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**Study of the structure and potential applications
of mixed oxides prepared from hydrotalcites for
the valorization of alcohols**

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Abstract

The doctoral thesis focuses on the synthesis, characterization, and testing of mixed oxides with different chemical compositions for the valorisation of alcohols. The interest was also focused on the investigation of using butanol (a product of ethanol valorisation) as a co-solvent in the transesterification of rapeseed oil. The mixed oxides were prepared by calcination of hydrotalcites, which were synthesised by a co-precipitation method. Firstly, the effect of the chemical composition of MgAl and MgFe mixed oxides doped with transition metals on the structure and catalytic activity in ethanol valorisation was studied. The reactions were carried out in a microflow reactor at different reaction temperatures. The reaction scheme for the valorisation of ethanol using mixed oxides was proposed on the base of a detailed analysis of the products. Another task was to study the effect of butanol (a product of ethanol valorisation) on the transesterification reaction of methanol with rapeseed oil, considering different molar ratios of components, reaction temperatures, catalyst masses, and the use of homogeneous (KOH) and heterogeneous (MgFe mixed oxide) catalysts. The last task was to study the effect of zinc in CuZnAl mixed oxide on the structural and textural properties and catalytic activity in the hydrogenolysis of glycerol to propane-1,2-diol.

Abstrakt

Disertační práce se zabývá syntézou, charakterizací a testováním směsných oxidů s různým chemickým složením ve valorizaci alkoholů a studiem možností použití butanolu jako kosolventu v transesterifikaci řepkového oleje. Směsné oxidy byly připraveny kalcinací hydrotalcitů, které byly syntetizovány pomocí koprecitační metody. Nejprve byl studován vliv složení MgAl a MgFe směsných oxidů dopovaných o další přechodový kov (Co, Ni, Cu, Mn, a Cr) na strukturu a katalytickou aktivitu ve valorizaci etanolu na látky s vyšší přidanou hodnotou. Reakce byla studována v mikro průtokovém reaktoru se zaměřením na analýzu vznikajících reakčních produktů, zejména butanol, hexanol, acetaldehyd, ethyl-acetát, atd. Na základě detailní analýzy produktů bylo navrženo reakční schéma jejich vzniku. Byl popsán vliv teploty a přechodového kovu na konverzi etanolu, selektivitu (a výtěžek) k vybraným produktům. Dále byl zkoumán vliv butanolu (produkt valorizace etanolu) jako kosolventu na transesterifikační reakci metanolu s řepkovým olejem za různých molárních poměrů složek, reakční teploty a množství katalyzátoru s použitím katalyzátoru homogenního (KOH) a heterogenního (MgFe směsný oxid). Posledním cílem bylo studium vlivu zinku v CuZnAl směsném oxidu na strukturní a texturní vlastnosti a katalytickou aktivitu při hydrogenolýze glycerolu (vzniká jako vedlejší produkt při transesterifikaci) na propan 1,2 diol.

Keywords

Hydrotalcite, mixed oxides, valorization of alcohols, ethanol, glycerol, butanol

Klíčová slova

Hydrotalcity, směsné oxidy, valorizace alkoholů, etanol, glycerol, butanol

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Introduction

Growing knowledge about environmental issues such as declining reserves of fossil raw materials (oil, coal, natural gas) and chemical pollution produced by their uses, leads to the promotion of research of new substances derived from renewable sources. One large group of renewable sources is biofuels. Biofuels are currently most often divided based on raw material for their production into (i) conventional (produced from food crops) and (ii) modern (non-food biomass) [1]. The best-known and most widely used biofuels are ethanol, which is produced by the fermentation, and fatty acid methyl esters (FAME), which are produced by the transesterification of vegetable oils or fats [2, 3]. Ethanol, FAME, and glycerol can also use as feedstocks to produce other commercially important raw materials. For example, ethanol could be transformed into - acetaldehyde, ethyl acetate, butanol, hexanol, and others [4, 5]. From glycerol could be prepared propane-1,2-diol, propane-1,3-diol, ethane-1,2-diol, acrolein, carboxylic acids, and others [6, 7]. These substances are important because they used in many fields of human activity such as chemical, food, pharmaceutical, and clothing industries.

Catalysts are an important part of the chemical industry, without which many chemical processes would not be possible to realize. Catalysts are substances that positively influenced the rate of a thermodynamically feasible chemical reactions. Approximately 90 % of the products of the chemical industry are produced by catalytic processes (petroleum processing - cracking, alkylation; plastics production - PVC, polyethylene, polypropylene; ammonia production, transesterification of oils) [8]. Catalysts are also used in common applications such as ecology (reducing pollutants in car exhaust), the food industry (production of solidified fats), and many others.

In the aspect of the catalyst state in relation to the input reaction components, catalysts are divided into homogeneous and heterogeneous. The advantage of homogeneous catalysts is their high activity, easier description of the catalyst activity, and study of the kinetics of the catalyzed reaction. The disadvantages are the difficult separation from the reaction mixture and generally lower thermal stability than heterogeneous catalysts. Heterogeneous catalysts have many advantages such as easy separation from the reaction mixture, the possibility of having multiple types of active centres on the catalyst surface, the possibility of space selectivity, and many others. The disadvantages are harder description of the catalyst behavior, the reduction of the reaction rate due to the transport of mass and heat to the active centers on the surface, the deactivation of the catalyst, and generally the necessity to use more energy-intensive reaction conditions (higher temperature, pressure, concentration of starting materials [9, 10]. Based on distribution of active centres in the catalyst, catalysts are divided into bulk and supported catalysts (the active component is located on the surface of the support, usually with a high specific surface area value). The most well-known heterogeneous catalysts include, for example, noble metals (Pt, Pd, Ru) [11], zeolites [12], oxides (V_2O_5 , Al_2O_3 , SiO_2) [13], mixed oxides (MgAl, MgFe, CuZnAl) [14], transition metals (Raney-Ni, Cu, Co) [6], and others.

Aims of doctoral thesis

- The synthesize hydrotalcites and mixed oxides with different type of metal and they molar ratios (MgAl, MgFe and CuZnAl).
- The characterize synthesised materials (hydrotalcites, mixed oxides, and reduced mixed oxides) by various characterization techniques such as XRD, N₂-physisorption, NH₃ and CO₂-TPD, H₂-TPR
- Test MgAl and MgFe mixed oxides with and without the addition of transition metal (Co, Ni, Cu, Mn, Cr) in the valorization of ethanol to add-values products (butanol, acetaldehyde, ethyl acetate) at different reaction temperatures
- The use of butanol as a co-solvent in the transesterification of rapeseed oil using heterogeneous (MgFe mixed oxides) and homogeneous catalysis (KOH) at different reaction conditions
- The use of CuZnAl mixed oxides with different molar ratios of zinc as catalysts in the hydrogenolysis of glycerol to propane-1,2-diol in a batch reactor
- Describe the effect of zinc on the structure of mixed oxide, the size of copper particles on the surface and the catalytic activity in glycerol hydrogenolysis

1. Hydrotalcites

Hydrotalcites (HT, LDH - layered double hydroxides) are natural or synthetic substances with a characteristic layered structure. Crystallographically, the structure of hydrotalcites is derived from magnesium oxide (brucite). The basic building unit of hydrotalcite is the magnesium cation (Mg^{+II}), around are octahedrally coordinated six hydroxide anions. The connection of the basic units forms continuous flat layers which are bonded together by hydrogen bonds. In the hydrotalcite structure, part of the magnesium cations is replaced by trivalent aluminium cations (Al^{+III}). This gives the layer a positive charge (cationic layers). For electroneutrality of material, the cationic layers had to be compensated by anions (A^{n-}) in the space between the layers (anionic layers). The size of the anionic layer depends mainly on (i) the type of compensating anion and their spatial orientation, and (ii) the molar ratio of divalent to trivalent cation in cationic layers. Water molecules are also located in the space of the anionic layers [15]. A schematic of the basic building unit and structure of hydrotalcite is shown in Fig. 1.

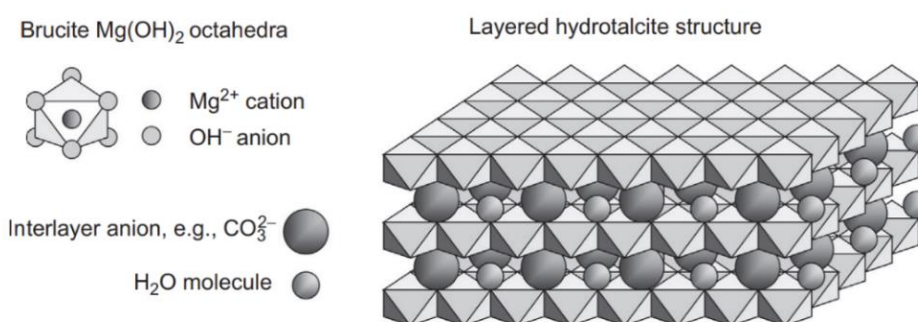


Fig. 1 Layered structure of hydrotalcite [16]

The important parameters of hydrotalcites are a_{HT} and c_{HT} , where a_{HT} indicates the average distance between two metal cations and c_{HT} indicates the value of three times the average distance between the centres of two neighboring cationic layers.

The hydrotalcites have growing interest in recent years demonstrated by many new publications and industrial patents. Hydrotalcites find applications in various fields of human activity. They are used as neutralizing additives, flame retardants, catalysts, precursors for the preparation of mixed oxides, and others. The advantages of hydrotalcites are their low toxicity, biocompatibility, relatively cheap production, and easy availability [15].

1.1. Hydrotalcites synthesis

Several synthesis methods have been developed for the synthesis of hydrotalcites. The synthesis method, together with the changing chemical composition, determines the structural and physicochemical properties of the prepared materials. All hydrotalcite materials, described in this work, were synthesised by the coprecipitation method [14]. Another option is the modified coprecipitation method, using a solution of M^{+II} and M^{+III} metal salts in a solution of hydrolyzing urea for the preparation of hydrotalcites. The solution with urea and metal cations is homogeneous up to approximately 90 °C. Urea slowly decomposes with increasing temperature, which cause that the pH increases. The

decomposition process is slow, and pH is constant throughout a reaction. The hydrotalcites, which were prepared by this synthesis method, show a high proportion of crystalline phase and a narrow particle size distribution [17].

The sol-gel method is other technique for hydrotalcites synthesis. The metal precursor, which is the most often organic substances (alkoxides, acetylacetonates), is first dissolved and hydrolyzed in water or an organic solvent (a sol is formed). Subsequently, a strong acid (HCl, HNO₃) is added to the solution to promote peptization. The mixing of the colloidal metal suspensions and adjusting the pH (basic) leads to the formation of a gel. The solid hydrotalcite material is formed after washing, filtration, and drying [18].

1.2. Calcination of hydrotalcites and formation of mixed oxides

The mixed oxides (MO) are formed by thermal decomposition (calcination) of hydrotalcites. The process of transformation of hydrotalcite to mixed oxide has several steps, which are the most often studied by thermogravimetric analysis. This method is also used for determination of the optimal calcination temperature. In general, the thermal transformation of hydrotalcites has three steps, which may not always be observable. The first step (up to a temperature of about 200 °C) involves the release of water molecules (i) bound at the surface and (ii) bound in the anionic layer of the hydrotalcite. In the next step (250–500 °C), the hydroxyl groups in the form of water are removed (dehydroxylation) and the compensating ions that have been localized between the layers are removed. Most often, carbonate ions are found between the layers and leave in the form of carbon dioxide (decarboxylation). In the last step mixed oxide is transformed to spinel, which are double oxides characterized by a very low specific surface area. The calcination temperature of hydrotalcite is usually chosen so that the formation of spinel structure is avoided. The TGA analysis recordings for (TM)MgAl (TM - transition metal) and CuZnAl hydrotalcites are shown in Fig. 2. No significant differences were observed between hydrotalcites with similar compositions on the TGA curves during the temperature transformation of HT to MO. The calcination temperatures were chosen for the studied hydrotalcites follows: CuZnAl - 350 °C, (TM)MgAl - 450 °C and (TM)MgFe - 500 °C.

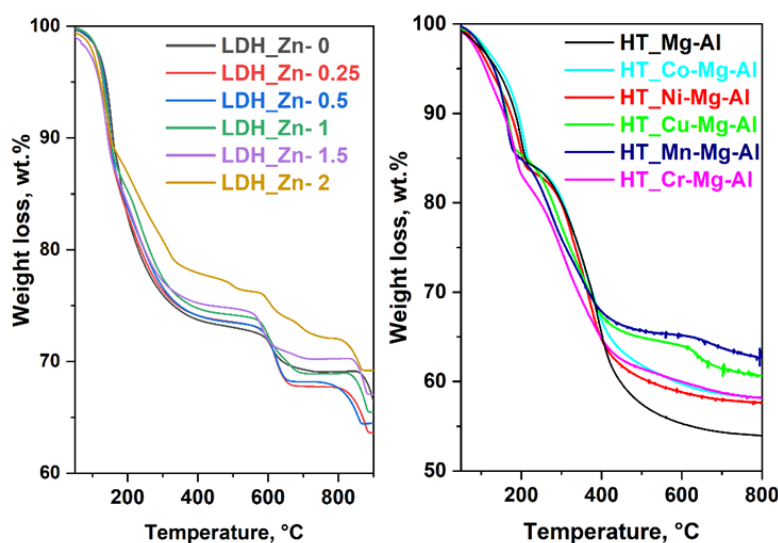


Fig. 2 TGA curves of CuZnAl (left) and (TM)MgAl (right) hydrotalcites

2. Ethanol valorization

Ethanol is an important chemical produced mainly from renewable sources by fermentation processes. Ethanol is usually used as a solvent, disinfectant, extraction agent, or as a bio-component in petrol. Ethanol can also serve as a feedstock for the preparation of other substances that are currently produced mainly from non-renewable sources. The dehydrogenation of ethanol can produce acetaldehyde, which is currently produced by the oxidation of ethylene mainly by PdCl₂ and CuCl₂ catalysts. Acetaldehyde is mainly used as a feedstock for the preparation of other important chemicals such as acetic acid, butanol, 2-ethyl hexanol and others. Several other dehydrogenation catalysts have also been tested for the preparation of acetaldehyde from ethanol, i.e., VO_x/ZrO₂ vanadium, VO_x/TiO₂, or copper supported on activated carbon [13, 19]. Acetaldehyde also formed as an intermediate in several ethanol valorization reactions.

The Guerbet reaction is a catalytic reaction of lower alcohols to preparation of higher alcohols (butanol, hexanol). The aldol mechanism is the most widely used mechanism for the Guerbet reaction and consist of alcohol dehydrogenation to the corresponding aldehyde (ethanol → acetaldehyde) in the first step. This step takes place on oxidation-reduction catalysts but can also take place at high temperatures on basic catalyst centres. In the second step a new C-C bond is formed by the aldol condensation of two aldehydes [20], and water is removed (acetaldehyde → crotonaldehyde). This reaction step takes place at the acid-base centres of the catalyst. The last step: the aldehyde group and the double bond are hydrogenated to formed of the desired product (ethanol → butanol) [5, 20]. The proposed scheme of the Guerbet ethanol valorization reaction with possible by-products is shown in Fig. 3. The scheme was proposed based on determination of products by catalytic tests at MgAl and MgFe mixed oxide dopped by other transition metal.

The first heterogeneous catalysts that have been published for the Guerbet reaction are hydroxyapatites (Ca₁₀(PO₄)₆(OH)₂) with different Ca/P molar ratios and substituted hydroxyapatites. Other tested catalysts include bifunctional zeolite-type catalysts containing palladium and zirconium, calcium carbide, oxide-based catalysts - MgO, Al₂O₃, mixed oxides - mainly MgAl and mixed oxides doped with noble or transition metals (Pd, Ir, Cu, Ni, and others) [21, 22].

Other type of reaction, which can process in the system is Tishchenko reaction - catalytic reaction of two identical or different aldehydes to form the corresponding ester. Tishchenko reaction is a common side reaction of the Guerbet reaction as it take place on the same type of catalyst. Another possible route for ethanol valorization is catalytic dehydration to form ethylene. The dehydration takes place on acidic catalysts and usually uses, i.e., γ-Al₂O₃ and zeolite ZSM 5 [4, 23]. The by-product of the dehydration of ethanol to ethylene is diethyl ether.

The focus of dissertation was test the possibility of using MgAl and MgFe mixed oxides without and with addition of Co, Ni, Cu, Mn, and Cr in the structure as catalysts for valorization of ethanol. The aim was compared the effect of transition metal on (i) the structures of the synthesis catalysts and (ii) the catalytic properties in ethanol valorization at different temperatures (280, 300, and 350 °C), the constant pressure

(10 MPa) and weight hourly space velocity (4.5 h^{-1}).

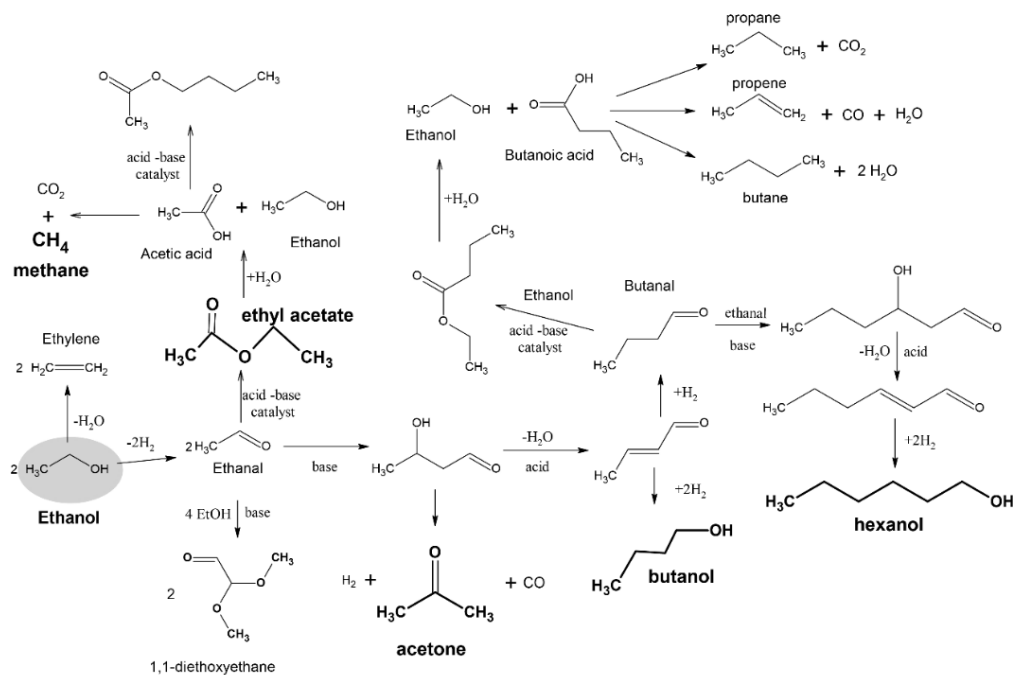


Fig. 3 Proposed scheme of the Guerbet reaction including side reactions

2.1. Effect of transition metal on the structure of (TM)MgAl MO and aMO

The six (TM)MgAl (TM = X, Co, Ni, Cu, Mn, Cr) hydrotalcite with a theoretical molar ratio of 0.25:2:1 (TM:Mg:Al) was synthesized by coprecipitation method. The molar ratio of metals was determined by ICPOS and the difference between the theoretical and real molar ratios was less than 5%.

XRD analysis was used to confirm the formation of hydrotalcite (HT) structure and to study the crystalline phase in mixed oxides (MO) and reduced mixed oxides (aMO). The characteristic diffraction lines at $2\theta = 11.6, 23.2, 34.1, 38.2, 59.9,$ and 60.9° were observed for all synthesized (TM)MgAl HT. No other diffraction lines were observed, which confirmed the synthesis of pure MgAl HT. After calcination at 450°C the diffraction lines for HT disappeared and diffraction lines at $2\theta = 35.6, 43.7,$ and 62.7° , which corresponded to MgO were observed. Diffraction lines for transition metal oxides were not observed because (i) their maxima are obscured by the dominant MgO signals (e.g., diffraction lines $2\theta = 35.6, 38.7$ and 48.8° correspond to tenorite-CuO), or (ii) their content is relatively lower than MgO, or (iii) they form an amorphous phase. The (TM)MgAl MO was reduced in a hydrogen atmosphere before the catalytic test (formation of aMO) for increasing the reduced ability. The reduction of aMO increased the intensity of the diffraction lines for MgO. Diffraction lines for the separated metal phase (Co, Ni, Cu, Mn, and Cr) for aMO were not observed due to (i) rapid oxidation in the air atmosphere before the XRD analysis or (ii) the transition metals did not form continuous crystallographic planes.

An important dehydrogenation process is the valorization of ethanol to required products. The dehydrogenation process takes place mainly on metal centres on the catalyst surface, and therefore it was used H_2 -TPR method. The reduction temperature

of MO before the catalytic test was set up to 450 °C (calcination temperature). According to the published results and experimental verification, the reduction of MgAl MO does not occur in the temperature interval of TPR analysis (30–1000 °C) [24]. From this it can be concluded that all peaks on the TPR record correspond to the reduction of transition metal oxides. It was determined that MO with added metals Cu, Mn and Cr were completely reduced at lower temperature than the 450 °C, while others (Co and Ni) were completely reduced at higher temperatures. However, a higher temperature for reduction is not possible, because the spinel phase is formed. Spinel cannot be reduced and has a very low (i) specific surface area and (ii) acid-based properties, which causes negligible catalyst activity.

The acid-base centres of the catalyst are important for many of studied reactions as dehydrogenation or aldol condensation. TPD were used for a selective determination of the basicity and acidity of catalyst, the curves of (TM)MgAl aMO are shown in Fig. 4. The amount of basic and acid centres was determined by integrating of obtained TPD curves within the respective temperature interval limits (for CO₂ 35–450 °C; for NH₃ 70–450 °C). The measured CO₂-TPD curves peaked at 110–140 °C, depending on the composition of (TM)MgAl aMO. All curves are tailed at the high temperature side, mirroring the presence of more types of basic centres on (TM)MgAl aMO. This observation is in parallel with the formation of weak (OH⁻ groups), medium strong (Meⁿ⁺-O²⁻ pairs) and strong basic centres (O²⁻) on the surface of such oxides [25]. The concentration of basic centres (CBS) are related to the aMO (TM)MgAl oxide composition. The presence of the transition metal in the (TM)MgAl MO causes a significant change in the total concentration of the basic centres. The highest CBS was observed for NiMgAl oxide, followed by CrMgAl with comparable CBS; consequently, MnMgAl, CoMgAl, MgAl, and finally CuMgAl had the lowest concentrations of CBS.

In general, lewis acid centres are formed by unsaturated metals on the surface of mixed oxides. In this case Al and TM can form acid centres. The measured NH₃ TPD curves for (TM)MgAl and MO (Fig. 4) show a temperature maximum of desorption in the temperature interval 155–188 °C. All desorption curves are nearly symmetric but show a slight taper at higher desorption temperatures. The acidic properties of aMO are also affected by the presence of transition metal in the structure. The measured CAS values decreased in order: Cr > Mn > Ni > Co > MgAl > Cu.

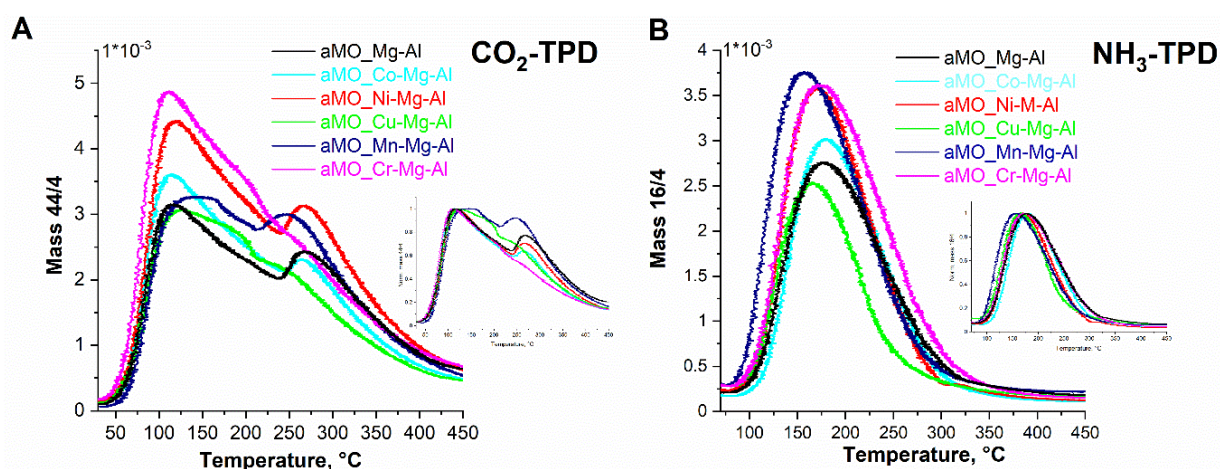


Fig. 4 CO₂-TPD (A) and NH₃-TPD (B) of aMO (TM)MgAl (insets depict normalized curves 0-1)

2.2. Effect of transition metal on the structure of (TM)MgFe MO and aMO

Six (TM)MgFe HT with a theoretical molar ratio of 0.25:2:1 (TM:Mg:Fe) were synthesised by coprecipitation method. The difference between the theoretical and real molar ratio of metals, determined for MO was in the range of 2–4 % [26]. XRD analysis was performed on the (TM)MgFe synthesised materials, where sharp characteristic diffraction lines for HT were observed (HT structure was confirmed). After the reduction process of MO in hydrogen, diffraction lines were observed at all (TM)MgFe aMO diffractograms for (i) MgO, (ii) metallic iron (44.7° and 65.1°) and (iii) FeO (42.2°). Diffraction lines for the separated metallic phase were not found. The exception is CuMgFe aMO where the diffraction lines at $2\theta = 43.2^\circ$ and 50.6° (Cu^0) was observed.

The reduction process of (TM)MgFe MO is significantly different than the reduction of (TM)MgAl MO. In (TM)MgFe MO structure are reduced oxides of two transition metals (Fe and TM), which interact during the reduction. The MgFe MO reduction curve shows two main reduction peaks (temperature maxima of 374 and 545 °C) corresponding to the reduction of iron oxides. Because of TM in the MgFe MO structure, the reduction curves of (TM)MgFe MO are not identifiable, because the reduction peaks overlap. The exception is CuMgFe MO, where a sharp reduction peak with a temperature maximum of 137 °C is observed. The reduction temperature of copper oxides in MgFe MO is significantly lower than the reduction of bulk CuO, which usually takes place at 200–300 °C [27]. Although for other MOs the reduction contributions of the individual metal oxides are not as clearly identified as in the case of CuMgFe MOs, however, the same conclusions can be drawn about the decrease in the reduction potentials of the transition metals for (TM)MgFe MO.

The acid-base properties of (TM)MgFe aMO were studied by NH_3 and CO_2 TPD techniques under identical conditions as (TM)MgAl aMO. (TM)MgFe aMO disposes of a lower amount of CAS and CBS than (TM)MgAl aMO, which agrees with previously published results measured on MgAl and MgFe MO. The amount of CAS and CBS affects the catalytic activity and product selectivity.

2.3. Catalytic properties of mixed oxides in ethanol valorization

The scheme of valorization of ethanol (MgAl and MgFe MO) with a focus on the Guerbet reaction (transformation of ethanol to butanol) including significant side reactions is depicted in Fig. 3. The side reactions were suggested based on the detailed analysis of substances in the reaction mixture, which was analyzed every 4 h including liquid and gas phases. The reaction was carried out at microflow reactor Vinci technologies at temperatures 280, 300, and 350 °C, atmospheric pressure and WHSV was 4.5 h^{-1} .

2.3.1. Catalytic properties of (TM)MgAl aMO

The catalytic properties of (TM)MgAl aMO are described by the ethanol conversion (X_E) and selectivity to butanol (S_B) (Tab. 1). The lowest ethanol conversion was observed for the catalyst without added TM (aMO MgAl) - $X_E = 15\%$ at 350 °C. This indicate that by the used reaction conditions the base centres of the MgAl catalyst are not significantly active in the first dehydrogenation step of the Guerbet reaction. Similar results were published by Leon et al. who achieved 12% ethanol conversion at 350 °C with MgAl catalyst (Mg/Al molar ratio 3:1, WHSV = 0.215 h^{-1}) [22].

Tab. 1 Conversion of ethanol (X_E) and selectivity to butanol (S_B) for (TM)MgAl aMO at different reaction temperatures (280, 300 and 350 °C; b - beginning, e - end)

Type of catalyst	X_E^{300b} %	S_B^{300b} %	X_E^{350} %	S_B^{350} %	X_E^{280} %	S_B^{280} %	X_E^{300e} %	S_B^{300e} %
aMO_MgAl	5	45	15	53	–	–	–	–
aMO_CoMgAl	29	39	62	12	10	52	19	37
aMO_NiMgAl	44	44	62	16	19	68	26	56
aMO_CuMgAl	52	7	73	7	39	12	48	11
aMO_MnMgAl	7	34	19	30	–	–	5	34
aMO_CrMgAl	6	42	18	46	–	–	5	39

Several (TM)MgAl catalysts have been observed to have many by-products. CuMgAl aMO catalyst shows the highest ethanol conversion values but has low selectivity to butanol (350 °C, $X_E = 73$ %, $S_B = 7$ %). The main products of ethanol valorization by CuMgAl catalyst at used conditions are esters (mainly ethyl acetate) formed by the Tishchenko reaction. Other products observed with this type of catalyst were 1,1-diethoxyethane (formed by the reaction of ethanol with acetaldehyde) and acetone (formed by the decomposition of acetaldol - an intermediate of aldol condensation). The formation of acetone was only observed with this type of catalyst and the amount of acetone increased with increasing temperature. The highest amount of hydrogen was also identified in the gaseous products compared to other MgAl aMO, because it is not consumed in the Tishchenko reaction. The highest selectivity to higher alcohols was observed for MgAl catalysts containing Ni and Co. At the lowest tested temperature (280 °C), the Ni catalyst achieved 19% ethanol conversion and 68% selectivity to butanol. The highest amount of hexanol was also observed for the Ni and Co catalysts, which is formed from acetaldehyde and butanal. The highest amount of water in the reaction products, which is a by-product of the Guerbet reaction, was also determined for these catalysts. As the reaction temperature increased, the selectivity for butanol decreased and the formation of by-products was promoted.

The stability of the MgAl catalysts was determined based on activity at 300 °C (the difference between activity at the beginning and end of the reaction). A decrease in activity was observed for MgAl catalysts up to 5 %, except for the catalysts containing Co and Ni which observed a higher activity decrease (Co - 10 % and Ni - 18 %). The decrease in activity was probably due to blocking of the active centres on the catalyst surface by carbon or b reaction products.

2.3.2. Catalytic properties of (TM)MgFe aMO

The catalytic properties of (TM)MgFe catalysts for ethanol valorization are described by the ethanol conversion (X_E) and the yield for each product (Y_P). The ethanol conversion for (TM)MgFe catalysts at reaction temperatures of 280, 300 and 350 °C is shown in Fig. 5.

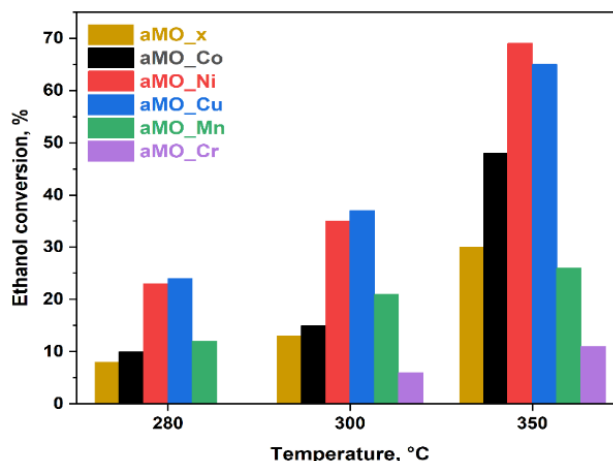


Fig. 5 Ethanol conversion at 280,300 and 350°C for (TM)MgFe aMO

It was determined that MgFe aMO (without TM) achieved twice higher ethanol conversion than MgAl aMO at all studied reaction temperatures. The higher ethanol conversion is due to the oxidation-reduction properties of iron, because (TM)MgFe aMO exhibits lower acid-base properties than (TM)MgAl aMO. The content of the second transition metal in the MgFe catalyst structure has a positive effect on the ethanol conversion. The exceptions are chromium, which has lower activity at all temperatures studied, and manganese with lower activity only at 350 °C. The catalysts containing Cu and Ni showed the highest ethanol conversion values at all studied temperatures ($X_E^{300,Cu} = 37\%$, $X_E^{300,Ni} = 35\%$). The activity of (TM)MgFe catalysts is dependent on the reaction temperature and their activity increases with increasing temperature ($X_E^{280,Ni} = 23\%$, $X_E^{350,Ni} = 69\%$).

The TM content in the MgFe catalyst also affects the composition of ethanol valorization products. The yields of the most represented liquid products for selected (TM)MgFe catalysts (TM = x, Co, Ni, Cu) are shown in Fig. 6.

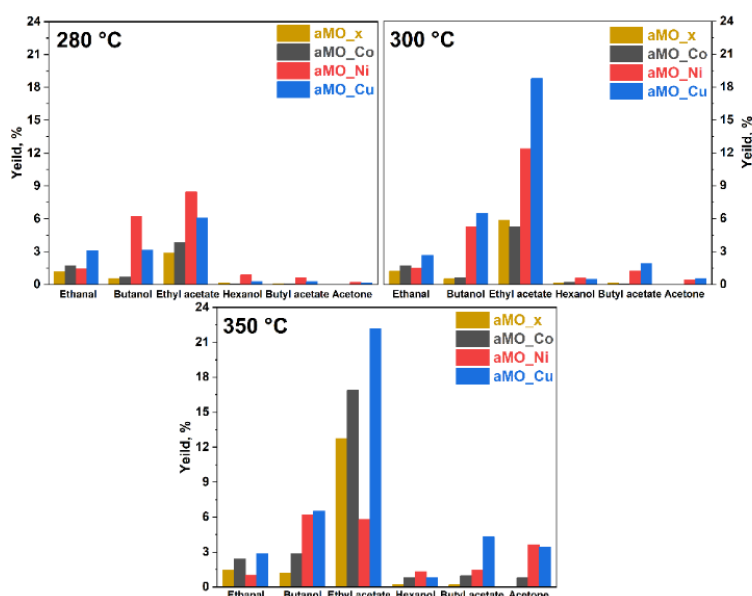


Fig. 6 Yields of ethanol valorization products for selected (TM)MgFe aMO at 280, 300 and 350 °C

The main product of ethanol valorization by (TM)MgFe catalysts is ethyl acetate, which in contrast to (TM)MgAl aMO. Other observed products are acetaldehyde, butanol, hexanol butyl acetate and acetone. At the lowest reaction temperature (280 °C), NiMgFe aMO achieves the highest yields of ethyl acetate and butanol compared to the other catalysts. With the increasing reaction temperature (300 and 350 °C), the CuMgFe catalyst shows the highest ethyl acetate and butanol yields. At the temperature of 350 °C show NiMgFe aMO high decrease of yields to the ethyl acetate.

The decrease is probably due to the decomposition of ethyl acetate (or other products) to methane and other hydrocarbons, which was detected in the gaseous products. The high amount of hydrogen in the gaseous products was indicated the ability of the MgFe catalyst to dehydrogenate ethanol. The TM (Co, Ni and Cu) in the structure of the MgFe catalyst has a positive effect on the dehydrogenation properties. MgFe catalysts have significantly fewer acid-base centres than MgAl catalysts. This is probably the reason, that MgFe aMO preferred the Tishchenko reaction over the Guerbet reaction.

3. Potential uses of butanol

The population growing and rising living standards bring increase consumption of fossil resources. However, the use of fossil fuels brings an environmental problem to our planet, and therefore their replacement with carbon-neutral alternatives is necessary [28]. The attention is focused on the transport and chemical industries, which are the source of a significant amounts of pollution. The transports industry has implemented stricter limits on emissions and the addition of biofuels (bioethanol and biodiesel) to the conventional fuels. The disadvantage of bioethanol is water affinity, which can cause corrosion of metal parts of the car. A solution is to replace ethanol with a higher alcohol (butanol) which is not hydroscopic and has a higher energy density [29]. Butanol cannot be added directly to diesel fuel, but it can be added to the biodiesel production process.

Biodiesel is produced by transesterification, which is a catalytic reaction between triglycerides (oils or fats) and alcohol (usually methanol). The homogeneous basic catalysts (NaOH, KOH) are most used today, but several heterogeneous catalysts are also intensively studied, which have the advantage of easy separation from the reaction mixture and reusability [30]. Some of the heterogeneous catalysts studied include CaO, MgAl MO, CaMgO, and CaZnO [31]. The most used alcohol for transesterification is methanol because of its high reactivity and low cost. Less common is the use of other types of alcohol such as ethanol or butanol. Methanol and ethanol are immiscible with triglycerides, so a heterogeneous mixture is formed, and the reaction takes place only at the interface [32]. To reduction of reaction time, the mixture must be intensively stirred because of increase the size of the phase interface.

On the other hand, butanol is miscible with triglycerides and therefore the reaction can proceed in the whole volume. The solution to the immiscibility of methanol and ethanol with triglycerides is the use of a co-solvent. Several cosolvents have been published for homogeneously catalyzed transesterification which does not react in transesterification as dimethyl ether, isopropyl ether, or methyl tert-butyl ether [33, 34]. Butanol can also be used as a co-solvent, but it reacts with triglycerides to form of butyl esters. When butanol is used in transesterification, a higher reaction temperature (around 110 °C) and a higher molar ratio of butanol than methanol is usually used, because it is less reactive.

The advantage of using butanol in transesterification is the higher energy value of butyl esters (BE) than methyl esters (ME; about 7-10 %) [35]. The dissertation work is focused on using butanol as a co-solvent in the transesterification of rapeseed oil with methanol, using a homogeneous and heterogeneous catalyst. The aim was to describe the influence of the molar ratio of oil, methanol, and butanol, reaction temperature, and the way of stopping of the transesterification on the properties of the products, mainly the ester phase (EP).

3.1. Butanol as co-solvent in transesterification of rapeseed oil

First, the ternary plots for methanol (M), rapeseed oil (O) and butanol were determined at the two reaction temperatures of 25 and 60 °C. The aim was to find the molar ratios of the components that result in a homogeneous reaction mixture because the miscibility depends on the molar ratio of components. The heterogeneous region was larger at 25 °C, which was expected because the miscibility usually increases with increasing temperature.

3.2. Transesterification by homogeneous catalyst (KOH)

Firstly attention was focused on the study of the effect of the molar ratio of O:M:B on the transesterification reaction (keeping other reaction parameters constant - 60 °C, 0.8 wt% catalyst to oil). A total of 3 reaction mixtures with different O:M:B molar ratios were studied. The reaction mixture without cosolvent with the commonly used O:M molar ratio (1:6) was tested as a reference. The molar ratio of butanol was chosen as the lowest possible to produce a homogeneous mixture based on the ternary diagram. The dependence of the ester content of EP (w_{ester} , wt%) on the reaction time is shown in Fig. 7.

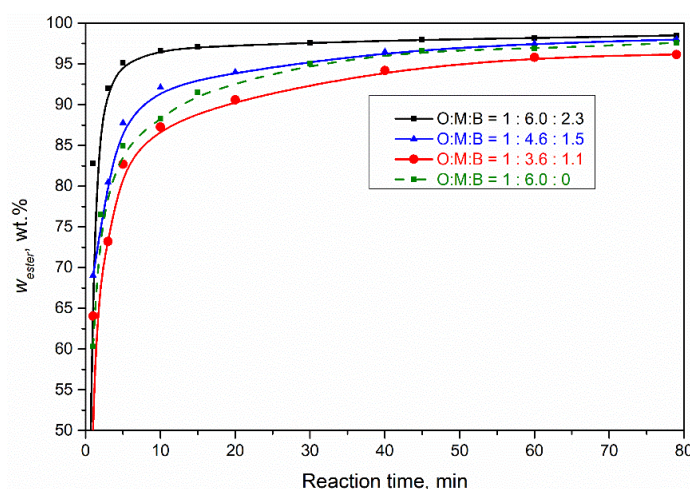


Fig. 7 Dependency of w_{ester} in the EP on the reaction time for different molar ratios of alcohols to oil at 60 °C and 0.8 wt% of catalyst to oil

When the molar ratio O:M:B was 1:6:2.3, which is the same as commonly applied for single methanol (O:M=1:6), the w_{ester} in the EP was 97% after 10 min. In the case of transesterification with methanol only, the same yield was achieved after 80 min of reaction (under the same reaction conditions). The same conclusions for referent mixture have been published previously by Komers et al [36]. The butanol content in the reaction mixture has a positive effect on the rate of the transesterification, thus reducing the necessary reaction time. Butanol at the selected reaction temperature (60 °C) also reacted

with rapeseed oil and 15 mol% of butyl esters (BE) was determined in the ester phase (EP). A decreasing reaction rate and lower mol % BE in EP (7 - 9 mol %) with decreasing molar ratio alcohols to oil was observed.

The acid number of the EP was always less than $0.2 \text{ mg KOH g}^{-1}$ because both methods of transesterification stopping ensured a low acid number. EP containing ME and BE achieved higher viscosity values than the reference EP and increases with increasing amounts of BE in the EP (BE viscosity is approximately 32 % higher than ME). The method of stopping the reaction has no effect on the viscosity value of the EP. A flash point higher than $130 \text{ }^\circ\text{C}$ was also determined for the EP, which means that the residual content of alcohols is less than 0.08 wt% for methanol and 0.13 wt% for butanol. When butanol was used as cosolvent, the EP contained significantly higher amount of water and potassium contents than those determined in the EP of the reference measurement. The amount of potassium in EP is greatly influenced by the amount of butyl ester formed, as potassium ions dissolve better in butyl esters than in methyl esters, which was also confirmed by independent experiments.

3.3. Transesterification by heterogenous catalyst (MgFe)

The transesterification with the heterogeneous catalyst was also tested. The MgFe mixed oxide with a molar ratio 3:1 was used as a heterogeneous catalyst. The precursor (hydrotalcite) for the preparation of MgFe mixed oxide was synthesised by a coprecipitation method with using of activated carbon. The MgFe mixed oxide synthesized with active carbon was compared with mixed oxide synthesised without the active carbon. Active carbon was removed by calcination of the hydrotalcite at $450 \text{ }^\circ\text{C}$. In hydrotalcite, the real molar ratio of MgFe of 2.9:1 was determined by ICP analysis i.e., almost the same as expected. The formation of MgFe mixed oxide was confirmed by XRD analysis and the diffractogram was compared with the reference MgFe MO synthesised without activated carbon. The diffraction lines were found at $2\theta = 43.5$ and 63° (belong to MgO) for both mixed oxides samples. Diffraction lines for carbon were not observed, which indicates successful removal from the MO structure.

The surface area of Mg/Fe 3:1 with 1.25 wt% of coal was $132 \text{ m}^2\text{g}^{-1}$, which was compared with that of hydrotalcite MgFe 3:1 without addition of active coal ($101 \text{ m}^2\text{g}^{-1}$). The high surface area is important because transesterification occurs on the surface of the catalyst.

The catalytic activity of MgFe MO was tested in the transesterification of rapeseed oil with (i) methanol, (ii) butanol and (iii) different molar ratios of methanol and butanol. The best results were obtained for TR using a mixture of methanol and butanol with a molar ratio of 1:1. The ester content in EP reached 97.5 wt% in after 4 h of reaction, while in the TR using MgFe MO and methanol only 70 wt% of esters in EP was achieved after 6 h of reaction (published by Hajek et al. [37]). The use of butanol as a cosolvent significantly increases the rate of heterogeneously catalyzed TR of rapeseed oil, because only two phases are presented in the reaction mixture instead of the three phases (O:M:cat). Unfortunately, the butyl esters has negative affect of the quality of the EP, as they increase the amount of water and the viscosity. The same phenomenon was also observed by using of a homogeneous catalyst.

4. Glycerol valorization

The production of glycerol, as by-product of transesterification, increase due to the increasing production of FAME. Nowadays glycerol is as an important chemical, but also as a potential feedstock to produce other important chemicals. Glycerol can be transformed by different technological processes such as (i) biological processes (production of propane-1,3-diol, ethanol), (ii) chemical processes (production of polyglycerols, ethers), (iii) thermochemical processes (production of hydrogen, CO) and (iv) catalytic processes (production of propane 1,2-diol, acrolein, acetal) [7]. An important catalytic processing of glycerol is hydrogenolysis (dehydroxylation). The products of the reaction are propan-1,2-diol, propan-1,3-diol, or ethan-1,2-diol [38], which depends on the type of used catalyst and reaction conditions. Most of the research is focused on the preparation of propan-1,2-diol, which has a wide application in many sectors of human activity. Propane-1,2-diol is currently produced from propylene, which is commonly produced from fossil sources. Glycerol as a substitute for propylene in propan-1,2-diol production is a promising way of utilizing renewables in the petrochemical industry [39].

The materials based on noble metals (Pt, Ru and Rh) or transition metals (Cu, Ni and Co) supported on various supports (Al_2O_3 , SiO_2 , ZnO , MgO , Zeolites) or incorporated in the structure of the catalyst (CuZnAl, NiAl) have been previously published as suitable catalysts for the preparation of propane-1,2-diol [12, 38]. From an economic point of view, copper-based catalysts are the most interesting group of catalysts, because they achieve comparable activity to noble metal-based catalysts, but their cost is significantly lower. For copper-based catalysts, an increase in catalyst activity in hydrogenolysis reactions by the addition of another component to the catalyst has been observed. The catalytic activity of copper can be influenced for example by the addition of P_2O_5 or metal such as Pt, Ag, Ni, or Zn [14, 38, 40]. Although zinc has been described several times as an effective modifier of Cu-based catalysts, no detailed study on its role in the structure of CuZnAl aMO prepared from hydrotalcite was published [40]. Six types of CuZnAl MO were synthesised with different zinc molar ratios $\text{CuZnAl} - 2:x:1$ ($x = 0, 0.25, 0.5, 1, 1.5$ a 2). The description of influence of zinc in CuZnAl mixed oxides. The work described the important influence of zinc on catalyst structure and the influence on hydrogenolysis glycerol in a batch reactor.

4.1. Influence of zinc on CuZnAl aMO structure

A series of CuZnAl HT with different metal molar ratios were prepared by the coprecipitation method. It was found that the real molar ratio values were slightly different from what was expected based on the input mass balance. The real ratio values of divalent v.s. trivalent cations $(\text{Cu}^{+II} + \text{Zn}^{+II}) / \text{Al}^{+III}$ were approximately 8–20% higher than theoretically expected. It is however in agreement with the literature as divalent cations have better ability to be built into the structure of HT, than trivalent cations [15].

The XRD patterns of LDH (HT), MO and aMO are shown in Fig. 8. In Figure 1, sharp, symmetric diffraction lines with high intensity at $2\theta = 11.7, 23.5, 34.6, 39.2, 46.7, 60.0$ and 63.3° can be seen. These lines are characteristic of the HT structure. Other diffraction lines were not observed.

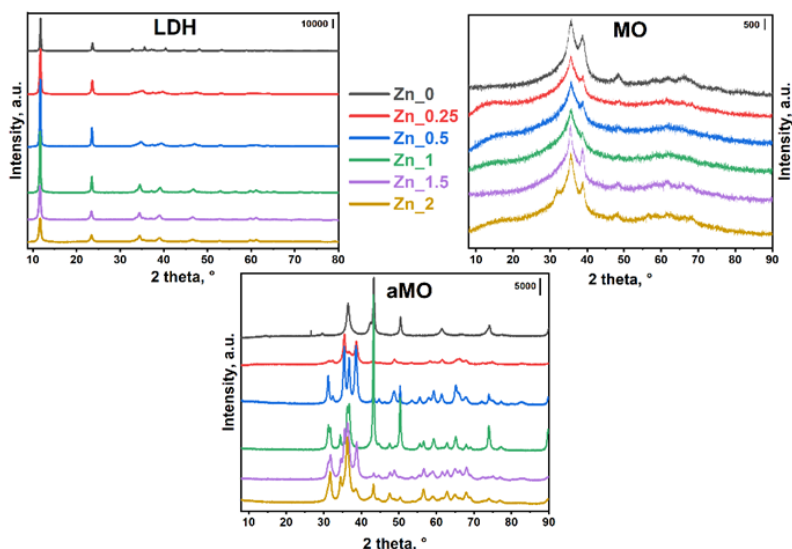


Fig. 8 XRD diffractograms of CuZnAl layered double hydroxides (LDH), mixed oxides (MO) and activated (reduced) mixed oxides (aMO)

For catalyst without the zinc (aMO_Zn 0) diffraction lines for Cu and Cu₂O were observed. While for the zinc-containing catalysts, only diffraction lines for CuO were observed. The absence of diffraction lines caused probably due oxidation of the materials between activation and before XRD analysis. Other diffraction lines observed for aMO containing zinc corresponded to gahnite (ZnAl₂O₄), which has a spinel structure. The possibility of spinel structure formation at low temperatures was confirmed in the publication of Divins et al. [41]. The gahnite diffraction lines were broader and of lower intensity for aMO_Zn-0.25 compared with aMO with higher Zn content. In catalysts with zinc molar ratio higher than 1 (aMO_Zn-1) also characteristic ZnO diffraction lines were observed. The diffraction lines for ZnO were sharper, and the intensity increased with increasing Zn content. This indicated the formation of well-ordered ZnO crystals. It can be concluded, that up to stoichiometric amount, practically all Zn is consumed by spinel formation. The excess Zn above this stoichiometric amount is converted to the ZnO phase during calcination.

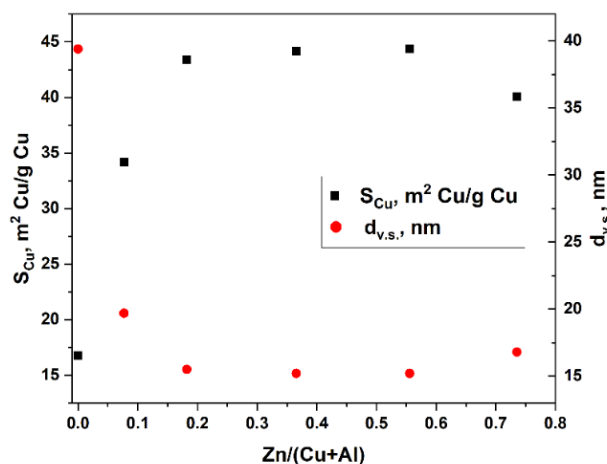


Fig. 9 Specific copper surface area and average volume-surface diameter against molar ratio Zn/(Cu+Al).

The specific copper surface area S_{Cu} ($m^2 Cu/g Cu$) and average volume-surface diameter $dv.s.$ (nm), were determined by H_2 -TPR with N_2O passivation. The calculation method was performed based on a previous study [42]. Based on hydrogen consumption during the reduction of the (i) total amount of copper and (ii) passivated copper, the Cu particle characteristics were calculated. The dependency of S_{Cu} a $dv.s.$ on the $Zn/(Cu+Al)$ molar ratio is shown in Fig. 9. It was found that the mixed oxides without zinc have lower values of S_{Cu} than the mixed oxides containing zinc. It is apparent that low amounts of Zn had a positive effect on the Cu specific surface area, and the maximum S_{Cu} was achieved at $Zn/(Cu+Al)=0.2$. A further Zn content increase had a rather negative impact.

4.2. Effect of zinc to glycerol hydrogenolysis

Glycerol conversion at 50 and 90 minutes of reaction time were chosen as the criteria for the comparison of catalyst activity. The values of selectivity to 1,2-propanediol at 65% glycerol conversion (iso-conversion data) were also compared for the whole set of catalysts studied.

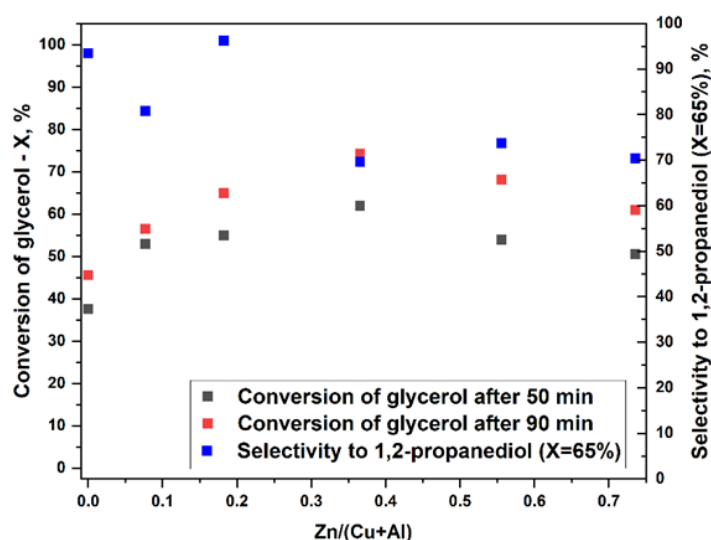


Fig. 10 Conversion of glycerol and selectivity to 1,2-propanediol against molar ratio $Zn/(Cu+Al)$.

The increase in activity with increasing Zn content, up to $Zn/(Cu+Al) = 0.35$, can be clearly seen in Fig. 10. For this molar ratio, the conversion at 90 min reached 75%, then it started to decline with a further increase in Zn content. A $Zn/(Cu+Al)$ molar ratio of approximately 0.35 ($Zn/Cu = 0.5$) was the optimum in terms of catalyst activity. The maximum activity was observed over the catalyst with the finest Cu particles and largest Cu surface area. It is therefore evident that Zn affected catalyst activity through its impact on the Cu surface.

In contrast, the selectivity at 65% glycerol conversion continued to decline with the Zn concentration in the same composition extent in which a positive effect of Zn on activity was observed. A selectivity of 75% was achieved with the catalyst of optimum activity, in which $Zn/(Cu+Al)$ was 0.35. The selectivity remained almost constant with a further Zn content increase.

5. Conclusion

The doctoral thesis is focused on using of mixed oxides (catalyst) in the valorization of alcohols and the use of butanol (the product of ethanol valorization) as a co-solvent in the transesterification of rapeseed oil. The hydrotalcites precursors were prepared by using coprecipitation methods. The studied catalysts and precursor forms were characterized by various instrumental methods (XRD, TPD, TPR, and others) to determine the influence of composition on the texture and structure of the catalysts and their catalytic activity.

Firstly, the effects of transition metals (Co, Ni, Cu, Mn, and Cr) on the physic-chemical properties of MgAl and MgFe mixed oxides is describe including the influence on catalytic activity of ethanol valorization at different reaction temperatures. It was found that transition metals significantly affect the activity and selectivity of the catalyst. Co, Ni, and Cu increased the activity of MgAl and MgFe catalysts, while Mn and Cr predominantly decrease the activity at the chosen temperatures. Generally, it can be concluded that (TM)MgAl catalysts produce higher amounts of higher alcohols, mainly butanol. An exception is the CuMgAl mixed oxide, which primarily produces ethyl acetate, which is also the main product in ethanol valorization by using (TM)MgFe mixed oxides. The quantity of other by-products depends on the transition metal and acid-base properties. Based on the analysis of reaction products, a scheme for ethanol valorization by using MgAl and MgFe MO was proposed. Based on the analysis of liquid and gaseous products, a reaction scheme for the valorization of ethanol using MgAl and MgFe MO was suggested.

Furthermore, the possibility of using butanol as a cosolvent in the transesterification of rapeseed oil with methanol was studied. The ternary plots for the methanol:butanol:rapeseed oil mixture at selected reaction temperatures were constructed. The molar ratios of the reaction components in which the feedstock mixture is homogeneous were determined. The use of butanol as a cosolvent was tested at different reaction conditions by homogeneous (KOH) and heterogeneous catalyst (MgFe MO). The use of butanol as a cosolvent significantly reducing the reaction time required to achieve 97 wt% esters in the ester phase. Furthermore, the properties of the ester and glycerol phases were analyzed in detail. It was found that the formed butyl ester affects the quality of the ester phase, because increases the caloric value, but also the viscosity and amount of water and potassium, which is negative.

The last study, CuZnAl mixed oxides with different molar ratios of zinc in the structure were tested in as catalysts for the hydrogenolysis of glycerol to propane-1,2-diol. It was found that zinc is effective structural modifier of the copper-based catalyst prepared by calcination of hydrotalcites. Only a small amount of zinc (molar ratio of $Zn/(Cu+Al) = 0.35$ at maximum) had a positive effect on the Cu particle surface and therefore on the catalyst activity in glycerol hydrogenolysis. However, a further increase in Zn content had no positive impact on either the Cu surface area or the catalyst activity, although a higher Zn content contributes to a higher concentration of acidic centers on the catalyst surface. An excess of Zn leads to the formation of ZnO crystals during catalyst calcination which causes deterioration of the Cu surface in the final, form of the catalyst. This also means that the acidic centers are not primarily important for the reaction mechanism in the case of bulk Cu based catalysts.

List of Published Works

Paper I: **J. Mück**, K. Frolich, Z. Tišler, J. Mück, L. Skuhrovcová, The parameters of Mg/Fe(Al) layered double hydroxides/mixed oxides related to the synthesis, Scientific Papers of the University of Pardubice, (2023)

Paper II: **J. Mück**, J. Kocík, **M. Hájek**, Z. Tišler, K. Frolich, A. Kašpárek, Transition metals promoting Mg-Al mixed oxides for conversion of ethanol to butanol and other valuable products: Reaction pathways, Applied Catalysis A: General, volume 626 (2021), IF – 5,723, Q1, <https://doi.org/10.1016/j.apcata.2021.118380>

Paper III: J. Mück, J. Kocík, K. Frolich, J. Šimek, M. Michálková, M. Hájek, Transition metal promoted Mg-Fe mixed oxides for conversion of ethanol to valuable products, volume 8 (2023), IF – 4,132, Q2, <https://doi.org/10.1021/acsomega.3c00182>

Paper IV: **M. Hájek**, A. Vávra, **J. Mück**, Butanol as a co-solvent for transesterification of rapeseed oil by methanol under homogeneous and heterogeneous catalyst, Fuel, volume 277 (2020), IF – 6,609, Q1, <https://doi.org/10.1016/j.fuel.2020.118239>

Paper V: K. Frolich, J. Kocík, **J. Mück**, J. Kolena, **L. Skuhrovcová**, The role of Zn in Cu-Zn-Al mixed oxide catalyst and its effect on glycerol hydrogenolysis, Molecular catalysis, volume 53 (2022), IF – 5,089, Q2, <https://doi.org/10.1016/j.mcat.2022.112796>

List of References

- [1] M.A. Hanif, F. Nadeem, R. Tariq, U. Rashid, Chapter 9 - Renewable energy from biomass, in: M.A. Hanif, F. Nadeem, R. Tariq, U. Rashid (Eds.) Renewable and Alternative Energy Resources, Academic Press, 2022, pp. 555-603.
- [2] A. Santha, R. Varghese, H. Joy Prabu, I. Johnson, D. Magimai Antoni Raj, S. John Sundaram, Production of sustainable biofuel from biogenic waste using CuO nanoparticles as heterogeneous catalyst, Materials Today: Proceedings, 36 (2021) 447-452.
- [3] G. Guan, N. Sakurai, K. Kusakabe, Synthesis of biodiesel from sunflower oil at room temperature in the presence of various cosolvents, Chemical Engineering Journal, 146 (2009) 302-306.
- [4] A.B. Gaspar, A.M.L. Esteves, F.M.T. Mendes, F.G. Barbosa, L.G. Appel, Chemicals from ethanol—The ethyl acetate one-pot synthesis, Applied Catalysis A: General, 363 (2009) 109-114.
- [5] X. Han, H. An, X. Zhao, Y. Wang, Influence of acid-base properties on the catalytic performance of Ni/hydroxyapatite in n-butanol Guerbet condensation, Catalysis Communications, 146 (2020) 106130.
- [6] T.S. de Andrade, M.M.V.M. Souza, R.L. Manfro, Hydrogenolysis of glycerol to 1,2-propanediol without external H₂ addition in alkaline medium using Ni-Cu catalysts supported on Y zeolite, Renewable Energy, 160 (2020) 919-930.
- [7] J. Kaur, A.K. Sarma, M.K. Jha, P. Gera, Valorisation of crude glycerol to value-added products: Perspectives of process technology, economics and environmental issues, Biotechnology Reports, 27 (2020) e00487.
- [8] S. Sukanuma, N. Katada, Innovation of catalytic technology for upgrading of crude oil in petroleum refinery, Fuel Processing Technology, 208 (2020) 106518.
- [9] D.J. Cole-Hamilton, R.P. Tooze, Homogeneous Catalysis — Advantages and Problems, in: D.J.

- Cole-Hamilton, R.P. Tooze (Eds.) *Catalyst Separation, Recovery and Recycling: Chemistry and Process Design*, Springer Netherlands, Dordrecht, 2006, pp. 1-8.
- [10] Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando, Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review, *Applied Catalysis A: General*, 363 (2009) 1-10.
- [11] P. Kots, A. Zabilska, Y. Grigor'ev, I. Ivanova, Ethanol to Butanol Conversion over Bifunctional Zeotype Catalysts Containing Palladium and Zirconium, *Petroleum Chemistry*, 59 (2019) 925-934.
- [12] H. Mitta, P.K. Seelam, S. Ojala, R.L. Keiski, P. Balla, Tuning Y-zeolite based catalyst with copper for enhanced activity and selectivity in vapor phase hydrogenolysis of glycerol to 1,2-propanediol, *Applied Catalysis A: General*, 550 (2018) 308-319.
- [13] P. Čičmanec, Y. Ganjkhanlou, J. Kotera, J.M. Hidalgo Herrador, Z. Tišler, R. Bulánek, The effect of vanadium content and speciation on the activity of VO_x/ZrO₂ catalysts in the conversion of ethanol to acetaldehyde, *Appl. Catal., A*, 564 (2018).
- [14] J. Kolena, L. Skuhrovcová, J. Kocík, J. Lederer, Modified hydrotalcites as precursors for catalysts effective in the hydrogenolysis of glycerol to 1,2-propanediol, *Reaction Kinetics, Mechanisms and Catalysis*, 122 (2017).
- [15] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: Preparation, properties and applications, *Catalysis Today - CATAL TODAY*, 11 (1991) 173-301.
- [16] S.A. Rackley, 7 - Adsorption capture systems, in: S.A. Rackley (Ed.) *Carbon Capture and Storage (Second Edition)*, Butterworth-Heinemann, Boston, 2017, pp. 151-185.
- [17] M.M. Rao, B.R. Reddy, M. Jayalakshmi, V.S. Jaya, B. Sridhar, Hydrothermal synthesis of Mg-Al hydrotalcites by urea hydrolysis, *Materials Research Bulletin*, 40 (2005) 347-359.
- [18] M. Bolognini, F. Cavani, D. Scagliarini, C. Flego, C. Perego, M. Saba, Mg/Al mixed oxides prepared by coprecipitation and sol-gel routes: a comparison of their physico-chemical features and performances in m-cresol methylation, *Microporous and Mesoporous Materials*, 66 (2003) 77-89.
- [19] J. Ob-eye, P. Praserthdam, B. Jongsomjit, Dehydrogenation of Ethanol to Acetaldehyde over Different Metals Supported on Carbon Catalysts, in: *Catalysts*, 2019.
- [20] G. Garbarino, G. Pampararo, T.K. Phung, P. Riani, G. Busca, Heterogeneous Catalysis in (Bio)Ethanol Conversion to Chemicals and Fuels: Thermodynamics, Catalysis, Reaction Paths, Mechanisms and Product Selectivities, *Energies*, 13 (2020).
- [21] T.W. Birky, J.T. Kozlowski, R.J. Davis, Isotopic transient analysis of the ethanol coupling reaction over magnesia, *Journal of Catalysis*, 298 (2013) 130-137.
- [22] M. León, E. Díaz, S. Ordóñez, Ethanol catalytic condensation over Mg-Al mixed oxides derived from hydrotalcites, *Catal. Today*, 164 (2011) 436-442.
- [23] K. Inui, T. Kurabayashi, S. Sato, Direct synthesis of ethyl acetate from ethanol over Cu-Zn-Zr-Al-O catalyst, *Appl. Catal., A*, 237 (2002) 53-61.
- [24] C. Cui, J. Ma, Z. Wang, W. Liu, W. Liu, L. Wang, High Performance of Mn-Doped MgAlO_x Mixed Oxides for Low Temperature NO_x Storage and Release, in: *Catalysts*, 2019.
- [25] L. Smoláková, K. Frolich, I. Troppová, P. Kutálek, E. Kroft, L. Čapek, Determination of basic sites in Mg-Al mixed oxides by combination of TPD-CO₂ and CO₂ adsorption calorimetry, *Journal of Thermal Analysis and Calorimetry*, 127 (2017) 1921-1929.
- [26] M. Hájek, J. Kocík, K. Frolich, A. Vávra, Mg-Fe mixed oxides and their rehydrated mixed oxides as catalysts for transesterification, *Journal of Cleaner Production*, 161 (2017) 1423-1431.
- [27] Z. Wang, Z. Niu, Q. Hao, L. Ban, H. Li, Y. Zhao, Z. Jiang, Enhancing the Ethynylation Performance of CuO-Bi₂O₃ Nanocatalysts by Tuning Cu-Bi Interactions and Phase Structures, *Catalysts*, 9 (2019) 35.
- [28] R. Kumar, N. Enjamuri, S. Shah, A.S. Al-Fatesh, J.J. Bravo-Suárez, B. Chowdhury, Ketone formation of oxygenated hydrocarbons on metal oxide based catalysts, *Catalysis Today - CATAL TODAY*, 302 (2018) 16-49.

- [29] J.M. Conesa, M.V. Morales, N. García-Bosch, I.R. Ramos, A. Guerrero-Ruiz, Graphite supported heteropolyacid as a regenerable catalyst in the dehydration of 1-butanol to butenes, *Catalysis Today - CATAL TODAY*, (2023) 114017.
- [30] L.C. Meher, D. Vidya Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, *Renewable and Sustainable Energy Reviews*, 10 (2006) 248-268.
- [31] Y.H. Taufiq-Yap, H.V. Lee, M.Z. Hussein, R. Yunus, Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel, *Biomass and Bioenergy*, 35 (2011) 827-834.
- [32] M. Demirbas, M. Balat, H. Balat, Potential Contribution of Biomass to the Sustainable Energy Development, *Energy Conversion and Management*, 50 (2009) 1746-1760.
- [33] G. Guan, K. Kusakabe, N. Sakurai, K. Moriyama, Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether, *Fuel*, 88 (2009) 81-86.
- [34] Z.B. Todorović, O.S. Stamenković, I.S. Stamenković, J.M. Avramović, A.V. Veličković, I.B. Banković-Ilić, V.B. Veljković, The effects of cosolvents on homogeneously and heterogeneously base-catalyzed methanolysis of sunflower oil, *Fuel*, 107 (2013) 493-502.
- [35] M. Jha, A. Gupta, V. Kumar, Kinetics of transesterification on *jatropha curcas* oil to biodiesel fuel, in: *Proceedings of the World Congress on Engineering and Computer Science 2007*, WCECS 2007, 2007, pp. 1-4.
- [36] K. Komers, F. Skopal, R. Stloukal, J. Machek, Kinetics and mechanism of the KOH — catalyzed methanolysis of rapeseed oil for biodiesel production, *European Journal of Lipid Science and Technology*, 104 (2002) 728-737.
- [37] M. Hájek, A. Tomášová, J. Kocík, V. Podzemná, Statistical evaluation of the mutual relations of properties of Mg/Fe hydrotalcites and mixed oxides as transesterification catalysts, *Applied Clay Science*, 154 (2018) 28-35.
- [38] L.C. Meher, R. Gopinath, S.N. Naik, A.K. Dalai, Catalytic Hydrogenolysis of Glycerol to Propylene Glycol over Mixed Oxides Derived from a Hydrotalcite-Type Precursor, *Industrial & Engineering Chemistry Research*, 48 (2009) 1840-1846.
- [39] A. Ruppert, K. Weinberg, R. Palkovits, ChemInform Abstract: Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals, *Angewandte Chemie (International ed. in English)*, 51 (2012) 2564-2601.
- [40] J. Aubrecht, V. Pospelova, A. Martínez, P. Concepción, O. Kikhtyanin, P. Straka, D. Kubička, CuZnAl hydrotalcites as suitable precursors for chromium-free ester hydrogenolysis catalysts, *Applied Catalysis A: General*, 644 (2022) 118811.
- [41] N. J. Divins, D. Kordus, J. Timoshenko, I. Sinev, I. Zegkinoglou, A. Bergmann, S. Chee, S. Widrinna, O. Karşlıoğlu, H. Mistry, M. Luna, J. Zhong, A. Hoffman, A. Boubnov, J. Boscoboinik, M. Heggen, R. Dunin-Borkowski, S. Bare, B. Roldan Cuenya, Operando high-pressure investigation of size-controlled CuZn catalysts for the methanol synthesis reaction, *Nature Communications*, 12 (2021).
- [42] C.J.G. Van Der Grift, A.F.H. Wielers, B.P.J. Jogh, J. Van Beunum, M. De Boer, M. Versluijs-Helder, J.W. Geus, Effect of the reduction treatment on the structure and reactivity of silica-supported copper particles, *Journal of Catalysis*, 131 (1991) 178-189.