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Preparation of Methyl Ester by Heterogeneous Catalysed Esterification and Transesterification

Martin Hájek, Jaroslav Kocík, Lucie Smoláková, Pert Kutálek, Libor Čapek

Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic
martin.hajek2@upce.cz

The aim of this work is to study and test two types of catalyst – acid and basic for the preparation of methyl esters. The first goal is to describe the transesterification catalysed by Mg-Al mixed oxides in a broad range of Mg/Al ratio (from 1.0 to 8.4) including the relation between the variables by statistical analysis and catalyst stability. The mixed oxides with a different Mg/Al molar ratio were synthesized by thermal pre-treatment of hydrotalcite at 450 °C. The influence of the Mg/Al molar ratio on the yield of ester, leaching of magnesium and catalyst properties such as the concentration of basic sites, crystallite size of MgO and specific surface area were studied. It was found that the crystallite size and the yield of ester increases and the concentration of basic sites decreases with an increasing Mg/Al molar ratio; the specific surface area does not depend on the Mg/Al molar ratio. The relation between the variables was described by statistical analysis (the correlation matrix and principal component analysis). There was observed only negligible magnesium leaching from solid Mg/Al mixed oxides to the liquid phases.

Five types of zeolites (MOR-C and D, ZSM-5, Y and mesoporous BEA) were tested in the esterification of oleic acid and the results were compared with pure alumina. The highest yield exhibited mesoporous BEA. The comparison of catalytic and non-catalytic esterification was carried out at the same reaction conditions.

1. Introduction

Methyl esters (biodiesel) are an ecological fuel and are produced by transesterification of triglycerides contained in vegetable oils by low molecular alcohols. Reaction is usually catalysed by a basic homogeneous catalyst (KOH or NaOH). This way has several disadvantages (e.g. saponification of oil, reuse of catalyst is impossible), therefore nowadays research has turned to heterogeneous catalysts, one of them is mixed oxides as a basic catalyst or zeolites as an acid catalyst. Other sources such as animal fats, waste and frying oils can also be used. The disadvantage of these sources is that they contain a higher amount of free fatty acids and water, which supports the saponification reaction (reaction between hydroxide and oil) and therefore reduction in the product yield. For this reason, use of a basic catalyst is not possible. The first step of ester production is the decreasing of fatty acids by acid-catalysed esterification and the second step is basic-catalysed transesterification. Therefore two different catalysts are necessary and in this paper both types were studied.

The Mg/Al mixed oxides are advantageously prepared by thermal pre-treatment of Mg/Al hydrotalcites. Hydrotalcites are layered materials known also as anionic clays or layered double hydroxides with a general formula. The symbol M represents bivalent or trivalent metallic cations, A represents an anion and x is the molar ratio of M3+. The combination and ratio of metallic ions influence the structure and chemical properties of hydrotalcites. A controlled thermal decomposition of hydrotalcite-like precursors leads to the formation of finely dispersed mixed oxides with a large surface area. This oxide possesses strong surface basicity, high surface area and a high quantity of defects resulting from the incorporation of Al^{3+} in the MgO lattice. Mg-Al mixed oxides are attractive catalysts for reactions such as transesterification (Castro et al., 2013) – focusing on basicity and (Shumaker et al., 2008) focusing on the structure, as well as aldol or Knoevenagel condensation (Abello et al., 2008). Many authors study the system (catalyst characterization and transesterification) separately for narrow range of molar ratio Mg/Al (usually 2-4) (Carvalho et al., 2012). However, we study the system together.

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Zeolites are natural substances, with a general formula M2/nO.Al2O3.xSiO4.yH2O, where M is the type of cation, n is valence, x is the amount of SiO4, which is always more than 2 and y is the number of bonded water. Zeolites have a channel structure with the size of each channel ranging from 2.5 to 10 Å and have a large specific surface area and they can be used as a catalyst or carrier of active components. In this paper, Mg/Al mixed oxides with a different Mg/Al molar ratio and several zeolites were tested in the transesterification and esterification by methanol. For mixed oxides, XRF, XRD, N_2 adsorption and TPD-CO_2 were used for the determination of chemical composition, surface area and basic strength. The relation among specific surface area, ester yield, crystallite size of MgO and concentration of basic sites as dependent variables on the Mg/Al molar ratio (independent variable) was described. The comparison of esterification with and without a catalyst was carried out and it was found that the highest yield has mesoporous BEA.

2. Experimental part

2.1 Preparation of heterogeneous catalyst

The Mg/Al hydrotalcites at different Mg/Al molar ratios were synthesized by the co-precipitation method with two solutions. Water was put into a batch reactor (1 L) and stirred. Then, 450 ml of the solution 1 (aqueous solution with different concentrations of $Al(NO_3)_3$ and $Mg(NO_3)_2$) was added to the reactor at a constant flow rate of 7.5 cm^3 min^{-1}. During addition, the pH value was kept constant at 9.5±0.1 by adding solution 2 (aqueous solutions of potassium basic precursors (K_2CO_3 + KOH)). The formed suspension was stirred for 1 h (75 °C, 1,400 rpm) and then filtered off and dried for 12 h at 105 °C. The precipitates were pre-treated at 450 °C for 4 h in the air to obtain Mg/Al mixed oxide. Zeolites were purchased from the company Zeolites and calcined at 450 °C or 700 °C for 4 h in air and then used in the esterification reaction.

2.2 Transesterification of oil and esterification of oleic acid

Rapeseed oil (cold-pressed, filtered rapeseed oil, acid number 1.2 mg KOH g^{-1}, water content 610 mg/kg, produced by RPN Slatiňany) and methanol p.a. (0.04 wt.% water) were used for the transesterification. Oil, methanol (methanol to oil molar ratio of 24:1) and catalyst (4 wt.% of catalyst based on the weight of rapeseed oil) were put into the pressure steel reactor and heated to the reaction temperature of 117 °C and the stirring intensity was set to 320 rpm. The volume of the reactor was 150 cm^3, while the total volume of oil and methanol was 130 cm^3. According to the Antoine equation, temperature and free volume of reactor (20 cm^3) was calculated that virtually all methanol was present in the liquid phase. After the reaction (8 h), the heterogeneous catalyst was filtered off and the methanol was evaporated from the reaction mixture (2 kPa and 65 °C). After separation, the methyl esters were determined in the ester phase and magnesium ions were determined in both phases. The esterification was carried out in the same type of reactor under the same conditions, but using oleic acid (not rapeseed oil).

The content of methyl esters (or methyl oleate) in the ester phase (EP) was determined by the GC method according to EN 14105 using Shimadzu GC-2010 with the help of linear calibration curves of pure methyl esters. The standard deviation of this method is less than 0.001 % (Oostdijk, 2011). The methyl esters were identified in the chromatogram and their calibrations were prepared by homogeneous transesterification from the same oil. The magnesium ions were extracted from the ester phase to water and its concentrations were determined by atomic absorption spectroscopy SensAA (GBC, Australia) with the help of a calibration curve.

2.3 Characterization of Mg/Al materials

The chemical compositions were determined by energy-dispersive XRF spectrometer Elva X equipped with a W anode X ray tube. Specific surface area was measured at the boiling point of liquid nitrogen. X-ray diffractograms were recorded with a Bruker AXS D8-Advance diffractometer using Cu Kα radiation. The average crystallite size of MgO-like phase of mixed oxides was calculated by the use of Scherrer's formula. Temperature programmed desorption of carbon dioxide as a probe molecule (TPD-CO_2) was carried out in an AutoChem 2920 equipped with a TCD detector and quadrupole mass spectrometer (Capek at al., 2013).

2.4 Statistical analysis

The program STATISTICA 10 (StatSoft®) was used for statistical analysis. The regression and statistical testing were performed with respect to the regression triplet at the statistical significance level of 0.05. The principal component analysis (PCA) and the correlation matrix were calculated to determine the relation between dependent variables, which are unknown from the natural patterns.

3. Results and discussion

3.1 Basic catalyst - Mg/Al mixed oxides

The characterization of the catalyst: the list of Mg/Al mixed oxides is summarized in Table 1, which also states their properties such (dependent variables) as the chemical composition (Mg/Al molar ratio), crystallite size (*D*), concentration of basic sites (*CBS*) and specific surface area (S_{BET}). These dependent variables are depicted on the Mg/Al molar ratio as an independent variable in Figure 1.

Table 1: List of Mg/Al mixed oxides

Mg/Al molar ratio	*D(MgO)* (nm)	*CBS* (μmol CO_2/g)	S_{BET} (m^2/g)	Y_{ester} (wt.%)	Mg leaching (wt.%)
1.0	2.1	402.2	334.5	50.4	0.8
1.8	3.1	367.9	112.9	60.7	0.31
2.7	3.4	258.1	235.9	61.4	0.35
3.5	4.6	165.1	173.8	59.5	0.12
4.4	5	133.1	244.3	62	0.68
8.4	5	140.4	221.3	65.1	0.29

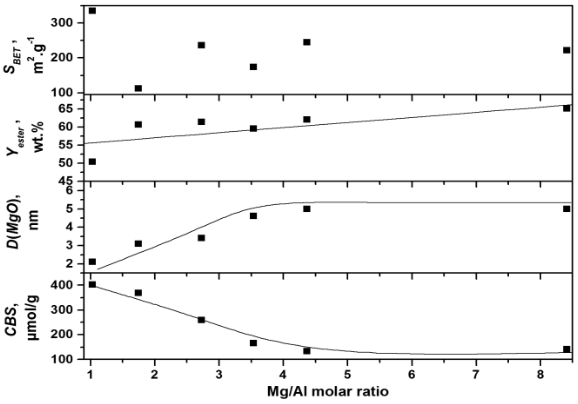

Figure 1: dependence of specific area, ester yield, crystallite size and concentration of basic sites on Mg/Al

Figure 2A shows the Mg/Al hydrotalcite with the Mg/Al molar ratio 1.0-8.4. The intensive lines (at 11.0, 22.2, 34.2, 38.2, 45.1, 59.9 and 61.3 °) are typical for this structure and show the double-layered structure. Fig. 2B shows the diffractograms of mixed oxides: two intensive lines (43.0 and 62.4 °) are characteristic to MgO-like phase or magnesia–alumina solid solution in Mg/Al mixed oxides (Kustrowski et al., 2004). These lines indicate destruction of the hydrotalcite structure after thermal pre-treatment.

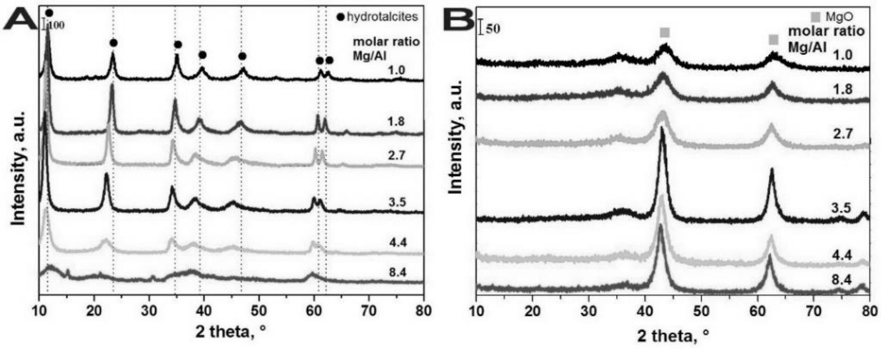

Figure 2: diffraction lines of Mg/Al hydrotalcites (A) and Mg/Al mixed oxides (B)

The crystallite size of MgO was calculated from the diffraction line at 62 ° by using the Scherrer's formula. It increases linearly with an increasing Mg/Al molar ratio to 4 and then has approximately a constant value (Table 1, Figure 1). This outcome is difficult to compare with other papers, because authors usually do not determine the crystallite size for mixed oxides (only for hydrotalcite). For hydrotalcite, an increase in the Mg/Al molar ratio caused increasing (Perez et al., 2004), decreasing (Olfs et al., 2009) and no significant effect (Di Serio et al., 2004) on crystallite size of Mg/Al hydrotalcites, therefore this dependency is ambiguous.

TPD-CO_2 profiles of Mg/Al mixed oxides are shown in Figure 3. CO_2 desorption peak was observed between 25 and 475 °C, which could be attributed to desorption of CO_2 from weak, medium and strong basic sites (Bolognini et al., 2002). Total concentration of basic sites (*CBS*) was calculated as total amount of desorbed CO_2 (Table 1).

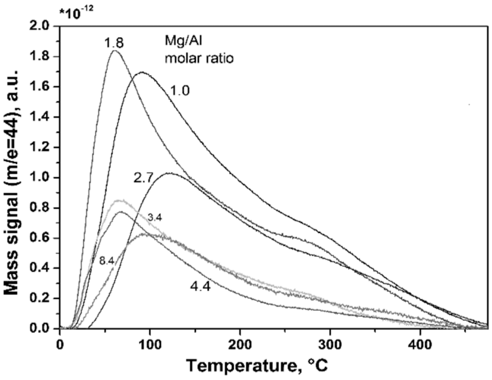

Figure 3: TPD-CO_2 profiles of Mg/Al mixed oxides pre-treated at 450 °C

The concentration of basic sites decreased with an increasing Mg/Al molar ratio and was limited to approximately the same value 130-140 μmol CO_2/g (Table 1). This is in contrast to observations by other authors studying the basicity of Mg/Al mixed oxides. Bolognini et al. (Bolognini et al., 2002) reported no unambiguous dependence of the amount of basic sites on the Mg/Al molar ratio ranging from 1.8-3.7 and Veloso et al. (Veloso et al., 2008) reported an increasing amount of basic sites with the Mg/Al molar ratio ranging from 2.3-4. Jinesh et al. (Jinesh et al., 2010) observed an increase in the amount of basic sites from 2.1 to 2.8 Mg/Al molar ratio and after that its decrease from 2.8 to 4.3. The reason for various observed dependencies is the fact that the dependent variables can be influenced by other parameters or by each other. Thus, we have performed statistical analysis of these hidden dependencies, which is published in this work for the first time.

The specific surface area (S_{BET}) has no clear relation to the Mg/Al molar ratio (Figure 1). Our results are in agreement with observations of other authors who investigated stability (Abello et al., 2008) and also looking into soybean oil as raw material (Kustrowski et al., 2004), who also did not find any clear relation between the S_{BET} and the Mg/Al molar ratio. On the other hand, Veloso et al. (Veloso et al., 2008) and Pérez et al. (Perez et al., 2004) published that the specific surface area of Mg/Al mixed oxides increases with an increasing of the Mg/Al molar ratio from 2.3 to 4. This is in contrast to Jinesh et al. (Jinesh et al., 2010) who observed that the S_{BET} decreases with an increasing Mg/Al ratio from 2.1 to 4.3.

Table 2: The correlation matrix

	D(MgO) (nm)	*CBS* (μmol CO_2/g)	S_{BET} (m^2/g)	Y_{ester} (wt.%)	Mg leaching (wt.%)
D(MgO) (nm)	1	**-0.986**	-0.087	**0.812**	-0.069
CBS (μmol CO_2/g)	**-0.986**	1	0.029	**-0.771**	-0.145
S_{BET} (m^2/g)	-0.087	0.029	1	-0.086	0.106
Y_{ester} (wt.%)	**0.812**	**-0.771**	-0.086	1	-0.105
Mg leaching (wt.%)	-0.069	-0.145	0.106	-0.105	1

Transesterification: The mixed oxides showed the ester yield from 50 to 65 wt.% and increased with an increasing Mg/Al molar ratio. Since the activity of Mg/Al mixed oxides was studied at various catalyst synthesis and reaction conditions by authors (Georgogianni et al., 2009; Silva et al., 2010), it is difficult to draw clear conclusions and comparison. Furthermore, the content of K and Mg metals was determined in liquid products. Firstly, the potassium ions can remain in Mg/Al mixed oxides after their synthesis. It can leach during the reaction and affect the final apparent activity by acting as a homogeneous catalyst. The potassium concentration was determined in all samples and it was always less than 4 mg kg^{-1} and could not affect the final activity of the mixed oxides. Secondly, Table 1 contains the amount of magnesium leached from the solid Mg/Al mixed oxide catalyst into liquid products. The leaching of Mg was 0.12-0.8 wt.% Mg, i.e. all prepared catalysts were relatively stable during the reaction. In literature, the activity and stability of Mg/Al mixed oxides is still a matter of discussion. Zeng et al. observed that Mg/Al mixed oxides prepared by the urea method were stable at least for 5 cycles, or 3 cycles (Zeng et al., 2008), but the catalytic activity decreased sharply then.

The statistical analysis: Complex statistical analysis of all results was carried out, which is in contrast to other papers, where variables are usually studied individually. The correlation matrix (Table 2) was calculated to determine the relation between dependent variables. This analysis helps to better understand the mutual relations between variables. The nonparametric Spearman's rank correlation coefficients were used for a calculation of the correlation matrix, numbers highlighted in bold correspond to a pair of parameters that show a correlation: positive (+) or negative (-).

It can clearly be seen from Table 2 that the magnesium leaching has no correlation with other variables. The MgO crystallite (D(MgO)) size has a positive correlation with the ester yield and a negative correlation with CBS, i.e. the higher the crystallite size, the higher the yield of ester and the lower CBS. The yield of ester has a positive correlation to the crystallite size and a negative correlation to CBS. The results of PCA confirm the results of the relation from the correlation matrix. This statistical analysis is valid for the whole range of Mg/Al.

3.2 Acid catalyst – zeolites

Five types of acid heterogeneous catalysts calcined at 450 °C were used for esterification of oleic acid (Table 3) and compared with pure alumina. The highest yield of ester has mesoporous BEA (76 wt.% for the first and 71 wt.% for the second used), which is probably caused by the highest channels in the zeolite structure (Egeblad et al., 2007). The yield of the second use of the catalyst was always lower than the first, which is probably caused by the inactivation of some active centres.

Table 3: Comparison of various heterogeneous acid catalysts (calcined at 450 °C)

Type of catalyst	Yield of esterification (wt.%)	
	First use	Second use
pure alumina	36	-
MOR-C – DEAL*	42	31
MOR-D – DEAL*	45	36
ZSM-5 – DEAL*	59	34
Y – DEAL*	54	36
mesoporous BEA	76	71

* DEAL means dealumined

Table 4: Comparison of conversion for esterification with and without catalyst (mesoporous BEA)

Reaction temperature (°C)	Molar ratio methanol/oleic acid	Catalyst	Conversion (wt.%)
117	6:1	no	53
		yes	56
	24:1	no	48
		yes	76
60	6:1	no	10
		yes	25
	24:1	no	3
		yes	20

It was found that the catalyst activity was influenced by the channel sizes and the thermal post-treatment. For ZSM-5 and Y zeolite calcined at 450 °C, the conversion 59 wt.%, resp. 54 wt.% was reached. The channel structure is obtained after calcination and both zeolites exhibit similar activity, however the zeolite ZSM-5 has strong acid sites, while zeolite Y has only moderate acid sites (Chung and Park, 2009). The reason for the similarity of both zeolites is in the different size of the channel: zeolite Y has a larger size of channel than zeolite ZSM-5 and therefore the internal diffusion of reactants is easy for zeolite Y. Both zeolites were also calcined at 700 °C: the activity of ZSM-5 increased to 75 wt.%, which can be attributed to the creation of defects and increases the number of strongly accessible acidic sites. On the other hand, the yield of zeolite Y was decreased to 10 wt.%, because the channel structure was broken.

The papers dealing with zeolites in an esterification reaction usually omit a comparison of esterification with and without a catalyst under the same reaction conditions. Therefore, the esterification by mesoporous BEA (which is the most active) was tested under various reaction conditions (two reaction temperatures – 60, 117 °C and two molar ratios methanol to oleic acid - 6:1, 24:1) and the results were compared with esterification without a catalyst under the same reaction conditions (Table 4). The catalyst has a positive effect on esterification, which was expected. The highest difference was reached in the case of 117°C and molar ratio 24:1.

4. Conclusion

The Mg/Al mixed oxides with different Mg/Al molar ratios from 1.0 to 8.4 were synthesized by thermal pre-treatment of hydrotalcite-like precursors at 450 °C. The relations of dependent variables (specific surface area, the ester yield, crystallite size of MgO and total concentration of basic sites) on the Mg/Al molar ratio as independent variable were described. It has been found that the MgO crystallite size and ester yield increase and concentration of basic sites decreases with an increasing Mg/Al ratio. On the other hand, the specific surface area has no clear relation to the Mg/Al molar ratio. Moreover, the relations between individual independent variables were described by the statistical analysis: the positive relation of the ester yield and the MgO crystallite size, negative relation of total basic sites between the ester yield and the MgO crystallite size and no relation of specific surface area to other variables. It has been found that the ester yield increased with an increase in the Mg/Al molar ratio, crystallite size of MgO and with a decrease in the total amount of basic sites. The significant of these relations consist in better understand of catalyst behavior in the reaction and so synthesis of catalyst with high catalyst activity and stability.

Zeolites: the comparison of esterification with and without a catalyst was carried out. It was shown, that zeolites are relatively stable and suitable catalysts, but only for higher ratios of methanol to oil. The highest yield has mesoporous BEA with the greatest channel size. In the case of 117 °C and ratio of methanol to oil 6:1, the zeolites have no significant effect.

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