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**Mg/Al MIXED OXIDES: PREPARATION,
PROPERTIES AND CATALYTIC ACTIVITY
IN TRANSESTERIFICATION OF RAPESEED OIL**

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This paper reviews the preparation, physicochemical properties and application of Mg/Al mixed oxides. Attention is focused on the activity of Mg/Al mixed oxides in transesterification of rapeseed oil. The mixed oxides were prepared from hydrotalcites by calcination and were characterized by XRD, FTIR and AAS. The aim of work was to study the effect of Mg/Al mixed oxides properties such as Mg/Al mass ratio (2-4), the temperature of calcination (450-1000 °C), time of calcination (4-17 h) and post-treatment rehydration of mixed oxides on the activity of Mg/Al catalysts in the transesterification reaction. The results show that the highest catalytic activity was observed for Mg/Al catalysts with Mg/Al mass ratio of 3, calcination temperature of 450 °C, time of calcination of 8 hours and rehydration by water. The leaching of magnesium to liquid phase was also determined and was always less than 0.1 wt. % — the catalyst was stable.

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Introduction

Hydrotalcites

Hydrotalcite is a natural, non-toxic, white mineral with lamellar structure (for a review see Ref. [1]). Its structure is derived from that of magnesium hydroxide (brucite), where a part of magnesium ions is substituted by trivalent ion (aluminium ion) and brucite-like layer is formed. Individual layers are stacked on each other and design layered structure. The cations can be different in brucite layer but they have to have similar ion radius as magnesium in the case of divalent cation or aluminium in the case of trivalent cation. The presence of d-elements in the hydrotalcite structure can cause a distortion in the octahedral coordination structure, and it causes the Jahn–Teller effect [2]. The brucite layer has positive partial charge, which has to be compensated by a negative charge. The negative charge is situated in the interlayer between two brucite-like sheets.

The compensating anions are situated in the anion layer. In the natural hydrotalcites, the carbonate anions are present as the compensating anions [3] but synthetic hydrotalcites can also contain different inorganic anions, such as fluorides, chlorides, sulphates, sulphites, nitrates, *etc.* [4], anions of organic acids such as adipic, malonic, *etc.* [5], or heteropolyacids anions, such as $(\text{PMo}_{12}\text{O}_{40})^{3-}$ and $(\text{PW}_{12}\text{O}_{40})^{3-}$ [6]. The positive charge in the brucite layer can also be compensated by two kinds of anions.

The hydrotalcite contains water, which is situated in a free space in anion layer [7]. The natural hydrotalcites have four molecules of water in one structural unit $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$, while the synthetic hydrotalcites contain less water. The amount of water decreases with an increasing amount of trivalent cations and size of anions [2].

The hydrotalcites are usually used as precursors for preparation of Mg/Al mixed oxides but can also be used for other applications, such as fire retardants [8], carriers for medications (Ibuprofen or various antibiotics) [9], anti-inflammatory salves or as antacid agents [2].

Preparation

The hydrotalcite can be prepared by three different methods: titration method [10], precipitation method at constant pH with high or low supersaturation of reactants solutions [11-12].

In the case of titration method, two solutions of nitrates with appropriate cations concentrations are prepared. These solutions are titrated with a solution of base — sodium carbonate or sodium hydroxide are often used. Firstly (in the pH range 4-4.5); the pure aluminum hydroxide is precipitated. The Mg/Al hydrotalcite

is formed if the pH is increased to the range of 7.7-8.5. Further increase in pH to 9.5 causes magnesium hydroxide to be formed. This method is not suitable for preparation of pure hydrotalcite [2].

The second method of preparation is the precipitation from solutions of nitrates (with appropriate cations) at a constant pH and high supersaturation of solutions. These solutions of nitrates are added very quickly to the solution of bases such as NaHCO_3 . By this method, we are able to prepare less crystalline material because of high numbers of crystallization nuclei arising in rapid precipitation. The amorphous hydrotalcites were prepared by this method [2].

The precipitation at a constant pH and with low-supersaturation solutions is one of the most frequently used methods. The solution of nitrates (with appropriate cations) is added very slowly into distilled water (heated to 70 °C), while pH is kept constant at the value of 9-10 by addition of bases solution. The mixture is stirred intensively during the precipitation. The hydrotalcite prepared by this method has a larger size of crystals in comparison with the method of high supersaturation solution [2].

Mixed Oxides

Properties

The properties of mixed oxides depend on many parameters, such as the type of mixed oxide, type and quantity of impurities present during catalyst preparation [2]. Their properties can also be influenced by the time and temperature of hydrotalcite synthesis, and calcination conditions such as heating rate, temperature, time and atmosphere of heat treatment [2,13,14]. The most important properties of prepared mixed oxides are acid-base properties [15], memory effect [16], paracrystallinity [17] and formation of non-stoichiometric spinels [2,18].

The acid-base properties of mixed oxides can easily be modified by introduction of suitable cations during preparation [2,13]. The strength of basic sites can also be influenced by the molar ratio of cations. In the case of the Mg/Al mixed oxides, the number of basic sites increases with an increasing amount of Mg [19]. The hydrotalcite with the ratio $\text{MgO}/\text{Al}_2\text{O}_3 = 5.23$ exhibited the highest number of Brønsted basic sites per unit of surface area [2]. Brønsted active centers are transformed by calcination into Lewis centers, which are more active. These mixed oxides have three types of active sites: the strongest O^{2-} surface basic sites, the medium strong O^- centers located near hydroxyl groups and the weak basic sites which are related to OH groups [13,20].

The mixed oxides prepared by calcination of hydrotalcite have memory effect, i.e., the reconstruction of the hydrotalcite lamellar structure by adsorption of various anions or water (e.g., from air) in mixed oxides. This process is suitable

for the preparation of hydrotalcites with different types of anions. The memory effect strongly depends on the type and amount of cations in brucite layer and the temperature of calcination. The lamellar structure of hydrotalcite cannot be reconstructed if the calcination temperature is higher than 450 °C [2].

Utilization

The significant applications of mixed oxides include their usage in the heterogeneous catalysis as an active component or support. Mixed oxides can catalyze many reactions, such as condensation [21-23], alkylation [24-26], aldolisation [27] or transesterification [28,29]. Therefore, they are intensively studied nowadays and their new applications are investigated.

The aldolisation is a reaction between two carbonyl compounds and a new C-C bond is formed. The reaction is usually homogeneously base catalyzed by sodium, barium or potassium hydroxides. As an example, the preparation of acrolein by the reaction of formaldehyde with acetaldehyde can be mentioned. The reaction was studied in the gas phase and Mg/Al mixed oxide was used as a catalyst [24]. It was found that the selectivity to acrolein is decreasing with an increasing amount of acid sites. The selectivity to acrolein was set by the action of acidic rather than by basic sites [24].

The aldol condensation of citral and acetone to pseudoionone was investigated by Abello *et al.* [30], and rehydrated Mg/Al mixed oxides modified by the presence of alkaline metals, such as sodium, potassium and lithium, were used as the catalyst. Abello *et al.* [30] found the Mg/Al mixed oxide catalyst doped with sodium to show the highest catalytic activity. Unfortunately, alkaline-promoted mixed oxide shows a significant leaching of the alkaline promoters to the reaction mixture in repeated cycles.

The catalytic methylation in the gas phase of imidazole was also studied by Grabowska *et al.* [31]. The Mg/Al mixed oxide with the molar ratio of 1:2 (Mg:Al) prepared by calcination of hydrotalcite at 500 °C was used as a catalyst. The catalyst was prepared by hydrothermal synthesis from magnesium and aluminium nitrates by co-precipitation method with low saturation. The reaction was carried out at 350 °C, and 94.2 % yield of *N*-alkylimidazole was obtained after 5 hours. The product can be used as an intermediate for pharmaceutical or agrochemical industry [31].

The transesterification of plant oils with low molecular alcohols is intensively studied nowadays [32], because it is one of the ways how biodiesel can be produced. In this reaction, the Mg/Al mixed oxides can be used as catalysts as well. Biodiesel is known as a renewable fuel that consists of fatty acid methyl ester (FAME), if methanol is used as alcohol in the reaction. Cantrell *et al.* [20] studied transesterification of glyceryl tributyrate with methanol. The mixed oxides were prepared by calcination at 500 °C. It was found that the conversion of oil after 3

hours was 74.8 %. The reaction was carried out at 60 °C. Albuquerque *et al.* [33] studied activity of the Mg/M mixed oxides (M = Ca or Al) in transesterification of sunflower oil with methanol. The Mg/Ca hydrotalcite had to be calcined at 800 °C, because that way it had a higher thermal stability than Mg/Al hydrotalcite. The transesterification was carried out at 60 °C and after 3 hours the yields of methyl esters were 92 % and 66.3 % for Mg/Ca and Mg/Al mixed oxides, respectively. The yield of methyl esters increased with an increasing basicity of catalysts [33]. The transesterification of methyl palmitate with isobutyl alcohol was also studied by Fraile *et al.* [34]. They studied the influence of alkaline metals, such as sodium and potassium on catalytic activity of mixed oxides. They found that conversion of oil and also basicity increases with an increasing amount of sodium and potassium in the structure of mixed oxides. When the amount of sodium was 10.6 wt %, the conversion increased above 94 %. On the other hand, the conversion decreased in repeated cycles [34]. They found out that sodium was leached from catalyst into reaction mixture during the reaction, and it caused a higher conversion. The conversion of methyl palmitate under the same reaction conditions was only 3 % when the commercial hydrotalcite (Hycite 713) from Süd-Chemie was used as a catalyst [34].

The mixed oxides containing transition metals can also catalyze decomposition of NO_x. Obalová *et al.* [35] studied degradation of nitrogen monoxide. Ni/Al and Co/Mn/Al mixed oxides prepared by calcination of hydrotalcites at 500 °C were used as catalysts. The suitability of these catalysts for a practical application was proved in a simulated steam process in the presence of O₂, NO, NO₂ and H₂O. A high catalytic activity was reached over all the tested catalyst [35].

Hydrogen provides a clean and environmentally friendly energy. The decomposition of methane is one way of hydrogen production. Ashok *et al.* [36] carried out steam reforming of CH₄ over Ni/Cu/Al layered double hydroxide converted to mixed oxide by calcination. The reaction was carried out at 600 °C and ambient pressure.

The dry reforming of methane to synthesis gas over Ru supported on an Mg/Al mixed oxide was studied by Tsyganok *et al.* It was found that the conversion after 4 hours was 100 % [37].

The mixed oxides are also significant sorbents; therefore, they are used for sorption of acid-forming gases (SO₂, NO₂, NH₃, mercaptans) or organic compounds (phenols, oils, amines, dyes).

Preparation

The mixed oxides are formed from the hydrotalcites (as precursor) during calcination. This method enables preparation of mixed oxide with a required molar ratio of cations (in this case Mg/Al) and was used in this study. The calcination

process can be divided into six heating stages, where in each of them the structure is changed. At first, water from interlayer is escaping in the temperature range of 70-190 °C (the lamellar structure is still preserved). Further, water, which is bound in the form of hydroxyl anions with Mg^{2+} or Al^{3+} , escapes in the temperature ranges of 190-280 °C and 280-405 °C. In the first temperature range (190-280 °C), the hydroxyl anions are bound to Al^{3+} , and in the second range (280-405 °C) they are bound to Mg^{2+} . The mixed oxides are formed in the temperature range from 405 °C to 580 °C. The degradation of lamellar structure and formation of amorphous phase occur in the temperature range of 280-405 °C. Further heating to 580 °C causes only evaporation of the carbon dioxide, which is bound in the form of carbonate anions (remnants from hydrotalcite synthesis). The spinel phase, which is mostly inactive in the heterogeneous catalysis, is formed after heating of the material up to 800 °C [38].

The mixed oxides prepared by calcination of hydrotalcite have advantages, such as a large surface area, and also they have generally a good dispersion of metal on their surface if they are used as supports [39].

The mixed oxides can also be prepared by different methods such as ceramic or co-precipitation method [40]. The ceramic method is based on mixing of individual powders of metal oxides or their carbonates and subsequent homogenization and calcination at high temperatures. This method is energy demanding; therefore, the co-precipitation method is used more often.

Experimental

Preparation of Catalysts

The Mg/Al hydrotalcites were synthesized by a co-precipitation method from two aqueous solutions as follows: an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ of the desired Mg/Al ratio (total metal concentration 1 mol l^{-1}) was slowly added to 200 ml distilled water at 75 °C. At the same time, a 3.5 mol l^{-1} solution of Na_2CO_3 (3 mol l^{-1}) and NaOH (0.5 mol l^{-1}) was added in order to maintain pH at the desired value (9.5 ± 0.5), and the mixture was stirred vigorously (1400 rpm) with a mechanical overhead stirrer (Heidolph® RZR 2020). When all the metal solution was added (1000 ml metal solution with total metal concentration 1 mol l^{-1}), the mixture was kept at 75 °C for 1 hour, and its pH value was maintained at 9.5. The solid catalyst was filtered off and washed several times with distilled water until the filtrate pH was 7. After the preparation, the hydrotalcites were dried for 24 hours at room temperature. Finally, the hydrotalcites were grained to 0.25-0.5 mm particle size. The mixed oxides are formed from hydrotalcites as precursors by calcination; therefore, the calcination of the hydrotalcites was performed. Additionally, the catalysts were calcined for various time periods in the air at various temperatures. For convenience, the

catalysts were named HTC-x, where HTC means hydrotalcite calcined and x refers to temperature of calcination (°C).

Additionally, the rehydration of mixed oxides was chosen as a post-treatment modification of the catalysts (reconstruction of lamellar structure). The rehydration was carried out as follows. Firstly, the catalyst was rehydrated by water when it was placed into distilled water at 85 °C, and the mixture was stirred with a magnetic stirrer (200 rpm) for 2 hours. After that, the mixture was heated up to the boiling point of water and excess water was evaporated. After evaporation, the hydrotalcites were dried for 24 hours at room temperature and grained to 0.25-0.5 mm particle size. Secondly, the catalyst was rehydrated by steam when it was placed in an oven and heated to the temperature between 130-150 °C. After that, the catalyst was treated with a flow of humidified air preheated to 60 °C for 4 hours. Finally, the catalyst was dried at oven temperature for 10 minutes to remove water, which might condense in the reactor. For convenience, the samples modified by different treatments were designated as HTC (AS), HTC (WT) and HTC (ST) for catalyst as synthesized (AS), treated with water (WT), and treated with steam (ST).

Characterization of Catalyst

X-ray diffraction (XRD) patterns of the powder materials were obtained using a D8 Advance diffractometer (Bruker AXS, Germany). FTIR spectra were obtained using a Nicolet 6700 spectrometer.

Reaction – Transesterification

The transesterification of rapeseed oil with methanol catalyzed by hydrotalcite was carried out at the temperature of 117 °C in a batch stainless steel reactor equipped with a manometer. The cold-pressed, filtered rapeseed oil, free of erucic acid (acid number 0.22 mg KOH g⁻¹, water content 600 mg kg⁻¹ and density 920 kg m⁻³, produced by RPN Slatiňany Corp., the Czech Republic) was used. The reactor, which was filled up with the reaction mixture, was put into a glycerol bath (117 °C) and the reaction started when the pressure on the manometer reached 550 kPa (the pressure close to the saturation vapor pressure of methanol). After the reaction, the catalyst was removed by filtration and the mixture was demethanolized (75 °C, 2.5 kPa). The ester (upper) and glycerol (lower) phases were separated in a separation funnel and analyzed. Nevertheless, the glycerol phase was not observed after the transesterification for all the catalysts. The ester phase was analyzed with respect to the content of ester in the ester phase (ester yield – wt.%), the amount of glycerides, the amount of free glycerol and the amount of magnesium in the

ester phase (Mg leaching – wt.%). The concentration of aluminium was determined by chelatometric titration, and aluminium leaching was found to be below the detection limit. The contents of mono-, di-, triglycerides and methyl esters were determined by the GC method according to EN 14105 by Shimadzu GC-2010 with the help of linear calibration curves. Monoolein (Sigma Aldrich), diolein (Sigma Aldrich), triolein (Acros Organics) and pure methyl ester (prepared by homogeneous transesterification from the same oil and purified by molecular distillation) were used as standards. The concentration of magnesium ions was determined by atomic absorption spectroscopy with the help of a calibration curve.

Results and Discussion

The Mg/Al mixed oxides with various Mg/Al mass ratio were studied as heterogeneous catalysts for transesterification of rapeseed oil. The catalytic activity of Mg/Al mixed oxides strongly depends on an Mg/Al molar ratio [41-42], temperature and time of pre-treatment [13,14] and post-treatment (rehydration) [43] or on the reaction conditions, namely reaction temperature and time, stirring speed, catalysts loading and oil to methanol molar ratio [43-45]. This work is focused on a systematic comparison of these effects on the catalytic activity. The most interesting finding is the effect of post-treatment rehydration on the catalytic activity. Post-treatment rehydration is advantageous in aldolisation [27] but the effect of post-treatment rehydration in transesterification of rapeseed oil has not been described in detail up to now.

The reaction conditions were as follows: methanol to oil molar ratio of 24:1, the reaction temperature of 117 °C, 4 wt. % of the catalyst (based on the weight of rapeseed oil) and a stirring speed of 320 rpm. These reaction conditions were derived from the series of tests, where we investigated the influence of each parameter on the catalytic activity, and under the above mentioned reaction conditions the catalyst shows the highest catalytic activity. The influence of these parameters on the catalytic activity is not discussed in this work.

Influence of Mg/Al Mass Ratio on Biodiesel Yield

Table I gives the catalytic activity of Mg/Al mixed oxides with Mg/Al mass ratios 2, 3 and 4. The highest catalytic activity was achieved with the Mg/Al mass ratio of 3; therefore, the catalyst with this mass ratio was used in following experiments. Table I also gives the amount of leached magnesium. Total amount of the magnesium leached from the catalyst structure was below 0.1 wt. %. Our results of the catalytic activity dependence are in agreement with studies of Zeng *et al.* [45] and Xie *et al.* [44], who reported similar trends in the catalytic activity. It is

Table I Influence of Mg/Al mass ratio in mixed oxides catalyst HTC-450 on yield of esters and stability of catalyst

Mg/Al mass ratio	2	3	4
Ester yield, wt. %	35.8	36.3	13.8
Mg leaching, wt. %	0.08	0.09	0.04

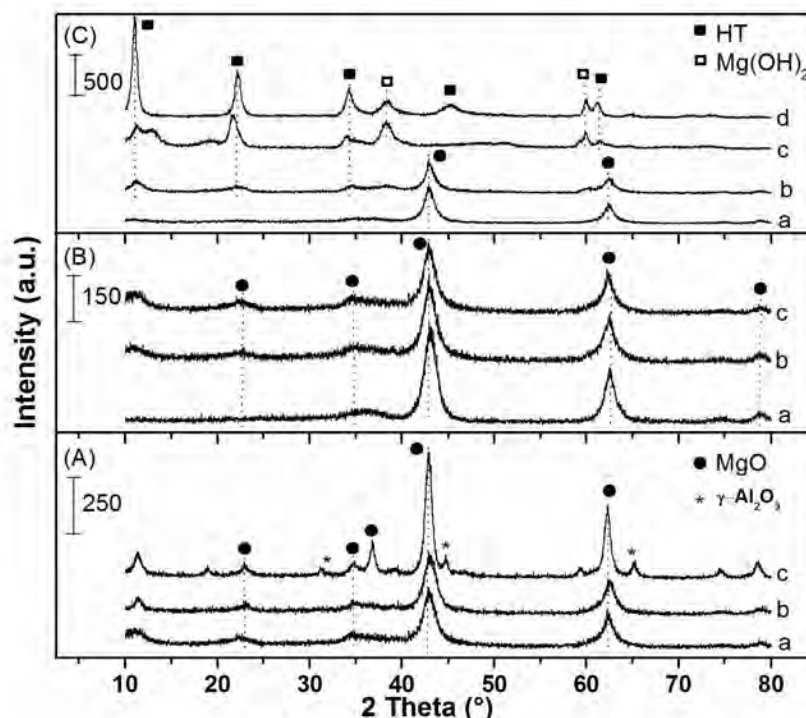


Fig.1 (A) XRD patterns of Mg/Al mixed oxides calcined at different temperatures: (a) 450 °C, (b) 600 °C, (c) 1000 °C. (B) XRD patterns of Mg/Al mixed oxides calcined at 450 °C for different time periods: (a) 4h, (b) 8h, (c) 17h. (C) XRD patterns of Mg/Al mixed oxides after various treatments: (a) without treatment, (b) treated with steam, (c) treated with water, (d) hydrotalcite before calcination

due to the formation of new weaker basic sites if the Mg/Al mass ratio is above 3. These weaker basic sites decrease the amount of strong basic sites; therefore, the catalytic activity is decreasing. The Mg/Al mass ratio of the catalysts does not influence the positions of characteristic diffraction maxima in XRD patterns, only their intensities.

Influence of Calcination Temperature on Biodiesel Yield

The results in Table II show that the catalytic activity was significantly affected by the temperature of calcination. It was found that the catalytic activity decreases with an increasing calcination temperature in the tested range from 450 °C to 1000 °C. The role of the thermal pre-treatment and the basicity of Mg/Al mixed oxides and their catalytic activity are still a matter of discussion. The results are in agreement with findings of Zeng *et al.* [45] and Xie *et al.* [44], who reported similar trends in the catalytic activity. They found that the catalytic activity increases with an increasing calcination temperature and reaches the maximum over the calcination temperature of 450-500 °C. When the temperature was higher, then the catalytic activity dropped considerably. The catalysts showed a very good stability: the total amount of magnesium leached was below 0.1 wt. %. The decomposition resulted in the formation of mixed Mg/Al oxides phase during calcination of hydrotalcites. This fact was confirmed by the XRD patterns as shown in Fig. 1 (A). For the Mg/Al mixed oxides calcined at 450 °C and 600 °C, the characteristic reflections observed clearly at 43° and 62° correspond to MgO-like phase [19]. This confirms that the mixed oxide was formed from Mg/Al hydrotalcite-like precursor (Fig. 1 (C) – d). In addition, the Mg/Al mixed oxide calcined at 1000 °C has shown characteristic reflections of MgAl₂O₄ spinel phase (spinel phase appeared at 19°, 31°, 37°, 45°, 59° and 65°). The spinel phase is inactive and may be one of the reasons for the decrease in the catalytic activity [44].

Table II Influence of calcination temperature of mixed oxides on yield of esters and catalyst stability

Catalyst	HTC-450	HTC-600	HTC-1000
Calcination temp., °C	450	600	1000
Ester yield, wt. %	27.6	19.9	17.3
Mg leaching, wt. %	0.04	0.06	0.04

Influence of Calcination Time on Biodiesel Yield

Although several authors tested mixed oxides prepared for different calcination times, almost all the authors stated that the calcination time did not affect the catalytic activity. Therefore, the effect of the calcination time on the catalytic activity was investigated in the range from 4 to 17 hours. The results in Table III show that the catalytic activity of the catalysts calcined for 4 and 8 hours is practically the same. On the other hand, the catalyst calcined for 17 hours showed a significant decrease in the catalytic activity. It was found, that the calcination

time has no influence on the catalyst structure (Fig. 1 (B)). All catalysts calcined for different amount of time showed characteristic reflections of MgO-like phase typical for mixed oxides. Therefore, another FTIR measurement was performed to find what caused the decrease in the catalytic activity. The FTIR spectra of catalysts calcined for different periods of time are presented in Fig. 2. The band found at 620 cm^{-1} corresponded to the carbonate and Mg-O bond, and the band around 420 cm^{-1} was attributed to the presence of the Mg-O and Al-O bonds [44,46]. Both these bands (620 and 420 cm^{-1}) were similar for catalysts calcined for 4 and 8 hours. The catalyst calcined for 17 hours exhibited lower intensities of these bands; therefore, the catalyst showed a lower activity than those calcined for 4 or 8 hours.

Table III Influence of calcination time on yield of esters and stability of catalyst — HTC-450 catalyst

Calcination time (h)	4	8	17
Ester yield (wt.%)	27.6	28.4	18.4
Mg leaching (wt.%)	0.04	0.06	0.06

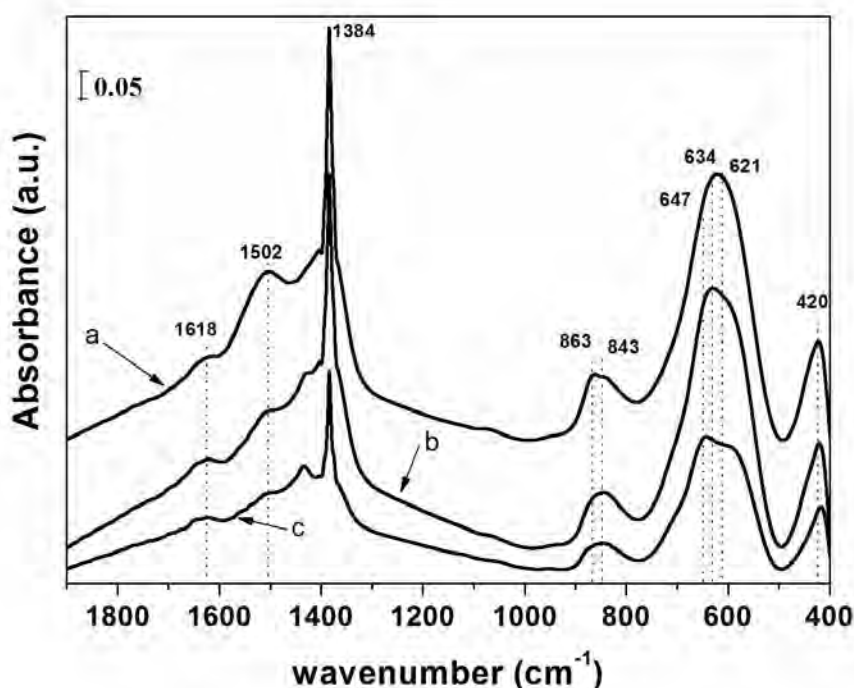


Fig.2 IR spectra of Mg/Al mixed oxides calcined for different time periods: (a) 4 h, (b) 8 h, (c) 17 h

Table IV Influence of catalyst treatment on yield of esters and catalyst stability

Catalyst	HTC (AS)-450	HTC (WT)-450	HTC (ST)-450
Treatment	without	water	steam
Ester yield (wt. %)	24.4	42.0	24.0
Mg leaching (wt. %)	0.06	0.02	0.06

Rehydrated Mixed Oxide

The influence of catalysts rehydration by water or steam on biodiesel yield is shown in Table IV. It was found that the catalyst reconstructed after rehydration by water was much more active than the mixed oxides obtained by calcination. The biodiesel yield was 24.4 % and 41.9 % for Mg/Al mixed oxides obtained by calcination and rehydration by water, respectively. The catalyst rehydrated by steam showed practically the same catalytic activity as the calcined catalyst. The significant improvement in the catalytic activity in the case of the catalyst rehydrated by water was due to a partial reconstruction of the layer structure typical of hydrotalcites, which was proved by XRD patterns. These patterns (Fig. 1 (C)) confirm that the rehydrated materials have shown characteristic reflections at 11°, 22°, 34°, and 38° corresponding to a hydrotalcite-like structure, which are not present in the sample after calcination. Additionally, the characteristic reflections for MgO-like phase for the rehydrated catalysts had a lower intensity. However, this is not so clearly seen in the case of the catalyst rehydrated by steam, which may be one of the reasons that the catalyst rehydrated by steam did not show an improvement in the catalytic activity in comparison with the calcined catalyst. The rehydration with water or with steam did not influence the catalytic stability; The total magnesium leaching was below 0.1 wt. %. However, the stability of Mg/Al mixed oxides dramatically decreased under air atmosphere, probably due to the interaction with atmospheric CO₂ (the catalytic activity of rehydrated catalyst after 3 months was practically the same as that of the calcined catalyst).

Conclusion

Firstly, this present paper reviews the preparation, physicochemical properties and application of Mg/Al mixed oxides.

Secondly, the paper describes the effect of Mg/Al mixed oxides properties, such as Mg/Al mass ratio, temperature and time of thermal pre-treatment and post-treatment rehydration of mixed oxides on the activity of the Mg/Al catalysts in the transesterification reaction.

The reaction conditions were as follows: the methanol to oil molar ratio of 24:1, the reaction temperature of 117 °C, 4 wt. % of the catalyst and the stirrer

speed of 320 rpm. The highest activity of the Mg/Al mixed oxides was observed for mixed oxide with the Mg/Al mass ratio of 3, pre-treated at 450 °C for 4-8 hours.

The study of the effect of calcination time and post-treatment rehydration showed that the catalytic activity of Mg/Al mixed oxides decreased with decreasing population of Mg-O bonds. The amount of these bonds and the catalytic activity of Mg/Al mixed oxides increased significantly after the post-treatment rehydration of catalysts with water.

References

- [1] Xu Z.P., Zhang J., Adebajo M.O., Zhang H., Zhou C.H.: *Appl. Clay Sci.* **53**, 139 (2011).
- [2] Cavani F., Trifiro F., Vaccari A.: *Catal. Today* **11**, 173 (1991).
- [3] Manasse E.: *Atti.Soc.Toscana. Sc. Nat. Proc. Verb.* **24**, 92 (1915).
- [4] Schutz A., Biloen P.: *J Solid State Chem.* **68**, 360 (1987).
- [5] Miyata S., Kumura T.: *Chem. Lett.* 843 (1973).
- [6] Drezdson M.A.: *Inorg. Chem.* **27**, 4628 (1988).
- [7] Allmann R., Jepsen H.P.: *N. Jhb. Miner. Mh.* **12**, 544 (1969).
- [8] Xu S., Zhang L., Lin Y., Li R., Zhang F.: *J. Phys. Chem. Solid.* – in press.
- [9] Kong X.G., Shi S.X., Han J.B., Zhu F.J., Wei M., Duan X.: *Chem. Eng. J.* **157**, 598 (2010).
- [10] Ross G.J., Kodama H.: *Amer. Min.* **52**, 1037 (1967).
- [11] Marchi A.J., Sedrau A.G., Apesteguia C.R.: *Prepr. IV th Int. Symp. on Scientific Bases for the Preparation of Heterogeneous Catalyst, Louvain-la-Neuve (B) H* (1986).
- [12] Mamhi A.J., Cosimo J.I.D., Apesteguia C.R.: *Proc. XI Ibero Amer. Symp. on Catalysis* **1**, 25 (1988).
- [13] Di Cosimo J.I., Diez V.K., Xu M., Iglesia E., Apesteguia C.R.: *J. Catal.* **178**, 499 (1998).
- [14] Shen J.Y., Tu M., Hu C.: *J. Solid. State Chem.* **137**, 295 (1998).
- [15] Miyata S., Kumura T., Hattori H., Tanabe K.: *Nippon Kugaku Zasshi* **92**, 514 (1971).
- [16] Sato T., Fujita H., Endo T., Shimada M.: *React. Solid.* **5**, 219 (1988).
- [17] Wright C.J., Windsor C.G., Puxley D.C.: *J. Catal.* **78**, 257 (1982).
- [18] Nielsen P.E.H.: *Nature* **267**, 822 (1977).
- [19] Kustrowski P., Chmielarz L., Bozek E., Sawalha M., Roessner F.: *Mater. Res. Bull.* **39**, 263 (2004).
- [20] Cantrell D.G., Gillie L.J., Lee A.F., Wilson K.: *Appl. Catal. a-Gen.* **287**, 183 (2005).
- [21] Abello S., Dhir S., Colet G., Perez-Ramirez J.: *Appl. Catal. a-Gen.* **325**, 121 (2007).
- [22] Abello S., Vijaya-Shankar D., Perez-Ramirez J.: *Appl. Catal. a-Gen.* **342**, 119

- (2008).
- [23] Abello S., Medina F., Tichit D., Perez-Ramirez J., Sueiras J.E., Salagre P., Cesteros Y.: *Appl. Catal. B-Environ.* **70**, 577 (2007).
- [24] Dumitriu E., Hulea V., Chelaru C., Catrinescu C., Tichit D., Durand R.: *Appl. Catal. a-Gen.* **178**, 145 (1999).
- [25] Manivannan R., Pandurangan A.: *Appl. Clay Sci.* **44**, 137 (2009).
- [26] Shimada H., Ogoshi T.: *B. Chem. Soc. Jpn.* **78**, 937 (2005).
- [27] Rao K.K., Gravelle M., Valente J., Figueras F.: *J. Catal.* **173**, 115 (1998).
- [28] Shumaker J.L., Crofcheck C., Tackett S.A., Santillan-Jimenez E., Morgan T., Ji Y., Crocker M., Toops T.J.: *Appl. Catal. B-Environ.* **82**, 120 (2008).
- [29] Trakarnpruk W., Porntangjitlikit S.: *Renew. Energ.* **33**, 1558 (2008).
- [30] Abello S., Medina F., Tichit D., Perez-Ramirez J., Rodriguez X., Sueiras J.E., Salagre P., Cesteros Y.: *Appl. Catal. a-Gen.* **281**, 191 (2005).
- [31] Grabowska H., Zawadzki M., Syper L., Mista W.: *Appl. Catal. a-Gen.* **292**, 208 (2005).
- [32] Helwani Z., Othman M.R., Aziz N., Fernando W.J.N., Kim J.: *Fuel Proc. Tech.* **90**, 1502 (2009).
- [33] Albuquerque M.C.G., Santamaria-Gonzalez J., Merida-Robles J.M., Moreno-Tost R., Rodriguez-Castellon E., Jimenez-Lopez A., Azevedo D.C.S., Cavalcante C.L., Maireles-Torres P.: *Appl. Catal. a-Gen.* **347**, 162 (2008).
- [34] Fraile J.M., Garcia N., Mayoral J.A., Pires E., Roldan L.: *Appl. Catal. a-Gen.* **364**, 87 (2009).
- [35] Obalova L., Kovanda F., Jiratova K., Pacultova K., Lacny Z.: *Collect. Czech. Chem. Commun.* **73**, 1045 (2008).
- [36] Ashok J., Subrahmanyam M., Venugopal A.: *Int. J. Hydrogen Energ.* **33**, 2704 (2008).
- [37] Tsyganok A.I., Inaba M., Tsunoda T., Suzuki K., Takehira K., Hayakawa T.: *Appl. Catal. a-Gen.* **275**, 149 (2004).
- [38] Yang W.S., Kim Y., Liu P.K.T., Sahimi M., Tsotsis T.T.: *Chem. Eng. Sci.* **57**, 2945 (2002).
- [39] Chibwe K., Valim J.B., Jones W.: *Abstr. Pap. Am. Chem. Soc.* **198**, 20 (1989).
- [40] Leitner J., Hampl M., Sedmidubsky D., Ružička K., Svoboda P.: *Chem. Listy* **104**, 147 (2010).
- [41] Alvarez M.G., Chimentao R.J., Figueras F., Medina F.: *Appl. Clay Sci.* **58**, 16 (2012).
- [42] Silva C.C.C.M., Ribeiro N.F.P., Souza M.M.V.M., Aranda D.A.G.: *Fuel Proc. Tech.* **91**, 205 (2010).
- [43] Liu Y., Lotero E., Goodwin J.G., Mo X.: *Appl. Catal. a-Gen.* **331**, 138 (2007).
- [44] Xie W.L., Peng H., Chen L.G.: *J. Mol. Catal. a-Chem.* **246**, 24 (2006).
- [45] Zeng H.Y., Feng Z., Deng X., Li Y.Q.: *Fuel* **87**, 3071 (2008).
- [46] Roelofs J.C.A.A., van Bokhoven J.A., van Dillen A.J., Geus J.W., de Jong K.P.: *Chem. Eur. J.* **8**, 5571 (2002).