

Article



Biodiesel: Modified Mixed Oxides as Catalyst for Transesterification of Rapeseed Oil

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Abstract: Biodiesel, as one of the alternative biofuels replacing the common fossil fuels, is prepared by transesterification of oils and fats. Commonly, the reaction is catalysed by either acidic or basic catalysts. The availability of the active sites to large triglyceride molecules is the key factor of the heterogeneous catalysts. The use of carbon fibres during the synthesis of Mg/Fe layered double hydroxides results in the formation of macropores during the calcination. The amount of carbon fibres showed an important effect on the textural properties of the resulting mixed oxides. The texture was determined by N₂-adsorption and Hg-porosity. The catalyst activity in the studied reaction was examined by determination of ester amount by gas chromatography and the activity was compared with unmodified mixed oxides. The highest ester yield (40 wt.%) was achieved by adding 1 wt.% of carbon fibres to the catalyst with the largest size of macropores.

Keywords: mixed oxides; carbon fiber; transesterification

1. Introduction

Increasing consumption of fossil fuels has led to an increased demand for renewable fuel resources. Biodiesel oil has emerged as a promising environmentally friendly replacement for diesel oil. As opposed to diesel oil, biodiesel is easily biodegradable and is essentially sulphur free. Furthermore, it has very similar combustion properties as diesel oil [1] and it is therefore acceptable to use it as fuel in diesel engines.

One of the possible routes for production of biodiesel oil is a catalysed transesterification reaction of triglycerides [2]. This reaction can be catalysed under mild reaction conditions ($T = 60 \degree C$, p = 100 kPa). However, in order to run the reaction without a catalyst, we would need to apply considerably higher pressures and temperatures (supercritical methanol conditions) [3]. Transesterification is a reaction between a triglyceride and an alcohol (the most often used one is methanol) and the products are esters in the ester phase (EP) and glycerol in the glycerol phase (GP) [4]. It is most often catalysed by homogeneous catalysts (e.g., KOH or NaOH) because of their low cost and high catalytic activity [5]. Unfortunately, usage of homogeneous catalysts creates several issues: (i) saponification side-reactions take place, which decrease the reaction yield and complicate the separation process, (ii) the catalyst has to be neutralised after finishing the reaction and (iii) the catalyst cannot be reused [6].

The aforementioned problems motivate research of alternative catalysis methods. Immobilized enzyme and heterogeneous catalysts are promising options, since they can be recovered from the reaction mixture and therefore be reused [7]. These types of catalysts are also considered as more environment friendly due to lower water consumption during the separation of a catalyst from the reaction mixture after reaction [8].

One of the problems associated with the use of heterogeneous catalysts for transesterification, is the large size of a triglyceride molecule, which limits diffusion of the molecules into the pores of the

catalyst. This causes the transesterification reaction to take place only on the surface of a catalyst. It is also believed that the surface reaction is a rate-limiting step of the process.

Mixed metal oxides have been widely used as heterogeneous catalysts for transesterification reactions [9]. They can be prepared from layered double hydroxides (LDHs) by calcination (i.e., heating in air). The LDHs belong to a class of ionic clays, they have layered structure and a general formula $\left[M_{1-x}^{II}N_{x}^{III}(OH)_{2}^{x+}\right](A_{x/n}^{n-})\cdot m$ H₂O, where M^{II} is a bivalent (e.g., Ca, Zn, Mg, etc.) and N^{III} a trivalent (e.g., Fe or Al) metallic cation. Moreover, *x* is the stoichiometric coefficient of N^{III} , A^{n-} represents an anion (such as carbonate, nitrate, etc.) and is a number of water molecules [10]. The LDHs and mixed oxides can be used without any modification.

Xu et al. used Mg/Fe mixed oxides, prepared by calcination of LDHs, which were synthesized by a co-precipitation method at constant pH = 9.3 and with various molar ratios of metals (2–4). The highest catalytic activity was observed for a catalyst with a 3:1 molar ratio of Mg/Fe. In addition, the reaction temperature was kept at 60 °C, the molar ratio of methanol to oil was 6:1 and the reaction was left to proceed for 1.5 h. Using this catalyst and under these conditions, the authors reported a 88 wt.% yield of esters. The catalyst activity correlated with a total number of basic sites, which were also determined. Moreover, the authors tested the catalyst stability and reusability and found that their catalyst is stable for at least four experiments [11].

Shumaker et al. tested the catalytic properties of three types of mixed oxides: Li/Al, Mg/Al, and Mg/Fe, which were synthesised from LDH precursors. Two transesterification reactions were studied: (i) transesterification of soybean oil with methanol (1 wt.% of catalyst, molar ratio of methanol to oil 15:1 and 2 h of reaction time) and (ii) glycerol tributyrate with methanol. The Li/Al mixed oxides provided the highest catalytic activity in both studied reactions. The Li/Al catalyst contained the smallest of the weakest basic sites determined by Hammet indicators, but on the other hand, the total number of basic sites measured by CO₂-TPD had Li/Al catalyst the highest, which corresponds with highest ester yield. This discrepancy is attributed to the fact, that the Hammet indicators determine only the number of Brønsted basic sites and not the number of more general Lewis basic sites [12].

In this work, Mg/Fe mixed oxides, which were synthesised from hydrotalcites doped with carbon fibres in various concentrations, were used to improve the properties of catalysts. We focused on preparation of a catalyst with a high content of macropores. Macropores were created by a template method (i.e., by addition of carbon fibre during the synthesis of hydrotalcites). Subsequently, the carbon fibres were burned by calcination. The hydrotalcites were synthesised by a commonly used co-precipitation method and then calcinated to produce mixed oxides. Both hydrotalcites and mixed oxides were characterised by various techniques such as XRD, N₂-adsorption, Hg-porosimetry, etc. The catalytic activity was tested in a transesterification reaction with methanol in a fixed-bed reactor.

2. Results and Discussion

2.1. Characterisation of the Catalysts

In order to characterise the catalysts, we used ICP-OES, XRD, N₂-adsorption, Hg-porosimetry, TPD-CO₂, and SEM techniques.

First of all, precise molar ratio of Mg/Fe with carbon was determined by ICP-OES. The results are shown in Table 1. All of them were in the interval of molar ratio $3(\pm 0.1)$. The structure of the mixed oxides was confirmed by XRD analysis because the characteristic diffraction lines for this type of catalyst were found (see Figure 1). The diffraction lines at 43.0° and 62.5°, which are typical for the MgO phase, were also observed [13]. We consider the presence of these lines to be a confirmation of a successful mixed oxide synthesis. Moreover, the crystallite size and the fraction of the crystalline phase (crystallinity) were calculated from the diffraction line at 62.5° (see Table 2 for results).

Catalyst	<i>w</i> (Mg), wt.%	<i>w</i> (Fe), wt.%	Molar Ratio Mg/Fe
0.1% C	37.2	29.2	2.93
0.5% C	37.4	29.37	2.93
1.0% C	36.7	28.6	2.95
1.5% C	37.9	29.9	2.91
2.5% C	36.7	28d.5	2.96
4.0% C	36.4	28.7	2.91

Table 1. Molar ratios of Mg/Fe in the prepared catalysts.

The crystal size of mixed oxides, doped with carbon, decreased with an increasing mass fraction of carbon in the catalyst. Crystal sizes of 72.5 nm and 64.7 nm were present in samples 0.5 wt.% and 2.5 wt.% respectively. On the other hand, crystallinity increases with an increasing amount of carbon in materials. The higher crystallinity of 33.9% was determined in materials with 2 wt.% carbon, while the lowest crystallinity of 20.3 wt.% was found in a catalyst with 0.5 wt.% carbon.



Figure 1. Diffractograms of the Mg/Fe mixed oxides, modified with different mass fractions of carbon fibres.

Specific surface area, volume of mesopores, volume of micropores, and total volume of pores were determined by the N₂-physisorption method. Specific surface areas S_{BET} were calculated by fitting the measured adsorption isotherms to isotherms arising from BET theory, whereas the porosity results were obtained by a BJH method. From the results in Table 2, we can deduce that the materials with mass fractions of carbon 0.1 wt.%, 0.5 wt.%, and 4 wt.% had the lowest specific surface area. This can be explained by the fact that a large amount of carbon leads to form large unstable pores which are partially deformed during the thermal treatment calcination. The highest specific surface area (almost 130 m²·g⁻¹) was observed in the material with 2.5 wt.% added carbon. Although, Kocik et al. found that the Mg/Fe mixed oxides (molar ratio of 3:1) without carbon addition had specific surface area of 95.3 m²·g⁻¹. This result confirms that addition of carbon fibres significantly influences the specific surface area.

Catalyst	Dcryst, nm	Crystallinity, %	$S_{\rm BET},{\rm m}^2{\rm g}^{-1}$	CBS, µmol g ⁻¹
0.1% C	71.1	24.5	104.2	111.3
0.5% C	72.5	20.3	128.5	90.6
1.0% C	67.9	30.3	120.2	88.6
1.5% C	71.2	27.2	122.9	54.1
2.5% C	64.7	31.2	101.9	61.8
4.0% C	65.8	30.7	100.1	63.2

Table 2. *D*cryst, crystallinity, S_{BET} , and concentration of basic sites (*CBS*) of Mg/Fe mixed oxides modified by carbon.

N₂-physisorption isotherms obtained for all materials closely resembled the type IV isotherm of the IUPAC classification, which is characteristic of mesoporous materials. None of the isotherms exhibited adsorption limitations at high relative pressures. This is typical of type H3 hysteresis loops of IUPAC classification. The H3 type of hysteresis loop is commonly observed in materials made of aggregates of plate-like particles, which tend to form slit-shaped pores. The materials with 1 wt.% and 2.5 wt.% of carbon fibres did not exhibit desorption isotherms and had the lowest total volume of pores (0.367 mL and 0.408 mL respectively) of all the materials. At the same time, these materials had different pore distributions and also contained smaller pores compared to other materials (see Figure 2).

N₂-physisorption was used to describe mesopores in the synthesized catalysts. However, this method is inadequate for characterisation of macropores. Hence, Hg porosimetry was applied.

The distributions of meso- and macropores were determined by Hg-porosimetry. The resulting distribution curves are shown in Figure 3. The mesoporous structure was observed in the sample with 2.5 wt.%, which was in accordance with the results of N₂-physisorption. However, no macropores were observed. On the other hand, mainly macroporous structure is observed by in all of the prepared Mg/Fe mixed oxides. Lastly, the maxima of macropores distributions lied between 157 nm and 305 nm.



Figure 2. Nitrogen Adsorption-desorption isotherms of prepared catalysts are plotted on the left, while the pore size (D_{pore}) distributions according to BJH method are plotted on the right.



Figure 3. Distribution of pore sizes of prepared catalysts, obtained by Hg-porosimetry.

The surface structure of materials was studied by SEM. The prepared Mg/Fe hydrotalcite with carbon fibres is shown in Figure 4A. On the other hand, in Figure 4B, we can see a Mg/Fe hydrotalcite after calcination. In the same figure, we can also observe holes, which were produced by burning of the carbon fibres during calcination.



Figure 4. SEM microphotography of hydrotalcites with carbon fibres (A) and calcinated hydrotalcites (B).

2.2. The Activity of Catalysts in Transesterification

All catalysts were tested in a fixed-bed reactor at the same conditions. The reactor was stabilised for 30 h at 120 °C, the data are not presented. The temperature was changed three times in total to 150 °C, to 180 °C, and finally back to 120 °C in 30 h, 60 h, and 90 h of reaction time respectively. In Figure 5, we show the dependence of mass fraction of esters in the product on the total reaction time for individual catalysts. During the first 12 h, there are no data since the reactor was stabilising. During this period, the oil conversion decreased or increased with changes in temperature. The differences in the ester amount are more pronounced at lower temperature, while at higher temperatures, the differences are

far less significant. The rates of reaction and mass transport increase with increasing temperature, which they have influenced the amount of esters. The usage of catalysts with high amount of carbon resulted in the lowest activity. The high activity showed the Mg/Fe mixed oxides with 1.0 wt.% and 1.5 wt.% of carbon. at 120 °C and 0.5 wt.% and 1 wt.% of carbon at a temperature of 150 °C.



Figure 5. Activity of carbon fibres modified mixed Mg/Fe oxides in a transesterification reaction at temperatures of 120–180 °C.

2.3. Relationship Between Properties of Catalysts and Activity in the Transesterification

In order to analyse the relationship between properties of the catalyst and catalytic activity, we performed a principal component analysis (PCA). The PCA describes correlations between dependent variables. If the angle between some two variables is close to 0°, we may say that they correlate positively, i.e., if one variable increases the other increases too. On the other hand, if the angle between the two variables is close to 180°, the variables are negatively correlated. Finally, if the angle is close to 90°, the variables are uncorrelated.

The correlations between variables can be deduced from Figure 6. The particles of sizes 3–10 nm, Y_{esters} at 120 °C, and specific surface area have a strong positive correlation, i.e., if the catalysts contain micropores than they will have a high specific surface area. This correlation is expected because smaller particles can fit more easily into a given volume of a porous material, i.e., the particles had a higher specific surface area [15]. Crystallinity of the materials (i.e., the proportion of the crystalline phase in the materials) weakly positively correlated with fractions of particles with sizes 10–1000 nm and 1000–10,000 nm. This indicates that larger particles tend to be composed of more crystalline materials. Higher crystallinity of materials means a smaller crystal size of these materials, which was confirmed by component weigh plot (CWP), i.e., the crystallinity has a negative correlation with crystal size. The crystal size of materials showed a positive correlation with yield of esters Y_{ester} at 150 °C and at 180 °C. Furthermore, these variables had a negative correlation with crystallinity and number of particles of sizes 1000–10,000 nm. It can be deduced, that at these temperatures, the reaction occurs on the surface of a catalyst or inside the macropores. This is the expected behavior concerning the fact that the triglycerides are made of relatively large molecules. At the highest temperature (180 °C), the reaction proceeds the fastest and occurs on the surface of catalyst, regardless of the crystal size and crystallinity of the materials.



Figure 6. The CWP of properties of the prepared mixed oxides and catalytic activity at 120 °C, 150 °C, and 180 °C.

The yield of esters Y_{ester} is related to the amount of carbon fibers in the catalyst as shown in Figure 7. First, as the amount of carbon fibres in catalyst increases, the Y_{ester} decreases. This effect was more pronounced and better visible at lower temperatures, especially at 120 °C. At 1.5 wt.% (120 °C) and 2.5 wt.% of carbon fibres (150 °C and 180 °C), the yield of obtained esters begins to rise again. The dependence of concentration of basic centres (*CBS*) on the amount carbon fibres had a similar trend as the dependence Y_{ester} on mass fraction of carbon in a catalyst at 120 °C. This finding is in agreement with Kutálek et al., who found that the yield of esters positively correlates with the concentration of basic centres [16].



Figure 7. The dependence of yields of esters Y_{ester} and concentration of basic sites CBS on the mass fraction of carbon fibres in the catalyst.

3. Materials and Methods

3.1. Relationship Between Properties of Catalysts and Activity in the Transesterification

The carbon fibres were synthesised by carbonisation of 100% cotton wool (Hartmann, Veverská Bítýška, Czech Republic) in a tubular reactor with a diameter of 29 mm and a length of 820 mm. The 35 g of cotton wool were placed into the isothermal zone of the reactor and heated for 8 h at a temperature of 450 °C in a stream of nitrogen (100 mL/h). Then, the reactor was cooled with a stream of nitrogen (50 mL/h). The obtained carbon fibres were dispersed by milling. Afterwards, the carbon fibres were used in a co-precipitation in 500 mL of demineralised water (UltraTurrax T25, 7000 rpm/10 min, IKA[®]-Werke GmbH & Co. KG, Staufen, Germany).

The precursors of LDHs were prepared by a co-precipitation method, which was conducted at a constant pH of 9.5 and a temperature of 60 °C. The preparation of catalysts was carried out in a glass precipitation reactor (volume of 5 L) Syrris Globe (Syrris Ltd., Royston, United Kingdom) equipped with two-piston (syringe) pumps and a propeller stirrer. At first, the dispersed carbon fibres were introduced into the reactor and 500 mL of demineralised water were added. Then, 1000 mL of cation solution was prepared by dissolving Mg(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O in deionized water (all Lach-Ner, s.r.o., Neratovice, Czech Republic) to obtain the total cation concentration of $1 \text{ mol}\cdot\text{dm}^{-3}$ and the molar ratio of Mg/Fe of 3. Afterwards, the cations were continuously added under intensive stirring (250 rpm) to the reactor vessel. During the synthesis of the LDHs, the pH was kept constant by adding a KOH/K₂CO₃ buffer solution ($C_{K(OH)} = 2 \text{ mol} \cdot dm^{-3}$, $C_{K2CO3} = 0.2 \text{ mol} \cdot dm^{-3}$). After the cation solution was depleted, the suspension was stirred at 60 °C for 1 h. The resulting suspension of LDHs was then filtered by press-filtration using S15N (Hobra, s.r.o., Broumov, Czech Rebublic) filter paper plates. Furthermore, the suspension was washed by demineralized water until the pH of the washing water decreased below a value of 7. Finally, the suspension was dried at 65 °C for 12 h. Mixed oxides were prepared by calcination, which was carried out at 450 °C for 3 h with a temperature ramp of $1 \,^{\circ}\mathrm{C} \,\mathrm{min}^{-1}$.

3.2. Characterisation of Catalyst

X-ray diffraction (XRD): The mixed oxides were characterized by powder X-ray diffraction with the All of JCPDS sheets PDF 2-2002, International Centre for Diffraction Data. Diffractograms were recorded by Bruker AXS D8 Advance (Bruker AXS GmbH, Karlsruhe, Germany) diffractometer using CuK α radiation with a secondary graphite monochromator. The intensity of diffraction was measured between 5° and 70° (2° steps). The crystal size of mixed oxides was calculated from the diffraction line at 43° by using the Scherrer formula:

$$D_{\text{cryst}} = (0.9 \cdot \lambda) / (\beta \cdot \cos \theta), \tag{1}$$

where D_{cryst} is the average crystal size, 0.9 is the value of the used shape factor, λ is the wavelength of the used CuK α radiation (0.154056 nm), β stands for the full width at half-maximum (FWHM), and θ is the diffraction angle.

 N_2 -physisorption: Nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) using ASAP 2020 equipment (Micromeritics, Norcross, GA, USA). Specific surface areas (S_{BET}) were determined by fitting the experimental data to BET isotherm, while the distributions of pore sizes were obtained by BJH method.

Temperature programmed desorption of CO_2 (TPD- CO_2): In order to determine a concentration of basic sites for each sample, we used TPD- CO_2 method. The measurement was carried out on the AutoChem II 2920 machine (Micromeritics), equipped with the OmniStarTM GSD 320 mass spectrometer (Pfeiffer Vacuum, Prague, Czech Republic). The complete measurement procedure was already described in our previous work. Mercury porosimetry: The macro-porous structural properties of the mixed oxides were determined using the AutoPore IV 9510 porosimeter (Micromeritics) in the pressure range of 0.7 kPa–413 MPa and at a temperature of 120 °C. Prior to each measurement, the mixed oxide samples were outgassed by applying vacuum. The measurement was performed in a stepwise manner with 10 s of equilibrium time at each pressure stage.

Scanning electron microscope (SEM) was used to study the surface structure of the mixed oxides. We used the Dual-beam scanning electron microscope with a focused ion beam (FIB/SEM, (LYRA3 GMH, TESCAN ORSAY HOLDING, a.s., Kohoutovice, Czech Republic), equipped with a magnetic field cancelling system, gas injection system and STEM detector, energy dispersive X-ray diffraction, and electron-beam lithography.

3.3. Transesterification in Fixed-Bed Reactor

The rapeseed oil without erucic acid (produced by Glencore Agriculture Czech, s.r.o., Ústí nad Labem, Czech Republic) was used in a transesterification reaction in a fixed-bed reactor. The relevant properties of the oil were: density = 920 kg·m⁻³, acid number = 0.3 mg·kg⁻¹, and water content = 470 ppm. The transesterification of rapeseed oil with methanol was realized in the fixed bed stainless steel reactor (length: 820 mm, insert diameter: 9.4 mm) with the 4871 process controller (Parr Instruments, Moline, IL, USA). Five g of mixed Mg/Fe oxide were placed into the middle part of the fixed-bed reactor. The 10 mL of silicon carbide (with a particle size of 0.1–0.2 mm) were placed above catalyst layer for better distribution of reaction mixture on catalyst particles. Free space of reactor was filled with silicon carbide (with a particle size of 1.2 mm). At first, the mixed oxides were thermally pre-treated at 115 °C (40 °C min⁻¹) for 4 h in a nitrogen atmosphere (10 dm³ h⁻¹). Molar ratio of rapeseed oil with methanol 1:24 was used and three temperatures (120, 150 and 180 °C) were tested. Mixed oxides were kept at the same temperature for 30 h. The weight hour space velocity, which can be defined as the ratio of rapeseed oil mass rate (g h⁻¹) to the mass of catalyst (g), was same for all experiments (1 h⁻¹). A sample was taken every four hours and then analysed by GC and ICP.

3.4. Analytical Methods

The content of glycerides (mono, di- and triglycerides) and the main products of a transesterification reaction (methyl esters) were determined in samples, which were taken every 4 h for each temperature (120 °C, 150 °C, 180 °C and finally repeated 120 °C). The determination was carried out on the gas chromatograph (GC)—GC-FID (7890A, MXT(R) Biodiesel TG column: 2 m/0.53 mm ID/0.32 µm, Agilent, Santa Clara, CA, USA) using the EN 14105 standard method. Liquid products of the reaction were collected in the low pressure separator. The excess of methanol was removed from the reaction mixture by distillation at 70 °C and lowered pressure and then the glycerol phase was separated from the ester phase. The samples for GC were derivatized subsequently: 5 µL of the EP was mixed with 60.8 µL of MSTFA (p.a., Sigma Aldrich, Prague, Czech Republic), 100 µL of pyridine (p.a. Lach:ner, Neratovice, Czech Republic), and 4 mL of cyclohexane (p.a., Lach:ner). The derivatization of each sample was derivatised at T = 25 °C for 40 min. Yield of esters Y_{esters} and conversion of triglycerides X_{TG} were calculated according to Equations (2) and (3):

$$Y_{esters} = (m_{esters}/m_{EP}) \cdot 100, \qquad (2)$$

$$X_{TG} = (m_{TG}^{before} - m_{TG}^{after})/(m_{TG}^{before}) \cdot 100$$
(3)

where m_{ester} is mass of all the esters in the sample, m_{EP} is the total mass of sample of the analysed EP. Finally, m_{TG}^{after} and m_{TG}^{before} are the masses of triglycerides in the reaction mixture after and before reaction respectively.

In order to evaluate the stability of the used catalysts, the amount of metals in the EP was determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 725). The same samples as in the previous paragraph were used for this experiment. Before determination,

the samples had to be mineralized according to the following procedure. Firstly, 10 mg of EP was mixed with *p*-toluenesulfonic acid (ca. 1 mg). Then, the mixture was stirred for ten minutes. Afterwards, the prepared mixture was inserted into the muffle oven, where the mixture was slowly heated until the temperature reached 500 °C. The obtained ashes were dissolved in 5 mL of sulphuric acid and the amount of metals was determined by a calibration curve method. The total amount of leached metals was evaluated after the experiment (i.e., after 120 h after the beginning of the reaction).

4. Conclusions

Layered double hydroxide-like precursors of Mg/Fe mixed oxides with various mass fractions of added carbon fibres (0.5, 1, 1.5, 2.5, and 4 wt.%) were prepared by a co precipitation method. The addition of carbon fibres significantly influenced the textural properties of the Mg/Fe mixed oxides although the amount of added carbon fibres had no significant effect on the activity of the catalysts. The increasing amount of added carbon fibres increased the portion of large macropores, which are necessary for transesterification of large molecules such as triglycerides. The modification of LDHs by carbon fibres improved the catalytic properties of Mg/Fe mixed oxides. Moreover, heterogeneous catalysts are more environmentally friendly as opposed to homogeneous ones since they do not require as much washing water. Owing to these benefits, the production of methyl esters with carbon fibres modified catalysts is more sustainable as the catalytic activity of modified catalyst is improved.

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