

Mixed metal oxides Mg-Cu-Fe obtained from hydrotalcites as catalysts for selective oxidation of ammonia to nitrogen and water vapour (SCO)

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Introduction

Hydrotalcite is a mixed layered magnesium-aluminum hydroxide of the summary formula of $Mg_6Al_2(OH)_6CO_3 \cdot 4H_2O$. The structure of hydrotalcite can be a model for synthetic materials, made from brucite-like network with the general formula of $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}A^{z-}_{x/z} \cdot nH_2O$, where M^{II} i M^{III} are two- and trivalent cations respectively, A – interlayer anions, while x is the molar ratio of the metal cations, whose value varies in the range 0.15-0.34 [1]. The brucite-like network consists of M^{II} and M^{III} metal cations octahedral coordinated by hydroxyl groups, so that any two octahedrons have a common edge (Fig.1).

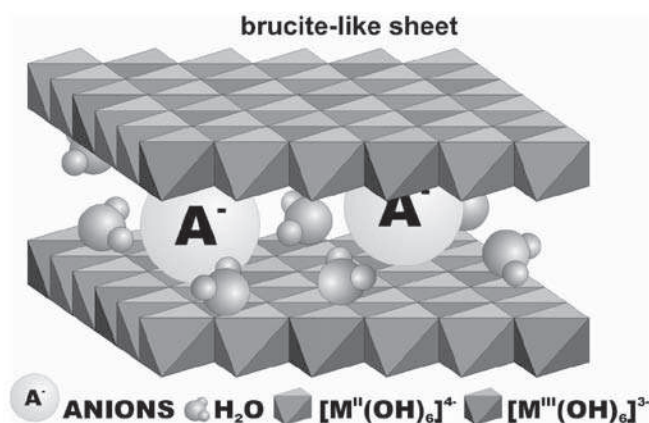


Fig.1. The structure of hydrotalcite

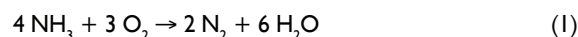
In the natural hydrotalcite some of the Mg^{2+} cations are replaced by trivalent Al^{3+} cations. The net positive charge is compensated by anions, which together with water molecules are located in the interlayer space.

It is possible to produce hydrotalcites in which some of the Mg^{2+} and/or Al^{3+} are replaced by other divalent and/or trivalent cations of similar diameter. Most of the M^{II} positions is occupied by cations such as Mg^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and the M^{III} positions by Al^{3+} , Cr^{3+} , Fe^{3+} [2,3]. In addition to modification of the layer composition, it is also possible to produce hydrotalcites containing large variety of different interlayer anions, which in large extend determine chemical properties and availability of the inner surface of hydrotalcites [4, 5].

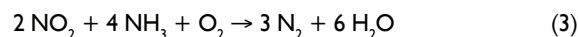
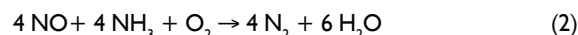
Thermal decomposition of hydrotalcites leads to a mixed oxides, characterized by a highly developed surface area (>200 m^2/g), homogeneous dispersion of components and high thermal stability. An additional advantage this class of materials is the possibility of synthesis of the samples containing different transition metals in a relatively wide range of content. The phase composition of the hydrotalcite originated metal oxide systems can be changed by

calcination conditions. An increase in calcination temperature promotes formation of the spinal phases, while amorphous mixed oxides are formed at lower temperatures. The acid/base properties can be adjusted by changing of the Mg/Al ratio in these materials [6].

Hydrotalcites were tested as precursors of catalysts of various catalytic processes such as: DeNOx process [6], selective oxidation of ammonia [7], N_2O decomposition [8]. Recently, an increasing interest in application of the hydrotalcite like materials as precursors of the catalysts for selective catalytic oxidation of ammonia to nitrogen and water vapour (SCO, equation 1) is observed:



The SCO process could be used for elimination of ammonia, unreacted in DeNOx process (equations 2, 3):



The implementation of the SCO converters in DeNOx installation in electric power stations as well as in exhaust systems in diesel cars (AdBlue technology) should improve effectiveness of NOx conversion without risk of ammonia leakage into atmosphere.

The studies of in the SCO process were focus on three groups of materials as potential catalysts of this reaction: noble metals (e.g. platinum [9], palladium [10], iridium [11]), transition metal oxides (e.g.: $Fe_2O_3-Al_2O_3$, $Fe_2O_3-TiO_2$, $Fe_2O_3-ZrO_2$ [12] $Fe_2O_3-SiO_2$ [13]) and zeolites modified with transition metals (e.g. zeolit Y, ZSM-5, mordenite, beta, ferrierite, chabazite [14]). Among the tested catalysts, the highest activity and selectivity to nitrogen was observed for systems containing copper and/or iron. The study of mixed metal oxides Cu-Mg-Al obtained from hydrotalcites as catalysts for the selective oxidation of ammonia, showed their high activity at low temperatures, however, the selectivity to nitrogen decreased with increasing reaction temperature [3,6,15]. In turn, the process performed in the presence of Mg-Fe-Al oxide systems was less effective with respect to ammonia conversion, but more selective to nitrogen. Therefore, studies were undertaken to develop active and selective catalyst based on Mg-Cu-Fe mixed metal oxides obtained from hydrotalcites for oxidation of ammonia.

Experimental part

Catalysts preparation

$Mg(II)Cu(II)Fe(III)$ hydrotalcites with the intended molar ratio of metals: 2:1:1, 2:0.5:1 and 2:0:1, were prepared by coprecipitation method using aqueous solution of suitable metal nitrates: $Mg(NO_3)_2 \cdot 6H_2O$

(Sigma), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (POCh). Metal nitrate solutions were dosed to an aqueous solution containing a stoichiometric excess of Na_2CO_3 (POCh). The synthesis was carried out at constant $\text{pH} = 11.0 \pm 0.2$, which was maintained by controlled addition of 1 M NaOH solution. The obtained slurry was vigorously stirred in the mother liquor at 60°C for 30 minutes, then filtered, washed and dried at 100°C for 24 hours. Finally, obtained hydrotalcites were calcined at 600°C for 12 hours. The resulting catalysts were stored in desiccator.

Catalysts characterization

The phases present in the precursors and calcined hydrotalcites were identified using the powder XRD method (Philips X'Pert APD). Copper lamp with $\text{K}\alpha$ radiation of wavelength $\lambda = 1.54056 \text{ \AA}$ was used. The surface area of calcined hydrotalcites was determined by the BET method. Measurements were performed using Quantasorb Junior sorptometer (Ankersmit). Prior to nitrogen adsorption at -196°C , each of the samples were degassed at 250°C for 2 hours. Measurements of temperature-programmed reduction (TPR) were performed in a fixed bed flow reactor system. Prior to measurement each sample (30 mg) was calcined at 600°C for 12 hours. Hydrogen consumption was recorded using TCD (Valco). Measurements were performed from room temperature to 1100°C with a linear heating rate of $5^\circ\text{C}/\text{min}$. A reducing mixture of 10 vol. % H_2 diluted in Ar (Messer), which flow rate through the reactor was 6 ml/min, was used. Water, being the product of reduction, was removed by cold-trap.

Catalytic tests

Calcined hydrotalcites were tested as catalysts of the selective oxidation of ammonia to nitrogen and water vapour. Catalytic tests were performed in a fixed bed flow reactor system, while the analysis of reaction products was performed using the QMS detector. A sample of catalyst (100 mg) was first degassed at 600°C for 1 hour in a flow of helium (20 ml/min). Catalytic tests were performed in a flow of the reaction mixture containing: $[\text{NH}_3] = 0.5 \text{ vol.}\%$, $[\text{O}_2] = 2.5 \text{ vol.}\%$, $[\text{He}] = 2.5 \text{ vol.}\%$. The total flow rate of the reaction mixture was 40 ml/min. The studies were performed in the temperature range of $150\text{--}450^\circ\text{C}$ with a linear heating rate of $10^\circ\text{C}/\text{min}$.

Results and Discussion

The surface areas of calcined hydrotalcites are summarized in Table I. It was shown that the surfaces area measured for the all studied catalysts are similar and ranged from 43 to $56 \text{ m}^2/\text{g}$.

Table I

Composition and specific surface area of prepared hydrotalcites

codes of the samples before calcinations	codes of the calcined samples	Mg/Cu/Fe molar ratio	BET surface area [m^2/g]
HT- $\text{Mg}_2\text{Cu}_1\text{Fe}_1$	$\text{Mg}_2\text{Cu}_1\text{Fe}_1$	2/1/1	43
HT- $\text{Mg}_2\text{Cu}_{0.5}\text{Fe}_1$	$\text{Mg}_2\text{Cu}_{0.5}\text{Fe}_1$	2/0.5/1	50
HT- $\text{Mg}_2\text{Cu}_0\text{Fe}_1$	$\text{Mg}_2\text{Cu}_0\text{Fe}_1$	2/0/1	56

The X-ray diffraction patterns recorded for the precursors and calcined hydrotalcites were presented in the Figure 2.

For all the samples reflections characteristic of hydrotalcite (1) were found [16]. In the case of a sample containing the largest

amount of copper (HT- $\text{Mg}_2\text{Cu}_1\text{Fe}_1$), also reflections characteristic of tenorite phase (CuO) were found. Calcination of hydrotalcites at 600°C resulted in formation of mixed metal oxides and spinel phases. The sample, in which there is no copper (HT- $\text{Mg}_2\text{Cu}_0\text{Fe}_1$), consists of poor-crystalline periclase (MgO) and magnesioferrite (MgFe_2O_4) [17,18]. However, it should be noted that, identification of possible spinel phases is difficult because the position of the reflections characteristic for MgFe_2O_4 and $\text{Fe}^{\text{II}}\text{Fe}_2\text{O}_4$ is virtually identical [17].

The introduction of copper into the structure of the material leads to the formation of additional phases. Reflections that appear in the diffractogram of the samples containing copper (HT- $\text{Mg}_2\text{Cu}_1\text{Fe}_1$, HT- $\text{Mg}_2\text{Cu}_{0.5}\text{Fe}_1$), at 36.4 , 42.3 , 61.3 and $29.6^\circ 2\theta$ can be assigned to cuprite phase (Cu_2O). In turn, reflections at 35.6 , 38.7 , 48.8 and $61.6^\circ 2\theta$, confirm the presence of tenorite (CuO), whose creation is conditioned by high content of copper in the sample. Analysis of the obtained X-ray diffraction patterns, did not show the presence of cuprospinel ($\text{Cu}^{\text{II}}, \text{Mg}$) Fe_2O_4 and $\text{Cu}^{\text{II}}\text{Fe}_2\text{O}_4$ [19].

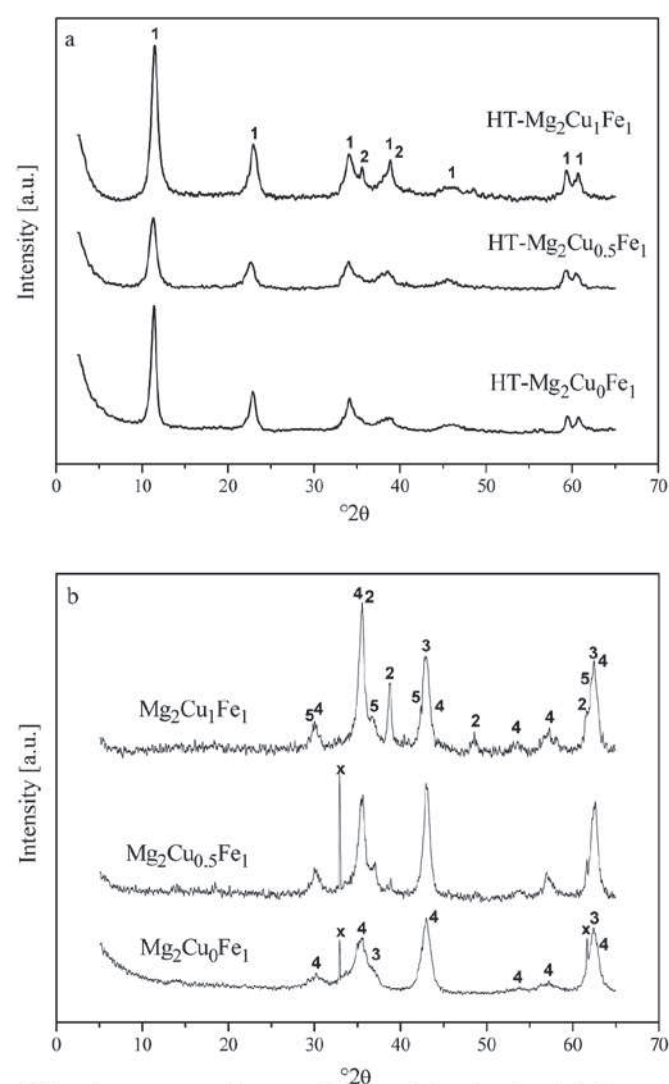


Fig. 2. X-ray diffractogram patterns obtained for hydrotalcites precursors: (a) and mixed metal oxides (b); 1 – hydrotalcite, 2 – tenorite, CuO , 3 – periclase, MgO , 4 – magnesioferrite, MgFe_2O_4 , 5 – cuprite, Cu_2O , x – Si holder

Additionally, the presence of amorphous iron oxides can not be excluded.

Redox properties of the catalysts were studied by temperature-programmed reduction (TPR). The results of these studies are presented in Figure 3.

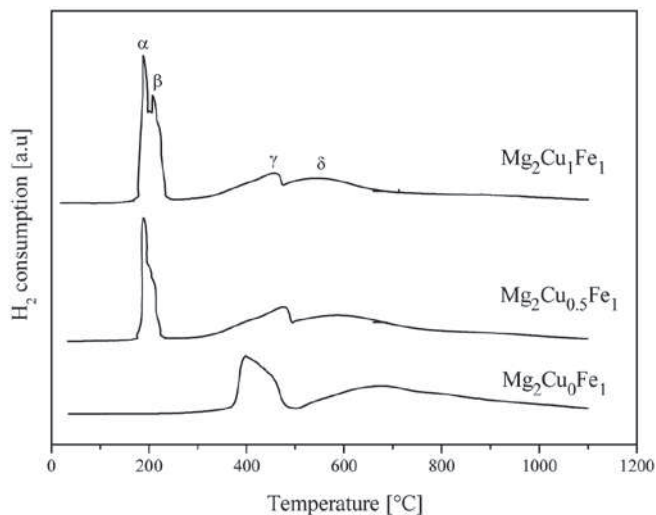
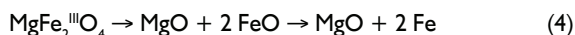


Fig. 3. TPR profile for calcined hydrotalcites. Reaction conditions: 30 mg catalysts, 10% H₂/Ar, total flow rate of 6 ml/min

Intensive reduction peaks associated with reduction of copper oxide species are located at 190-195°C (the α peak) and 200-205°C (the β peak). The α is associated with reduction of highly dispersed copper oxides, which include single copper ions and two- or three dimensional clusters [20÷23]. The β peak corresponds to the reduction of CuO phase, which contains large quantities of clusters and the crystallites of CuO. The intensity of this peak increases with increasing copper content in the sample. Maxima associated to the reduction of iron were found at 460-480°C and 540-620°C (marked as γ and δ, respectively). The structural studies of oxide systems have shown that iron could be present in the form MgFe₂^{III}O₄ and/or Fe^{II}Fe₂^{III}O₄. Unfortunately, the XRD method did not to allow unambiguously determine which of the spinel phase is present in the samples. Such information was obtained by analysis of the TPR results. Assuming that the iron, in both spinels, is reduced in two stages [23,24] process can be represented by equations 4 (reduction of MgFe₂^{III}O₄ spinel) and 5 (reduction of Fe^{II}Fe₂^{III}O₄ spinel):



During the reduction of iron in MgFe₂^{III}O₄ spinel, the hydrogen consumption ratio in both stages is 1:2, while in Fe^{II}Fe₂^{III}O₄ is 1:3. TPR analysis of the results showed, that for the studied oxide systems, this ratio varies depending on the copper content and is 1:2.27 for Mg₂Cu₁Fe₁, 1:2.14 for Mg₂Cu_{0.5}Fe₁ and 1:2.42 and Mg₂Cu₀Fe₁. The obtained results confirmed the presence of both spinel in the samples, although MgFe₂^{III}O₄ is a dominant spinel phase. Mixed metal oxides Mg-Cu-Fe obtained from hydrotalcites were tested in the role of catalysts of the selective oxidation of ammonia. Desired reaction products are nitrogen and water vapour, while the main by-products are NO and N₂O. The results of these studies are presented in Figure 4. The oxidation of ammonia begins at about 225-250°C, while the total conversion occurs in the 425-450°C. The exception is the catalyst without copper (Mg₂Cu₀Fe₁), for which the oxidation of ammonia begins at 325°C, but its complete removal is not achieved in the studied temperature range. Therefore, it seems that copper activates the catalytic systems for low temperature SCO process, but at higher temperatures the selectivity of the oxidation of ammonia to nitrogen oxides increases. Iron is catalytically active only at high temperature.

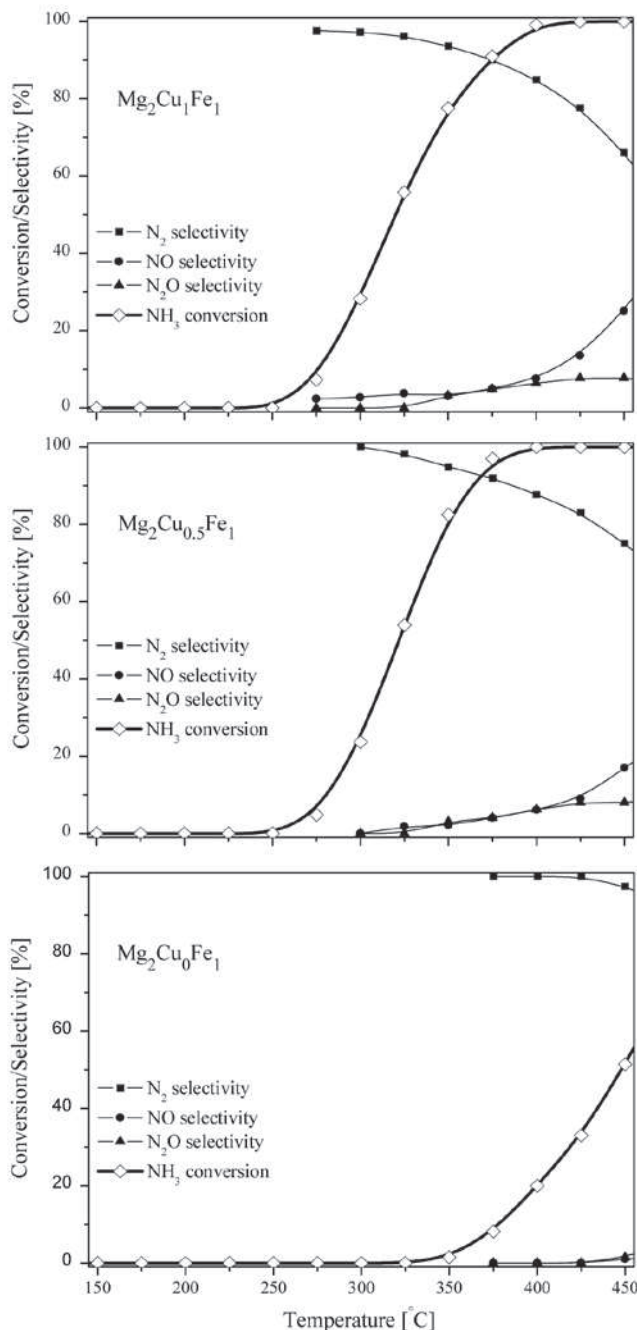


Fig. 4. Selective catalytic oxidation of ammonia to nitrogen and water vapour in the presence of Mg-Cu-Fe catalysts obtained from hydrotalcites. Reaction conditions: 100 mg catalysts, [NH₃] = 0.5%, [O₂] = 2.5%, [He] = 97%, total gas flow = 40 ml/min

Taking into account both high activity and selectivity to nitrogen, optimal results were obtained for the catalyst containing small amount of iron and copper (Mg₂Cu_{0.5}Fe₁). The total conversion of ammonia was achieved in the presence of this sample at 400°C, with selectivity to nitrogen of about 88%.

Conclusions

Mixed metal oxides Mg-Cu-Fe obtained from hydrotalcites are very interesting system for the selective catalytic oxidation of ammonia to nitrogen and water vapour. The activity and selectivity of catalysts obtained from hydrotalcite precursors strongly depends on the chemical composition of the samples. Optimal catalytic properties were found for the samples containing both copper and iron – Mg₂Cu_{0.5}Fe₁. Copper activates for the low-temperature process, but at higher temperatures is responsible for the formation of nitrogen oxides. Iron is catalytically active only in the high temperature region.

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