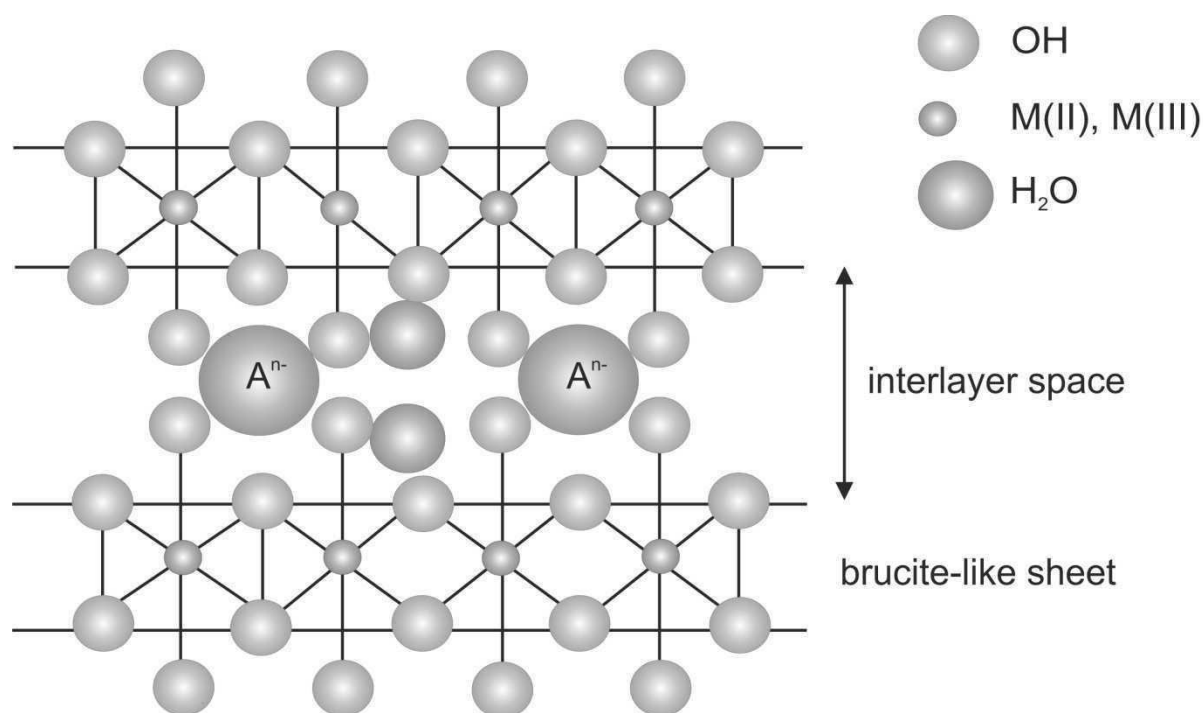


Fig. 1. Schematic representation of hydrotalcite-like materials [3].

## 2. Manganese-based hydrotalcite-like materials and their derivatives

Manganese is an interesting component of mixed oxide based catalysts for oxidation (e.g. oxidation of CO, methanol, ethylene, ammonia) and combustion reactions due to its ability to attain variable oxidation states (+2, +3, +4, and +7) [9]. Among them especial interesting properties of  $\text{Mn}^{2+}$ , such as its  $d^5$  paramagnetic structure, and its potential use in oxidation catalysts [10], natural minerals or synthetic hydrotalcite-like materials and their derivatives containing  $\text{Mn}^{2+}$  cations considered in recent years more attention.

Charmarite,  $\text{Mn}_4^{2+}\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 3\text{H}_2\text{O}$ , described by Chao and Gault [11], is  $\text{Mn}^{2+}$  containing layered double hydroxide occurring in nature. The first positive synthesis of a  $\text{Mn}^{2+}\text{-Al}^{3+}$  hydrotalcite-like materials, obtained by coprecipitation at constant pH, was reported by Malherbe et al. [10]. Mn-Al (Mn/Al = 2.0:1.0) hydrotalcite-like compounds was prepared by coprecipitation method at constant pH=7.0 using  $\text{MgCl}_2$  and  $\text{AlCl}_3$  solutions. The synthesis was performed in inert gas atmosphere and the precipitate was further washed with deoxygenated water. The manganese oxidation state in the material was +2.0 as it was proven by the results of comparative X-ray absorption near edge structure (XANES).

Hydrotalcite Mn-Al (Mn/Al = 2.0:1.0) materials containing various interlayer anions, such as  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  or dicarboxylic acids (DCA), were prepared the coprecipitation method by Aisawa et al. [12] to study their thermal decomposition. The synthesis was maintained under nitrogen. In the case of using  $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ , the solid products besides hydrotalcite-like structure included rhodochrosite ( $\text{MnCO}_3$ ) or shigaite ( $\text{Al}_4\text{Mn}_7(\text{SO}_4)_2(\text{OH})_{22} \cdot 8\text{H}_2\text{O}$ ) as by-products. Only materials containing  $\text{Cl}^-$  or

$\text{NO}_3^-$ , as interlayer anions, allowed the formation of structure of pure hydrotalcite-like materials. The rise of oxidation state of Mn ion (max. +2.2), determined by a redox titration with oxalic acid and  $\text{KMnO}_4$ , was observed at room temperature and it was suggested that a part of  $\text{Mn}^{2+}$  ions in the basal layer was oxidized by air during drying of the sample. Partial oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$ , evidenced by UV-vis-DRS, was also noted during the precipitation at constant pH of Mg-Mn-Al layered double hydroxides (Mg/Mn/Al = 3.0:0.0:1.0 – 0.0:3.0:1.0) [9].

Mainly the presence of  $\text{Mn}^{3+}$  was reported in the structure of hydrotalcite-like compounds [13-15]. Dunn et al. [13] described naturally occurring Mg-Mn layered double hydroxide - desautelsite,  $\text{Mg}_6\text{Mn}_2^{3+}(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ , which is a trivalent manganese analog of pyroaurite. The first attempt towards the synthesis of Mg-Mn hydrotalcite-like materials was carried out by Hansen and Taylor [14]. Mg-Mn (Mg/Mn = 1.0:1.0-1.0:8.0) layered double hydroxides were prepared by air oxidation of  $\text{MnCO}_3$  suspended in  $\text{Mg}(\text{NO}_3)_2$  solution at constant pH=9.0 and also by coprecipitation method using  $\text{Mg}(\text{NO}_3)_2$  or  $\text{MgCl}_2$  solution under strongly alkaline conditions. The average oxidation state of Mn (+3.0) in the synthetic desautelsite was determined by iodometry using the method proposed by Murray et al. [16]. The presence of the equal amounts of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  in the material was not dismissed.

Fernandez et al. [17] studied thermal stability of Mg-Mn (Mg/Mn = 3.0:1.0) hydrotalcite-like materials prepared by the coprecipitation method using a mixture of  $\text{Mg}(\text{NO}_3)_2$  and  $\text{MnCl}_2$ . According to the temperature programmed reduction analysis ( $\text{H}_2$ -TPR), the main part (84%) of  $\text{Mn}^{2+}$  was oxidized to  $\text{Mn}^{3+}$  during the synthesis.

Further studies were focused mainly on the investigation of the effect of transition metal (e.g. Cu, Co) introduction to the Mn-Al hydrotalcite-like structure. For example, Velu et al. [18] studied the physicochemical properties of Cu-Mn-Al (Cu/Mn/Al = 0.9:2.1:1.1, 1.6:1.5:1.0, 1.9:1.2:1.0) hydrotalcite-like samples. The obtained results revealed the formation of the crystalline and pure hydrotalcite phase. A systematic loss in crystallinity upon an increase in Cu content and the appearance of the other phases, such as malachite ( $\text{Cu}(\text{OH})_2\text{CuCO}_3$ ), manganite ( $\text{Mn}(\text{OH})_4/\text{MnO}(\text{OH})_2$ ) and rhodochrosite ( $\text{MnCO}_3$ ) were reported. On the contrary, Kovanda et al. [7] found that synthesis of Co-Mn-Al (Co/Mn/Al = 4.0:2.0:0.0 – 4.0:0.0:2.0) hydrotalcite-like compounds without the formation of  $\text{MnCO}_3$  phase was possible by using different  $\text{M}^{2+}(\text{Co}^{2+}$  and/or  $\text{Mn}^{2+})/\text{Al}^{3+}$  ratios, e.g. the ratio of 2 instead of 3. These findings were confirmed by Lamonier et al. [19], who reported that instead of Mn-Al hydrotalcite-type solid (Mn/Al = 6.0:2.0) the formation of charmarite-2H ( $\text{Mg}_4\text{Al}_2(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$ ) phase was also observed. Subsequently,  $\text{Mn}^{2+}$  species were available for the reaction with carbonates to produce  $\text{MnCO}_3$ .

Replacement of Al by Ni cations in the Mn-Al hydrotalcite-like structure has been studied widely. Barriga et al. [15] and Kovanda et al. [20] described the preparation of Ni-Mn hydrotalcite-like materials with the Ni/Mn ratios close to 2.0:1.0 and 3.0:1.0. Thermal behavior of Ni-Mg-Mn layered double hydroxides with the molar ratio of 1.0:1.0:1.0 was studied by Kovanda et al. [21]. It was reported that  $\text{Mn}^{2+}$  was oxidized to  $\text{Mn}^{3+}$  under alkaline conditions during the synthesis of hydrotalcite-like materials, what was confirmed by carbon analysis or temperature programmed reduction [15].

Further modification of the Ni-Mn catalytic system was based on the introduction of Co cations into the hydrotalcite-like structure [22-24]. Kosova et al. [24] studied the mixed Ni-Mn-Co hydroxide-like compounds synthesized by co-precipitation method under different conditions and with a variable Ni-Mn-Co ratio (Ni/Mn/Co = 0.8/0.1/0.1, 0.6/0.2/0.2, 0.33/0.33/0.33). It was shown by XPS that Mn cations were present in +3.0/+4.0 state.

Apart from the  $M^{2+}/M^{3+}$  molar ratio, the other key factors of the preparation procedure of Mn-containing hydrotalcite-like materials, including precipitate ageing time, pH and temperature of precipitation were rarely discussed. Some attempts were made by Zimowska et al. [25], who studied the effect of pH 6.0-9.0 on the synthesis of Cu-Mn precursor (Cu/Mn = 2.0:1.0). The impact of Zn and/or Al additives into the Cu-Mn structure on its catalytic activity in the process of toluene combustion was also investigated. The obtained results revealed that the addition of Al into the structure (Cu/Mn/Al = 6.0:2.0:1.0) was beneficial for its catalytic performance. The optimum pH was established to be 7.0.

### **3. Catalytic application of manganese-based hydrotalcite-like materials and their derivatives**

Manganese-containing oxides derived from hydrotalcite-like compounds, among other, were tested as catalysts for total VOCs oxidation [26]. The successful use of Mg-Mn-(Al) mixed metal oxides obtained from hydrotalcite-like materials in catalytic methane or toluene combustion was reported by Jiráťová et al. [27] and Velu et al. [9]. Otherwise, the Co-Mn-Al hydrotalcite derived catalysts were reported to be active in oxidation of toluene [19] and ethanol [7]. Lamonier et al. [19] found that the Mn-rich samples, especially Co-Mn-Al oxide systems (Co/Mn/Al = 2.0:4.0:2.0), exhibited higher activity in the oxidation of toluene. Moreover, various promoters, such as Pd, Pt, Ce, La, K or Li, deposited on the Co-Mn-Al mixed oxide catalysts, were found to considerably improve the properties of this catalysts [28]. Other modifications of the Co-based catalysts were connected with the introduction of different metals (e.g. Cu, Mg) to Mn-Al oxide system [26, 29]. The Cu-Co-Mn-Al oxide catalysts (Cu/Co/Mn/Al = 1.0:2.0:0.2:0.8) presented better activity than the Cu-Co/X-Al (X = Fe, La, Ce) catalysts in the process of methane oxidation [29]. In a series of the Mg-containing catalysts, the optimum catalytic performance in the process of the total VOCs oxidation was found for Co-Mn-Mg-Al mixed oxide (Co/Mn/Mg/Al = 1.0:2.0:8.33:3.77). The presence of the mixed phases containing both Mn and Co was suggested to be responsible for the formation of the structural defects, thus leading to the improvement of the oxygen mobility.

Other Co-containing mixed oxides obtained from the hydrotalcite-like samples (Co-Mn, Ni-Mn, Ni-Co-Mn, Ni-Cu-Mn, Co-Cu-Mn, Ni-Cu-Al, Co-Cu-Al, Co-Ni-Al), deposited on  $Al_2O_3$ /Al support (anodized aluminum foil) or grained alumina, were studied in total oxidation of ethanol by Kovanda and Jiráťová [30-32].

Apart from the VOCs decomposition, Co-Mn, Co-Mn-Al or Co-Mg-Mn-Al hydrotalcite-derived mixed oxides were also found to be promising catalysts for  $N_2O$  decomposition [7, 33, 34]. The catalytic decomposition of  $N_2O$  over calcined Co-Mg-



Mn-Al hydrotalcite compounds was reported to increase after the incorporation of Al<sup>3+</sup> cations into the Co-Mn oxide catalyst. The most active Co-Mn-Al (Co/Mn/Al = 4.0:1.0:1.0) catalyst exhibited both the optimum Mn/Al molar ratio and the optimum amount of components reducible in the temperature region of the catalytic process (350-450°C). It was suggested that the most active state of manganese was +3.0.

Only few reports were related to the applications of copper-based hydrotalcite-like derivatives. The catalytic behavior of the Cu-Mn-Al (Cu/Mn/Al = 3.0:3.0:1.0) mixed metal oxides for total oxidation of toluene was evaluated by Palacio et al. [35]. The comparison of the total oxidation of toluene reaction performed over calcined Cu-Mn-Al oxide system [25, 35], showed that the catalysts with the lower molar ratio of metals was much more active than the other ones [35]. The temperature needed for 50% conversion of toluene to CO<sub>2</sub> was among the lowest reported in literature describing the application of hydrotalcite derivatives for the catalytic toluene combustion [19, 25, 36, 37].

Only few papers reported other applications of Mn-containing hydrotalcites and their derivatives. For example, Mn-Al, Mn-Fe, Mn-Cr layered double hydroxides were applied as catalysts for solvent-free oxidation of benzyl alcohol to benzaldehyde [38]. Activity studies were also carried out for Mn-Mg-Al hydrotalcite-like materials in the catalytic isomerization of estragole to anethole [39]. On the other hand, layered double hydroxides containing Ni and Mn were widely studied as cathode materials [40-42]. Additionally, electrochemical behavior of Mn-Al and Zn-Mn-Al hydrotalcite-like materials was studied by Sampieri et al. [43].

#### 4. Conclusion and outlook

In this short report, an overview on the Mn-based hydrotalcite-like materials and their derivatives were addressed, mainly concerning the improvements toward catalysts composition and their activation in catalytic processes. It was shown that Mn-containing hydrotalcite-like materials, are considered as one of the most promising catalysts for total oxidation of VOC.

#### 5. References

- [1] F. Cavani, F. Trifiro, A. Vaccari, "Hydrotalcite-type anionic clays: Preparation, properties and applications.", *Catalysis Today* 11 (1991) 173-301.
  - [2] A. Vaccari, "Preparation and catalytic properties of cationic and anionic clays.", *Catalysis Today* 41 (1998) 53-71.
  - [3] S. Kannan, C.S. Swamy, "Effect of trivalent cation on the physicochemical properties of cobalt containing anionic clays.", *Journal of Materials Science* 32 (1997) 1623-1630.
  - [4] J.S. Valente, M. Sánchez-Cantú, E. Lima, F. Figueras, "Method for large-scale production of multimetallic layered double hydroxides: formation mechanism discernment.", *Chemistry of Materials* 21 (2009) 5809-5818.
  - [5] F. Millange, R.I. Walton, D. O'Hare, "Time-resolved *in situ* X-ray diffraction study of the liquid-phase reconstruction of Mg-Al-carbonate hydrotalcite-like compounds.", *Journal of Material Chemistry* 10 (2000) 1713-1720.
  - [6] K.-H. Goh, T.-T. Lim, Z. Dong, "Application of layered double hydroxides for removal of oxyanions: A review.", *Water Research* 42 (2008) 1343-1368.
-

- [7] F. Kovanda, T. Rojka, J. Dobešová, V. Machovič, P. Bezdička, L. Obalová, K. Jiráťová, T. Grygar, "Mixed oxides obtained from Co and Mn containing layered double hydroxides: Preparation, characterization, and catalytic properties.", *Journal of Solid State Chemistry* 179 (2006) 812-823.
- [8] B.F. Sels, D.E. de Vos, P.A. Jacobs, "Hydrotalcite-like anionic clays in catalytic organic reactions.", *Catalysis Reviews* 43 (2001) 443-488.
- [9] S. Velu, N. Shah, T.M. Jyothi, S. Sivasanker, "Effect of manganese substitution on the physicochemical properties and catalytic toluene oxidation activities of Mg-Al layered double hydroxides.", *Microporous and Mesoporous Materials* 33 (1999) 61-75.
- [10] F. Malherbe, C. Forano, J.P. Besse, "First coprecipitation of an LDH containing manganese as the divalent cation.", *Journal of Materials Science Letters* 18 (1999) 1217-1219.
- [11] G.Y. Chao, R.A. Gault, "Quintinite-2H, quintinite-3T, charmarite-2H, charmarite-3T, a new group of carbonate minerals related to the hydrotalcite-manasseite group.", *The Canadian Mineralogist* 35 (1997) 1541-1549.
- [12] A. Aisawa, H. Hirahara, H. Uchiyama, S. Takahashi, E. Narita, "Synthesis and thermal decomposition of Mn-Al layered double hydroxides.", *Journal of Solid State Chemistry* 167 (2002) 152-159.
- [13] P.J. Dunn, D.R. Peacor, T.D. Palmer, "Desautelsite, a new mineral of the pyroaurite group.", *American Mineralogist* 64 (1979) 127-130.
- [14] H.C.B. Hansen, R.M. Taylor, "Formation of synthetic analogues of double metal-hydroxy carbonate minerals under controlled pH conditions: II. The synthesis of desautelsite.", *Clay Minerals* 26 (1991) 507-525.
- [15] C. Barriga, J.M. Fernandez, M.A. Ulibarri, F.M. Labajos, V. Rives, "Synthesis and characterization of new hydrotalcite-like compounds containing Ni(II) and Mn(III) in the hydroxide layers and of their calcination products.", *Journal of Solid State Chemistry* 124 (1996) 205-213.
- [16] J.W. Murray, L.S. Balistrieri, B. Poul, "The oxidation state of manganese in marine sediments and ferromanganese nodules.", *Geochimica et Cosmochimica Acta* 48 (1984) 1237-1247.
- [17] J.M. Fernandez, C. Barriga, M.A. Ulibarri, F.M. Labajos, V. Rives, "Preparation and thermal stability of manganese-containing hydrotalcite,  $[\text{Mg}_{0.75}\text{Mn}^{\text{II}}_{0.04}\text{Mn}^{\text{III}}_{0.21}(\text{OH})_2](\text{CO}_3)_{0.11} \cdot n\text{H}_2\text{O}$ .", *Journal of Materials Chemistry* 4 (1994) 1117-1121.
- [18] S. Velu, C.S. Swamy, "Synthesis and physicochemical properties of a new copper-manganese-aluminium ternary hydrotalcite-like compound.", *Journal of Materials Science Letters* 15 (1996) 1647-1677.
- [19] J.-F. Lamonier, A.-B. Boutoundou, C. Gennequin, M. J. Pérez-Zurita, S. Siffert, A. Aboukais, "Catalytic removal of toluene in air over Co-Mn-Al nano-oxides synthesized by hydrotalcite route.", *Catalysis Letters* 118 (2007) 165-172.
- [20] F. Kovanda, T. Grygar, V. Dorníček, "Thermal behaviour of Ni-Mn layered double hydroxide and characterization of formed oxides.", *Solid State Sciences* 5 (2003) 1019-1026.
- [21] F. Kovanda, T. Grygar, V. Dorníček, T. Rojka, P. Bezdička, K. Jiráťová, "Thermal behaviour of Cu-Mg-Mn and Ni-Mg-Mn layered double hydroxides and characterization of formed oxides.", *Applied Clay Science* 28 (2005) 121-136.
- [22] S. Jouanneau, J.R. Dahn, "Preparation, structure, and thermal stability of new  $\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x(\text{OH})_2$  ( $0 \leq x \leq 1/2$ ) phases.", *Chemistry of Materials* 15 (2003) 495-499.
- [23] M.Y. Lee, Y.J. Kang, S.T. Myung, Y.K. Sun, "Synthetic optimization of  $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$  via coprecipitation.", *Electrochimica Acta* 50 (2004) 939-948.
- [24] N.V. Kosova, E.T. Devyatkina, V.V. Kaichev, "Mixed layered Ni-Mn-Co hydroxides: Crystal structure, electronic state of ions, and thermal decomposition.", *Journal of Power Sources* 174 (2007) 735-740.
- [25] M. Zimowska, A. Michalik-Zym, R. Janik, T. Machej, J. Gurgul, R.P. Socha, J. Podobiński, E.M. Serwicka, "Catalytic combustion of toluene over mixed Cu-Mn oxides.", *Catalysis Today* 119 (2007) 321-326.
- [26] D.A. Aguilera, A. Perez, R. Molina, S. Moreno, "Cu-Mn and Co-Mn catalysts synthesized from hydrotalcites and their use in the oxidation of VOCs.", *Applied Catalysis B* 104 (2011) 144-150.
- [27] K. Jiráťová, P. Čuba, F. Kovanda, L. Hilaire, V. Pitchon, "Preparation and characterisation of activated Ni (Mn)/Mg/Al hydrotalcites for combustion catalysis.", *Catalysis Today* 76 (2002) 43-53.
- [28] K. Jiráťová, J. Mikulová, J. Klempa, T. Grygar, Z. Basal, F. Kovanda, "Modification of Co-Mn-Al mixed oxide with potassium and its effect on deep oxidation of VOC.", *Applied Catalysis B* 361 (2009) 106-116.

- [29]J. Cheng, J. Yu, X. Wang, L. Li, J. Li, Z. Hao, "Novel CH<sub>4</sub> combustion catalysts derived from Cu-Co/X-Al (X = Fe, Mn, La, Ce) hydrotalcite-like compounds.", *Energy & Fuels* 22 (2008) 2131-2137.
- [30]F. Kovanda, K. Jiráťová, "Supported mixed oxide catalysts for the total oxidation of volatile organic compounds.", *Catalysis Today* 176 (2011) 110-115.
- [31]F. Kovanda, K. Jiráťová, "Supported layered double hydroxide-related mixed oxides and their application in the total oxidation of volatile organic compounds.", *Applied Clay Science* 53 (2011) 305-316.
- [32]J. Ludvíková, F. Kovanda, K. Jiráťová, "Mixed oxides of transition metals as catalysts for total ethanol oxidation.", *Chemical Papers* 66 (2012) 589-597.
- [33]L. Obalová, K. Jiráťová, F. Kovanda, K. Pacultová, Z. Lacný, Z. Mikulová, "Catalytic decomposition of nitrous oxide over catalysts prepared from Co/Mg-Mn/Al hydrotalcite-like compounds.", *Applied Catalysis B* 60 (2005) 289-297.
- [34]L. Obalová, K. Karásková, K. Jiráťová, F. Kovanda, "Effect of potassium in calcined Co-Mn-Al layered double hydroxide on the catalytic decomposition of N<sub>2</sub>O.", *Applied Catalysis B* 90 (2009) 132-140.
- [35]L.A. Palacio, J. Velásquez, A. Echavarría, A. Faro, "Total oxidation of toluene over calcined trimetallic hydrotalcites type catalysts.", *Journal of Hazardous Materials* 177 (2010) 407-413.
- [36]Z. Mikulová, P. Cuba, J. Balanová, T. Rojka, F. Kovanda, K. Jiráťová, "Calcined Ni – Al layered double hydroxide as a catalyst for total oxidation of volatile organic compounds: Effect of precursor crystallinity.", *Chemical Papers* 61 (2007) 103-109.
- [37]F. Kovanda, K. Jiráťová, J. Rymes, D. Koloušek, "Characterization of activated Cu/Mg/Al hydrotalcites and their catalytic activity in toluene combustion.", *Applied Clay Science* 18 (2001) 71-80.
- [38]V.R. Choudhary, D.K. Dumbre, B.S. Uphade, V.S. Narkhede, "Solvent-free oxidation of benzyl alcohol to benzaldehyde by tert-butyl hydroperoxide using transition metal containing layered double hydroxides and/or mixed hydroxides.", *Journal of Molecular Catalysis A* 215 (2004) 129-135.
- [39]D. Kishore, S. Kannan, "Catalytic isomerization of estragole to anethole over hydrotalcites and HT-like compounds.", *Journal of Molecular Catalysis A* 244 (2006) 83-92.
- [40]R.S. Jayashree, P. Vishnu Kamath, "Layered double hydroxides of Ni with Cr and Mn as candidate electrode materials for alkaline secondary cells.", *Journal of Power Sources* 107 (2002) 120-124.
- [41]L. Demourgues-Guerlou, C. Denage, C. Delmas, "New manganese-substituted nickel hydroxides: Part 1. Crystal chemistry and physical characterization.", *Journal of Power Sources* 52 (1994) 269-274.
- [42]L. Demourgues-Guerlou, C. Denage, C. Delmas, "New manganese-substituted nickel hydroxides: Part 2. Interstratification process upon ageing.", *Journal of Power Sources* 52 (1994) 275-281.
- [43]L. Demourgues-Guerlou, C. Denage, C. Delmas, "Electrochemical behavior of the manganese-substituted nickel hydroxides.", *Journal of The Electrochemical Society* 143 (1996) 561-566.
-