The basicity of mixed oxides and the influence of alkaline metals:

the case of transesterification reactions

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Abstract

Several M(II)/M(III) mixed oxides were prepared and tested in two different transesterification reactions, biodiesel production from sunflower oil and methanol, and the more demanding transesterification of methyl palmitate with isobutanol. The presence of residual alkaline ions after crystallization is the main source for the strong basicity in this kind of solids, as it happened with Mg/Al mixed oxides. The effect of these alkaline traces is more evident with the most demanding reaction, in which the alkaline-free solids did not show any catalytic activity. These results seem to indicate that the strong basicity in mixed oxides is always connected to the presence of alkaline metals, irrespective from the nature of M(II) and M(III).

Keywords: Transesterification, hydrotalcite, mixed oxide, basicity, leachable basicity.

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1. Introduction

The nature of the basic sites in heterogeneous catalysts [1] is still poorly understood and this is probably one of the reasons for the relatively scarce application of solid basic catalysts in organic reactions. Mg-Al mixed oxides and analogues with other divalent (Ca, Zn) and trivalent cations (La, Ga), prepared from mixed hydroxides with hydrotalcite structure of general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$ [2], have been reported as excellent basic catalysts for different organic reactions [3]. In the case of transesterification reactions, such as biodiesel production or analogous model reactions, several mixed oxides have been used as catalysts [4-11]. Solids were prepared by precipitation with sodium [5,7-11] or ammonium [4,11] bases, commercially available hydrotalcite was found active [6] or inactive [7] in different works, and the effect of the composition on activity was also found different in several papers [4,5,8,9,11], conforming a quite puzzling set of results.

In these solids several basic sites have been proposed from calorimetric and spectroscopic measurements [12], that have been identified as O^{2-} (strong), Mg-O pairs (medium), and OH^- (weak) groups. Discrepancies were observed in the number of basic sites determined by TPD/calorimetry of CO_2 [12,13] and titration using different Hammett indicators [5] over mixed oxides *a priori* prepared in the same way. Moreover soluble basicity was detected in several cases [5,11]. The term leachable basicity was introduced in a previous paper [14] to reflect the potential homogeneous character of the strong basic sites. As can be seen from those results, the nature and amount of the basic sites are intriguing features of the mixed oxides obtained from hydrotalcite calcination. The discrepancies observed in the basicity determination, even using the same method, may be due to the inconsistency of the method itself, or to the lack of reproducibility in

the hydrotalcite preparation, leading to solids with very different basic properties and hence difficult to compare from one work to another.

The presence of trace of alkaline metals was proposed as the origin of the strong and leachable basicity in Mg-Al mixed oxides [14,15]. The difficulty in reproducing the preparation method and the lack of strong basicity of the thoroughly washed solids make almost impossible the practical application of the Mg-Al mixed oxides in reactions requiring strong bases in quite polar reaction media.

Other mixed oxides have been reported as basic catalysts, such as Zn-Al and Mg-Zn-Al mixed oxides [9,16–18] or Mg-La mixed oxides [19], and they have been used in transesterification reactions. In this paper we explore the generality of the role of alkaline metals in the basicity of different mixed oxides, by their application in transesterification reactions.

2. Experimental

2.1 Mg-Zn-Al and Zn-Al catalysts preparation (general procedure)

250 ml of an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ of the desired Mg/Zn/Al ratio (total metal concentration 1M) were slowly added to 600 ml of distilled water at 333K. At the same time a 2.4 M solution of Na_2CO_3 and NaOH (Na_2CO_3/NaOH = 0.06) was added in order to maintain pH at the desired value (10 or 7 ± 0.2). The solids were named with the metals ratio and the precipitation pH: for example $Mg_8Zn_1Al_1(10)$ is a solid prepared with a Mg/Zn/Al ratio = 8:1:1 at pH = 10. When all the metal solution was added, the mixture was kept at 333K for two hours. The solid was filtered and washed with distilled water at 333K. Typically as-prepared solids were washed with 500 ml of water, whereas for thoroughly washed solids a volume of 3-4 l of water was used. Then the solid was dried overnight at 343K. The catalyst precursor was sieved at a particle size between 160 to 400 μm and calcined under N_2 flow at 723K for 14 h.

2.2 Preparation of $Zn_4Al_1(7-NH_4)$

200 ml of an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Zn/Al ratio = 4, total metal concentration 1M) was slowly added to 600 ml of distilled water at 333K. At the same time 40 ml of a 1 M solution of Na_2CO_3 was added in order to maintain pH at 7 ± 0.2 and, once consumed, the pH was maintained by addition of a 1M solution of NH_4OH.

When all the metal solution was added, the mixture was kept at 333K for two hours. The solid was filtered and washed with distilled water at 333K. Then the solid was dried

overnight at 343K. The catalyst precursor was sieved at a particle size between 160 to 400 μm and calcined under N_2 flow at 723K for 14 h.

2.3 Mg-La catalysts preparation (general procedure)

The catalyst was prepared according to the method described by De Vos and coworkers [20]. A solution of 0.132 mol of Na_2CO_3 in 100 ml of water was slowly added (rate of 1.6 ml/min) to 200ml of an aqueous solution of 0.09 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.01 mol of $La(NO_3)_3 \cdot 4H_2O$. When all the basic solution was added, the mixture was kept at 353K for one hour. The solid was filtered and washed with distilled water. Then the solid was dried overnight at 343K. The catalyst precursor was sieved at a particle size between 160 to 400 μm and calcined under N_2 flow at 713K or 873K for 14 h. $Mg_9La_1(NH_4)$ was prepared by the same method but the Na_2CO_3 solution was substituted by 100 ml of NH_4OH 30%.

2.4 Mg-Al and Mg-Ga catalysts preparation (general procedure)

An aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ or $Ga(NO_3)_3 \cdot xH_2O$ of the desired Mg/M^{+3} ratio (total metal concentration 1M) was slowly added to 700 ml of distilled water at 333K. At the same time a 2.4 M solution of Na_2CO_3 and NaOH (Na_2CO_3/NaOH = 0.06) was added in order to maintain pH at the desired value (10 ± 0.4). When all the metal solution was added, the mixture was kept at 333K for two hours. The solid was filtered and washed with distilled water at 333K. Then the solid was dried overnight at 343K. The catalyst precursor was sieved at a particle size between 160 to 400 μm and calcined under N_2 flow at 723K for 14 h.

2.5 Catalyst characterization

Analyses of metals (Mg, Ga, La, Zn, Al, Na) were carried out by plasma emission spectroscopy on a Thermo Elemental, IRIS Intrepid Radial emission spectrometer.

Step scanned X-ray diffraction patterns of oriented samples were collected at room temperature from 3º in 2θ up to 80º, using D-Max Rigaku system with a rotating anode.

XPS measurements were carried out on an Axis Ultra DLD (Kratos Tech.) with monochromatizedAl$K\alpha$ source (1486.6 eV) at 15 kV and 10 mA. Samples were evacuated at room temperature.

Surface areas were determined by N_2 adsorption (BET) using a MicromeriticsASAP 2020 apparatus. Typically, 0.2 g of calcined solid was used for measurements. Prior to N_2 adsorption, the sample was outgassed for 4 h at 423K.

Thermogravimetric analysis (TGA) was performed using a TA Instruments STD 2960 simultaneous TGA-DTA at a rate of 10ºC/min under synthetic air atmosphere. TGA data are given as the onset of decomposition curve. In addition, the first derivative of decomposition curve (DTGA) was read.

The quantitative determination of basicity was done by titration with benzoic acid [5, 21]. A suspension of calcined solid (0.15 g) in a toluene solution of phenolphthalein (2 ml, 0.1 mg/ml) was stirred for 30 min and then titrated with a toluene solution of benzoic acid (0.01 M) to determine the total basicity. A sample of calcined solid (0.5 g) was shaken in water (50 ml) for 1h at room temperature, the catalyst was filtered off, a methanol solution of phenolphthalein (5 ml, 0.1 mg/ml) was added to the filtrate, which was titrated with a methanol solution of benzoic acid (0.01 M) to determine the leachable basicity.

2.6 Transesterification reaction of sunflower oil with methanol

Transesterification reaction of sunflower oil with methanol was carried out in a round flask under reflux using 2g of oil, 3 ml of methanol and catalyst/oil ratio 10% (w/w) for 3 h. The catalyst was filtered off and washed with methanol and ether. The crude reaction mixture was analyzed by gas chromatography using eicosane as internal standard. The GC analysis was performed using an HP-5890-II chromatograph equipped with FID detector, an SPB-5^{TM} column: 30m x 0.25mm x 0.25 μm, He as carrier gas 20 psi temperature: 280 ºC; detector temperature: 300 ºC; oven program: isotherm 205 ºC (30 min), retention times: eicosane 6.9 min, methyl palmitate 5.7 min, methyl estearate 9.1 min, methyl oleate 9.2 min, methyl linoleate 9.8 min

2.7 Transesterification reaction of methyl palmitate with isobutanol.

Methyl palmitate transesterification was carried out in a round flask at 85ºC using 2.59 mmol of methyl palmitate (0.7 g), 0.25 g of catalyst, 40.63 mmol of isobutanol (3.75 ml) and 0.2 g of 1-methylnaphthalene as internal standard. After 4 h, the catalyst was filtered off and washed with CH_2Cl_2. The crude reaction mixture was analyzed by gas chromatography using the same apparatus as in transesterification of sunflower oil. Injector temperature: 250ºC; detector temperature: 280ºC; oven program: initial temperature 200 ºC (10 min) rate 5ºC/min, final temperature 250ºC (10min). Retention times: 1-methylnaphthalene (standard) 2.3 min, methyl palmitate 6.7 min, isobutyl palmitate 12.2 min.

3 Results and Discussion

3.1 Mg-Zn-Al mixed oxides

a) Preparation and characterization

Mg-Al mixed oxide with Mg/Al ratio of 9 was chosen as starting point, given the good results obtained with this solid in previous work [14]. Zn was introduced to substitute part of the Mg, and two solids were prepared by co-precipitation method at constant pH = 10, $Mg_8Zn_1Al_1(10)$ and $Mg_4Zn_5Al_1(10)$. The pH was controlled by means of a Na_2CO_3/NaOH solution. The precipitated precursor showed several crystalline phases (Figure 1A), including ZnO, hydrotalcite structure with low crystallinity, and $NaNO_3$, together with other unidentified peaks. The thoroughly washed material is composed only by ZnO and hydrotalcite with lower crystallinity than in the poorly washed material. In the case of the poorly washed precursor, calcination gives rise to a highly crystalline solid (Figure 1B), containing at least three identified crystalline species, ZnO, MgO and $NaNO_3$, whereas the thoroughly washed precursor produces only ZnO and poorly crystalline MgO.

<div align="center">Figure 1 near here</div>

The adequate incorporation of Zn, Mg, and Al within the mixed oxides was verified by elemental analysis. All the ratios (Table 1) were in good agreement with the composition of the starting solutions, demonstrating the suitability of the precipitation conditions. Unwashed (only filtered) Mg-Zn-Al mixed oxides retain an important amount of sodium from the precipitation solution, and thorough washing with a huge amount of water is necessary in order to eliminate almost completely ($\leq$ 0.25 mmol/g) the traces of Na present in the solids [3]. Solids with high sodium content present a very

low surface area, whereas the thoroughly washed solids show values in the expected range for Mg-Al mixed oxides. The disappearance of the highly crystalline $NaNO_3$ phase, together with the lower crystallinity of the remaining phases after thorough washing may account for this effect on surface area.

Table 1 near here

Several Zn-Al solids without Mg were prepared under different conditions. A solid with Zn/Al = 4 was prepared using the same procedure at pH 10. As Zn is less basic than Mg, lower pH can be used to precipitate the mixed hydroxide, and a solid with the same composition was prepared at pH 7. As can be seen in Fig. 2 both solids show completely different crystallinity. $Zn_4Al_1(10)$ (Fig. 2A) is a well crystallized hydrotalcite, that retains $NaNO_3$ together with other crystalline materials before thorough washing. $Zn_4Al_1(7)$ (Fig. 2B) is a poorly crystalline solid, with different Zn species, such as $Zn(OH)_2$ and $Zn_5(CO_3)_2(OH)_6$, in which hydrotalcite is only detectable after washing.

Figure 2 near here

Calcination of all those precursors mainly produced ZnO with low crystallinity (Fig. 3), with almost no influence of the structure of the precursor. The Zn/Al ratio (Table 1) was consistent with the composition of the solution, and the sodium amount in as-prepared solids was lower than in the Mg-Zn-Al solids and even lower when the synthesis was carried out at neutral pH.

Figure 3 near here

Another solid with Zn/Al=1 was prepared also at neutral pH. The structure was similar to that of $Zn_4Al_1(7)$, but with lower crystallinity (not shown). Composition of the as-synthesized solid was in agreement with the initial solution, but thorough washing reduced the amounts of both Al and Na (Table 1).

Trying to control the Na amount just in the as-synthesized precursor, another solid $Zn_4Al_1(7-NH_4)$ was prepared maintaining the pH first with Na_2CO_3 until a theoretical Na content of 2 mmol/g in the final solid, and then with NH_4OH. This precursor shows the peaks corresponding to $Zn(OH)_2$ and $Zn_5(CO_3)_2(OH)_6$ species (Fig. 4Aa), whereas the hydrotalcite structure is only clearly visible after thorough washing (Fig. 4Ab). After calcination (Fig. 4B) highly crystalline ZnO is easily identified in the case of the poorly washed precursor. As expected this solid contained much lower amount of Na than the analogous prepared with $Na_2CO_3/NaOH$ (Table 1).

<center>Figure 4 near here</center>

The total number of basic sites was determined by titration with benzoic acid using phenolphthalein as indicator in toluene. Leachable basicity was determined by washing the solid in water and titration of the leachate also with benzoic acid and phenolphthalein. Results are gathered in Table 2. As can be seen, the as-prepared Zn-Al solids show high basicity, both total and leachable, in agreement with the high sodium content (Table 1). However there is no direct correlation between both magnitudes, demonstrating the different nature of the sites involved. The big exception is the case of Mg-Zn-Al solids, whose total basicity is very low, in contrast with the high leachable basicity. This may be due to the very low surface area of the solids (<3 m^2/g), which hides the sodium sites inside the structure and prevents the titration in toluene, whereas water washing is able to leach those sites. Thoroughly washed solids show in general values of leachable basicity below the limit of 0.15 mmol/g, necessary to obtain good catalytic results in the case of Mg-Al mixed oxides [14].

<center>Table 2 near here</center>

b) Transesterification of methyl palmitate with isobutanol.

As the catalytic activity of (Mg)-Zn-Al mixed oxides in transesterification of oils had been already demonstrated in the literature [9,16–18], these solids were tested in a more demanding reaction, the transesterification reaction of methyl palmitate with isobutanol (Scheme 1), a branched primary alcohol [14]. Results are gathered in Table 3.

<center>Scheme 1 near here</center>

<center>Table 3 near here</center>

As the best results with Mg-Al mixed oxides had been obtained with $Mg_9Al_1(10)$, the first tests were carried out with Zn-containing solids keeping constant the M(III)/M(II) ratio. Both solids, $Mg_8Zn_1Al_1(10)$ and $Mg_4Zn_5Al_1(10)$, showed rather low catalytic activity, in spite of the high sodium content (Table 1). The disagreement between Na content, total basicity, leachable basicity and catalytic activity may come from the different nature of the media in which those measurements are carried out. In toluene, the highly crystalline species (Fig. 1Ba) are completely insoluble and the low surface area leads to a very low total basicity determined on the surface. In the transesterification medium, the solubility is higher, leading to a partial leaching of species and a catalytic activity higher than that of the solids with similar total basicity, such as the thoroughly washed Zn_4Al_1 solids (both prepared at pH 10 and 7). However, given the high solubility of the crystalline species in water, the leachable basicity is much higher in the solids with very high Na content, a result which has no correspondence with the catalytic activity in a different medium. The thoroughly washed solids led to even worse results, in agreement with their greatly reduced basicity, both leachable and total.

On the contrary as-prepared $Zn_4Al_1(10)$, with high sodium content and very high leachable basicity, showed as expected very high catalytic activity. With this solid was possible to reduce both the excess of isobutanol and the reaction temperature. However,

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the thoroughly washed solid, with leachable basicity below the 0.15 mmol/g limit, lost almost completely the catalytic activity. In the case of $Zn_4Al_1(7)$, the lower pH produced a reduction in the sodium content of the as-prepared solid, from 4.5 to 2.3 mmol/g (Table 1), and also in the leachable basicity, from 2.60 to 0.94 mmol/g (Table 2). However this new solid also showed very high activity (Table 3), even at mild reaction conditions, activity that again disappeared after thoroughly washing. A similar result was obtained with a different composition, $Zn_1Al_1(7)$.

The sodium content in the as-prepared solid was further reduced in $Zn_4Al_1(7\text{-}NH_4)$. As a consequence this solid showed much lower catalytic activity that utterly disappeared after thorough washing.

A simulation of the role of Na ions was carried out by doping of the thoroughly washed $Zn_4Al_1(7)$ and $Zn_1Al_1(7)$ with different amounts of sodium salts, followed by calcination. The results of catalytic activity are gathered in Table 4.

Table 4 near here

As can be seen the post-synthesis addition of Na is not able to reproduce the high catalytic activity of the as-prepared solids with similar Na content. Na_2CO_3 and $NaNO_3$ are the most efficient sodium salts for this purpose. Given that the optimal catalytic activity is obtained with solids containing 2.3-4.5 mmol Na/g, a value in this range (3.75 mmol/g) was chosen as optimal loading. In fact this seems to be also the case with added Na, given the detrimental effect of either lower loading (0.95 mmol/g) or larger excess of Na (5.66 or 7.55 mmol/g). A poorer Na dispersion on the surface may account for this effect. The role of sodium on the activity of mixed oxides is again confirmed in the case of Mg is substituted by Zn as divalent metal, either in part or completely.

3.2 Mg-M(III) mixed oxides

a) Preparation and characterization

Once proved the role of alkaline cations in different M(II)/Al mixed oxides, aluminum was substituted by other trivalent metals, gallium and lanthanum, in another set of experiments to test the generality of the alkaline effect on the strong basicity of mixed oxides. All the Mg/M(III) solids were prepared by co-precipitation method at constant pH. A M(III)/(Mg+M(III)) ratio of 0.1 was chosen due to the fact that previous results with Mg-Al mixed oxides indicated a maximum activity for this solid composition [14]. Elemental analysis was used to determine the adequate incorporation of M(III) and Mg. All the ratios (Table 5) were in good agreement with the composition of the starting solutions. The co-precipitation method involves the use of sodium salts solutions and, as observed for the solids containing Zn, in all cases a certain amount of sodium remains in the solids even after thorough washing. In view of that, a solid free from sodium, $Mg_9La_1(NH_4)$, was also prepared using ammonium bases as co-precipitation medium.

<center>Table 5 near here</center>

The structures of the precursors and the mixed oxides were studied by XRD (Figure 5). The hydrotalcite structure was identified in the precursors containing Al and Ga, whereas this type of structure was not observable in the case of Mg_9La_1 precursor. After calcination, the peaks corresponding to MgO were apparent in all the solids. A broad peak from $2\theta = 20$ to 34 seemed to indicate also the presence of an amorphous phase, more important in the case of Al- and Ga-containing solids. In the case of the solids containing lanthanum, calcination at 773 K did not seem to be enough to obtain a mixed oxide, since a peak corresponding to $La_2(CO_3)_3$ ($2\theta= 29$) was still present (Fig. 5Ba). In the thermogravimetric analysis of this solid, the DTGA curve showed losses of weight at 523 K (10.5%), at 713 K (35.0%), and a residual loss of 3.5% at 873 K. This result

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indicated the need of calcination above 873 K for a total decomposition of carbonate species. XRD patterns of the solid calcined at 973 K showed good crystallinity and typical signals of mixed Mg/La oxide, La_2O_3 and MgO (Figure 6).

Figure 5 near here

Figure 6 near here

Total basicity and leachable basicity were again determined by titration with benzoic acid using phenolphthalein as indicator. Results are gathered in table 6. As can be seen, those solids containing a significant sodium amount also present a significant leachable basicity. In the case of low or no sodium content, the solids still showed a residual leachable basicity (< 0.1 mmol/g), the same tendency observed for Zn containing solids.

Table 6 near here

The influence of the presence of sodium in the leachable basicity was demonstrated by the good correlation observed when representing both parameters for $Mg_9M(III)_1$ solids (Figure 7), whereas no correlation can be found for total basicity and sodium content.

Figure 7 near here

b) Transesterification of sunflower oil with methanol

The transesterification of sunflower oil with methanol (Scheme 2) was used as reaction test for $Mg_9M(III)_1$ catalysts. Results of fatty acid methyl ester (FAME) yields are gathered in Table 7.

Scheme 2 near here

Table 7 near here

As can be seen, all the catalysts prepared with sodium bases, and hence containing a significant amount of Na (see Table 5), show a very high catalytic activity in the sunflower oil transesterification, with almost quantitative yields both cases. On the

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contrary, solids with low sodium content or the solid prepared with ammonium bases presents very poor activity irrespectively of the nature of the trivalent metal in the solid. Those results do not show any correlation with total basicity of solids, determined by titration with indicators of different acidity (Table 6). In fact the solid prepared with ammonium bases shows a number of basic sites close to the maximum. But these results clearly show that the presence of a minimum amount of alkaline ions and therefore a leachable basicity over 0.1 mmol/g is compulsory to achieve moderate to good yields in transesterification of sunflower oil.

The recovery of the solids without reactivation led to very poor catalytic activity. However, calcination under the same conditions allows an efficient recovery, but activity drops from the third run. This fact was carefully studied for the catalyst Mg_9La_1 and the loss of activity was closely related to the decrease of sodium content in the solid, from 90 % to 34% yield in the fourth run and from 0.22 mmol Na/g in the fresh catalyst to 0.08 mmol Na/g in the recovered one.

Relationship between sodium content and activity was even more evident when the solids were used as catalysts in a more demanding transesterification reaction such as the reaction of methyl palmitate with isobutanol (Scheme 1). As can be seen in Figure 8, moderate to high yields can be obtained in this reaction only with catalysts having sodium content over 0.22 mmol per gram. Catalysts with low or no sodium content exhibited yields under 5%. This fact demonstrated the need of the presence of alkaline ions in the mixed oxides for a good activity in transesterification reactions.

Figure 8 near here

Conclusions

The source of strong basicity in M(II)-M(III) mixed oxides is always the presence of traces of alkaline cations from the precipitation medium, irrespective from the nature of both M(II) (Mg or Zn) and M(III) (Al, Ga or La). This is very clear with highly demanding reactions with respect to basicity, as some transesterification reactions such as that of methyl palmitate with isobutanol. In this reaction solids free from alkaline cations are completely inactive under mild conditions, whereas they are still partially active in the less demanding transesterification of sunflower oil with methanol. The basic sites corresponding to residual alkaline cations are leachable to solution, and the degree of leaching depends on the nature of the reaction medium. This slow release of alkaline to solution under reaction conditions allows only a partial recovery of the catalyst, with irreversible deactivation of the strong alkaline-based sites. These results show the intrinsic limitation of alkaline-free mixed oxides as catalysts for this kind of demanding reactions.

Acknowledgements

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Table 1. Composition and surface area of Mg-Zn-Al mixed oxides.

Catalyst	Al/(Mg+Zn+Al)		Mg/Zn		Na content (mmol/g)	Surface area (m^2/g)
	Theoretical	Experimental	Theoretical	Experimental		
Mg_9Al_1(10)	0.10	0.12	-	-	1.22	96
thoroughly washed	0.10	0.10	-	-	0.02	172
$Mg_8Zn_1Al_1$(10)	0.10	0.10	8.00	7.60	27.98	2
thoroughly washed	0.10	0.11	8.00	6.85	0.25	176
$Mg_4Zn_5Al_1$(10)	0.10	0.10	0.80	0.88	12.10	3
thoroughly washed	0.10	0.10	0.80	0.85	0.11	95
Zn_4Al_1(10)	0.20	0.20	-	-	4.49	26
thoroughly washed	0.20	0.21	-	-	0.23	98
Zn_4Al_1(7)	0.20	0.20	-	-	2.29	43
thoroughly washed	0.20	0.19	-	-	0.25	102
Zn_1Al_1(7)	0.50	0.52	-	-	3.56	31
thoroughly washed	0.50	0.36	-	-	0.03	119
Zn_4Al_1(7-NH_4)	0.20	0.15	-	-	0.78	85
thoroughly washed	0.20	0.21	-	-	0.02	124

Table 2. Basicity of Mg-Zn-Al mixed oxides.

Catalyst	Total basicity (mmol/g)	Leachable basicity (mmol/g)
$Mg_9Al_1(10)$	0.51	0.21
thoroughly washed	0.50	0.14
$Mg_8Zn_1Al_1(10)$	0.13	4.28
thoroughly washed	0.26	0.21
$Mg_4Zn_5Al_1(10)$	0.11	3.55
thoroughly washed	0.21	0.17
$Zn_4Al_1(10)$	1.70	2.60
thoroughly washed	0.15	0.07
$Zn_4Al_1(7)$	1.06	0.94
thoroughly washed	0.17	0.07
$Zn_1Al_1(7)$	2.13	0.85
thoroughly washed	0.28	0.03
$Zn_4Al_1(7-NH_4)$	0.25	0.11
thoroughly washed	0.40	0.01

Table 3. Results from transesterification reaction of methyl palmitate with isobutanol catalyzed by Mg-Zn-Al mixed oxides.

Catalyst	iBuOH/ palmitate	Temp. (ºC)	Yield (1 h)	Yield (4 h)
$Mg_9Al_1(10)$	16	85	78	98
thoroughly washed	16	85	7	12
$Mg_8Zn_1Al_1(10)$	16	85	12	28
thoroughly washed	16	85	10	21
$Mg_4Zn_5Al_1(10)$	16	85	20	46
thoroughly washed	16	85	2	6
$Zn_4Al_1(10)$	16	85	99	-
	16	50	40	66
	4	85	28	74
thoroughly washed	16	85	2	6
$Zn_4Al_1(7)$	4	85	99	-
	4	50	84	99
thoroughly washed	4	50	1	2
$Zn_1Al_1(7)$	4	50	90	95
thoroughly washed	4	50	1	2
$Zn_4Al_1(7-NH_4)$	4	50	5	12
thoroughly washed	4	50	1	2

Table 4. Results from transesterification reaction of methyl palmitate with isobutanol catalyzed by Na-doped Zn-Al mixed oxides.[a]

Starting solid	Sodium salt (mmol Na/g)	Calcination temp. (°C)	Yield (1 h)	Yield (4 h)
$Zn_4Al_1(7)$	-	530	1	2
	Na_2CO_3 (3.75)	530	65	83
	reuse	530	24	47
	Na_2CO_3 (5.66)	530	29	58
	CH_3COONa (3.75)	530	21	44
	$NaNO_3$ (3.75)	900	4	5
	$NaNO_3$ (3.75)	530	51	74
	reuse	530	2	2
$Zn_1Al_1(7)$	-	530	1	2
	Na_2CO_3 (0.95)	530	3	11
	Na_2CO_3 (3.75)	530	51	80
	Na_2CO_3 (7.55)	530	35	68
	$NaNO_3$ (0.60)	530	2	4

[a] Prepared from thoroughly washed solids. Reaction conditions: isobutanol/palmitate = 4:1; 50°C.

Table 5. Composition and surface area of $Mg_9M(III)_1$ mixed oxides.

Catalyst	M(III)/(Mg+M(III)) Theoretical	M(III)/(Mg+M(III)) Experimental	Na content (mmol/g)	Surface area $(m^2/g)^a$
Mg_9Al_1	0.10	0.12	0.24	96
thoroughly washed	0.10	0.10	0.02	169
Mg_9Ga_1	0.10	0.10	0.03	52
$Mg_9La_1^b$	0.10	0.12	0.22	65
thoroughly washed[b]	0.10	0.12	0.12	n.d.
$Mg_9La_1(NH_4)^c$	0.10	0.12	---	n.d

[a] n.d. = not determined. [b] Activated by calcination at 973 K. [c] Prepared with ammonium bases.

Table 6. Basicity of $Mg_9M(III)_1$ solids.

Catalyst	Total basicity (mmol/g)	Leachable basicity (mmol/g)	Na content (mmol/g)
Mg_9Al_1	0.51	0.19	0.24
thoroughly washed	0.35	0.01	0.02
Mg_9Ga_1	0.46	0.06	0.03
Mg_9La_1[a]	0.08	0.22	0.22
thoroughly washed[a]	0.09	0.08	0.12
$Mg_9La_1(NH_4)$[b]	0.41	0.07	---

[a] Activated by calcination at 973 K. [b] Solid prepared with ammonium bases.

Table 7. FAME yields in sunflower oil transesterification with methanol catalyzed by $Mg_9M(III)_1$ mixed oxides.[a]

Catalyst	FAME yield (3 h)
Mg_9Al_1	93.0
thoroughly washed	31.0
Mg_9Ga_1	34.3
Mg_9La_1[b]	90.5
thoroughly washed	3.8
$Mg_9La_1(NH_4)$[c]	7.8

[a] Blank reaction does not produce any measurable yield of FAME. [b] Activated by calcination at 973 K. [c] Prepared with ammonium hydroxide and carbonate.
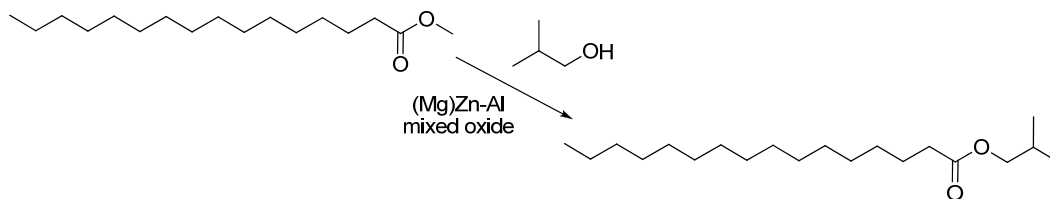
Scheme 1. Transesterification of methyl palmitate with isobutanol.
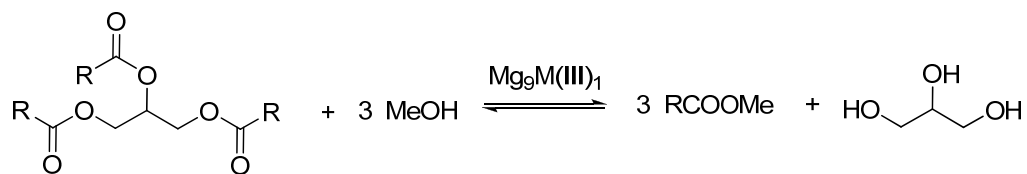
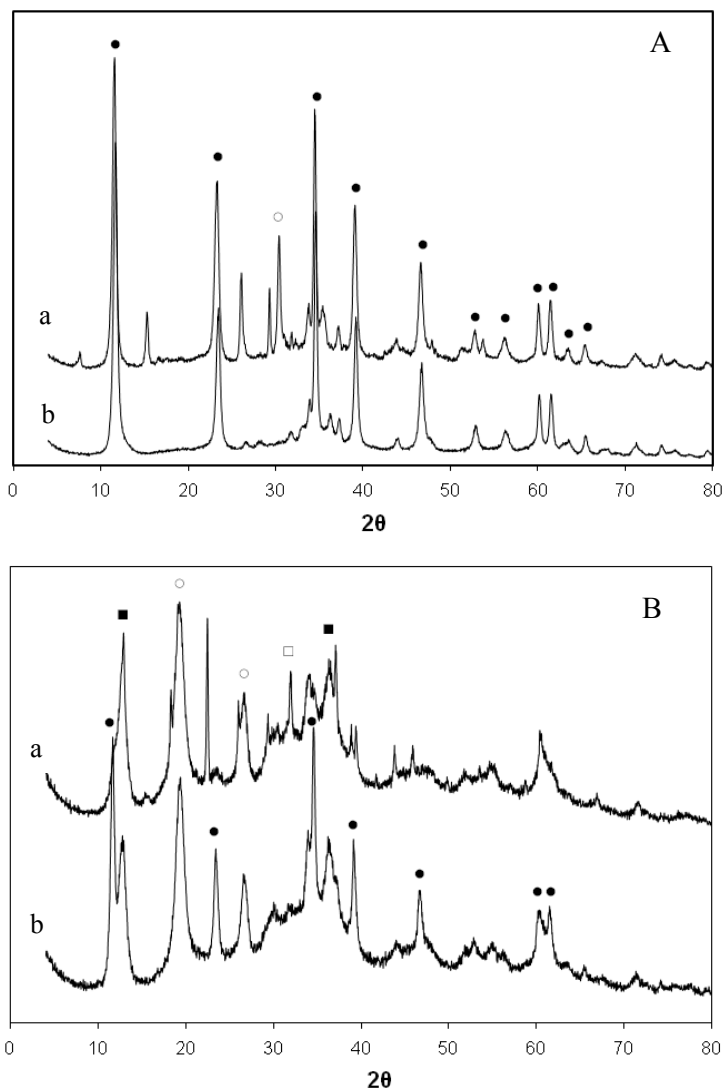**Scheme 2.** Transesterification of sunflower oil with methanol.
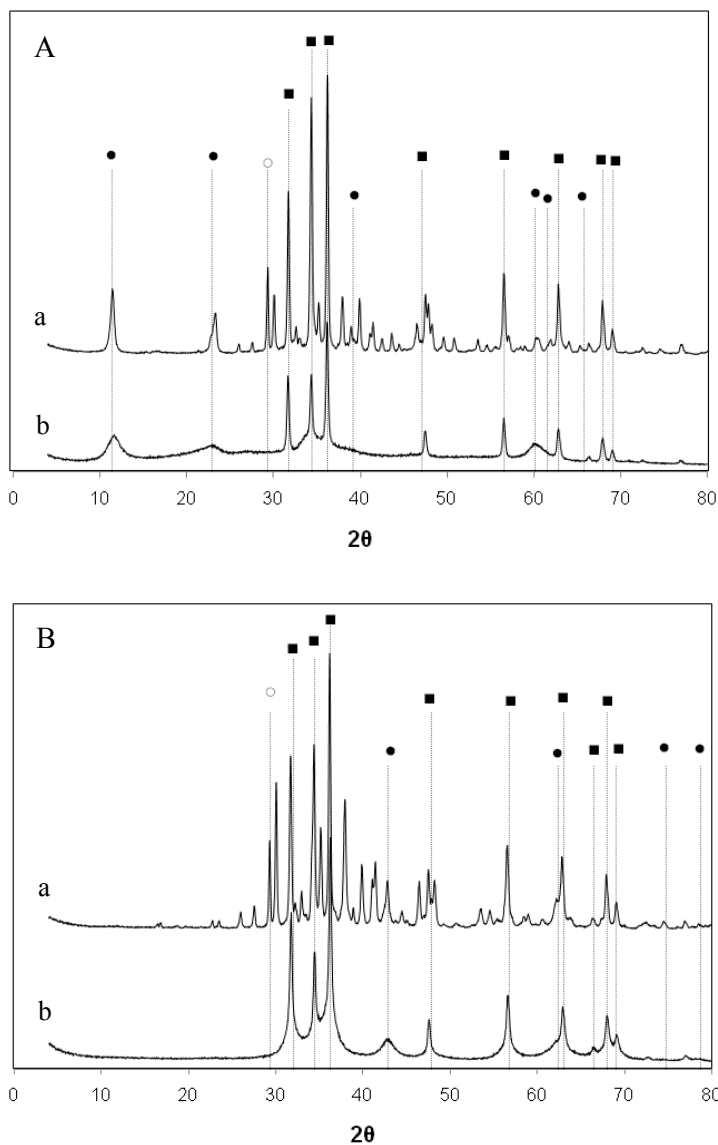
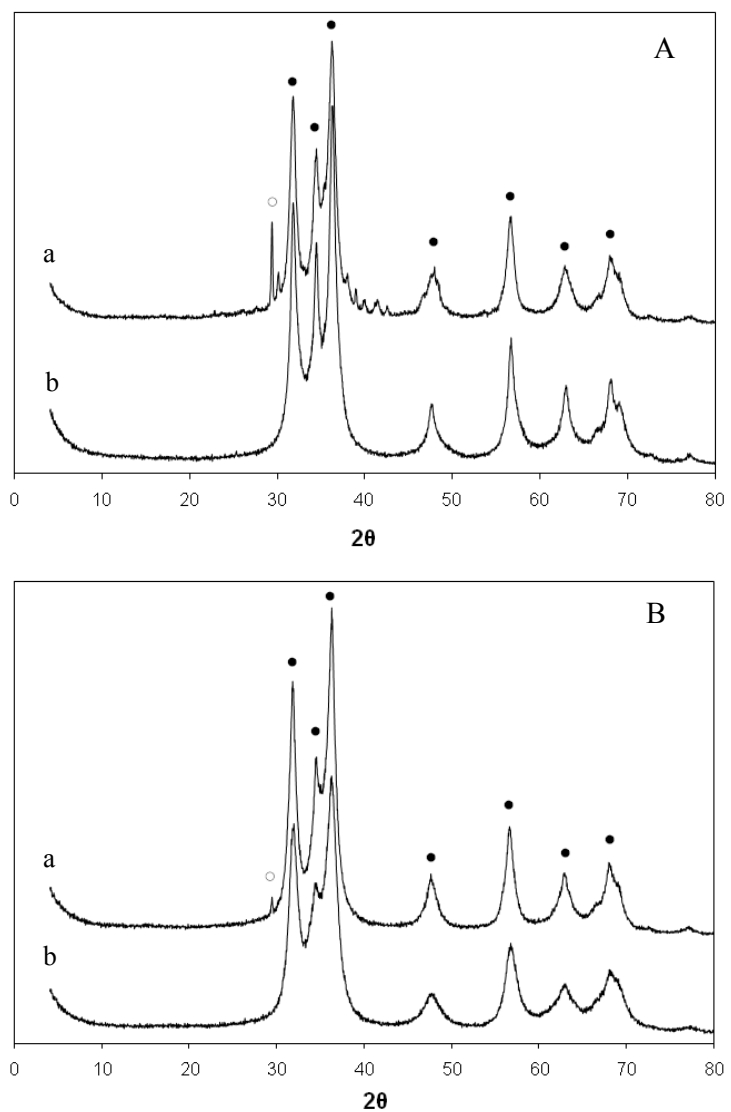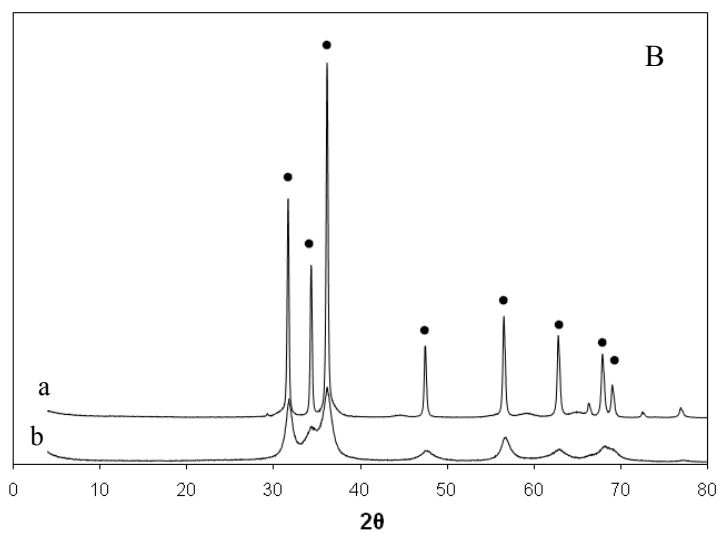**Figure 1.**A) XRD patterns of $Mg_4Zn_5Al_1(10)$ precursors, poorly washed (a) and thoroughly washed (b). Identified species: hydrotalcite (●), $NaNO_3$ (○), and ZnO (■). B)XRD patterns of $Mg_4Zn_5Al_1(10)$ mixed oxides prepared by calcination of the same precursors. Identified species: MgO (●), $NaNO_3$ (○), and ZnO (■).

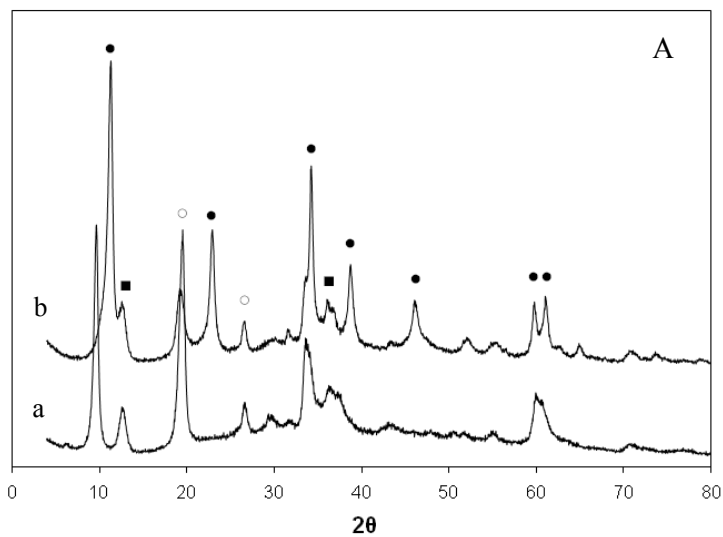**Figure 2.** A) XRD patterns of $Zn_4Al_1(10)$ precursors, poorly washed (a) and thoroughly washed (b). Identified species: hydrotalcite (●) and $NaNO_3$ (○). B) XRD patterns of $Zn_4Al_1(7)$ precursors, poorly washed (a) and thoroughly washed (b). Identified species: hydrotalcite (●), $Zn(OH)_2$ (○),$NaNO_3$ (□), and $Zn_5(CO_3)_2(OH)_6$ (■).

Figure 3.A) XRD patterns of $Zn_4Al_1(10)$ mixed oxides prepared by calcination of the precursors shown in Fig. 2A. B) XRD patterns of $Zn_4Al_1(7)$ mixed oxides prepared by calcination of the precursors shown in Fig. 2B. Identified species: ZnO ($\bullet$) and $NaNO_3$ ($\circ$).

Figure 4. A) XRD patterns of $Zn_4Al_1(7\text{-}NH_4)$ precursors, poorly washed (a) and thoroughly washed (b). Identified species: hydrotalcite (●), $Zn(OH)_2$ (○), and $Zn_5(CO_3)_2(OH)_6$ (■). B) XRD patterns of $Zn_4Al_1(7\text{-}NH_4)$ mixed oxides prepared by calcination of the same precursors. Identified species: ZnO (●).
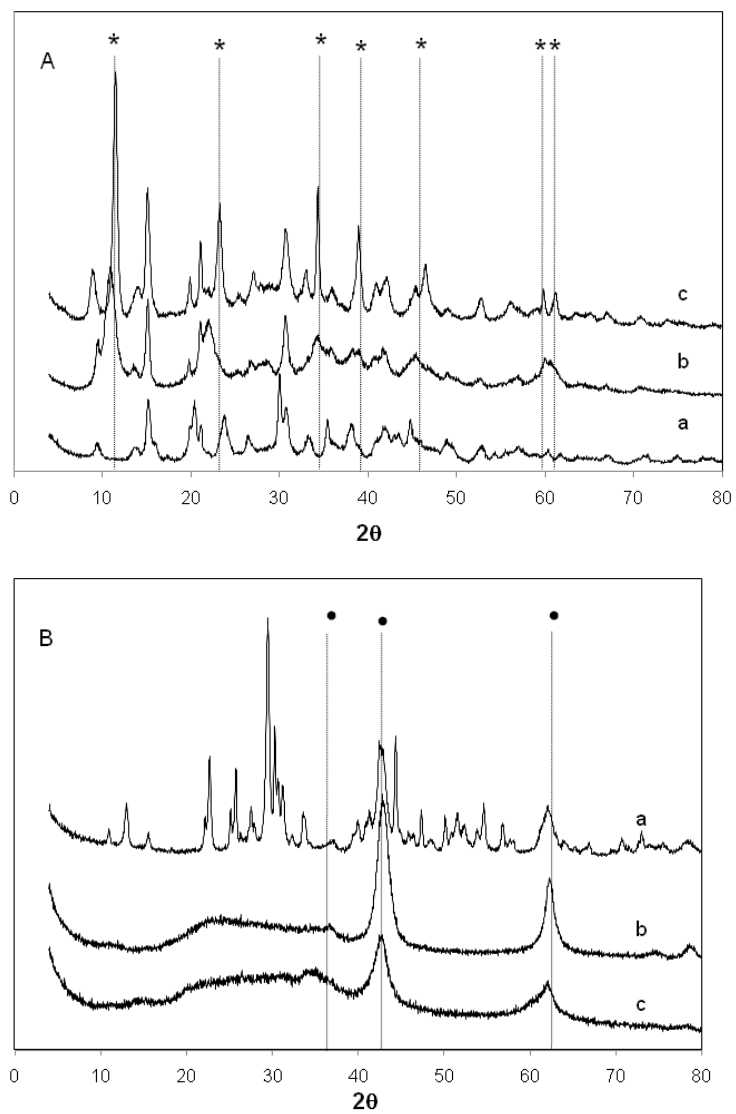
Figure 5. XRD patterns of Mg/M(III) solids. a) Mg_9La_1, b) Mg_9Al_1, c)Mg_9Ga_1. A) Precursors. Identified species: hydrotalcite (*). B) Mixed oxides prepared by calcination at 723 K. Identified species: MgO (●).
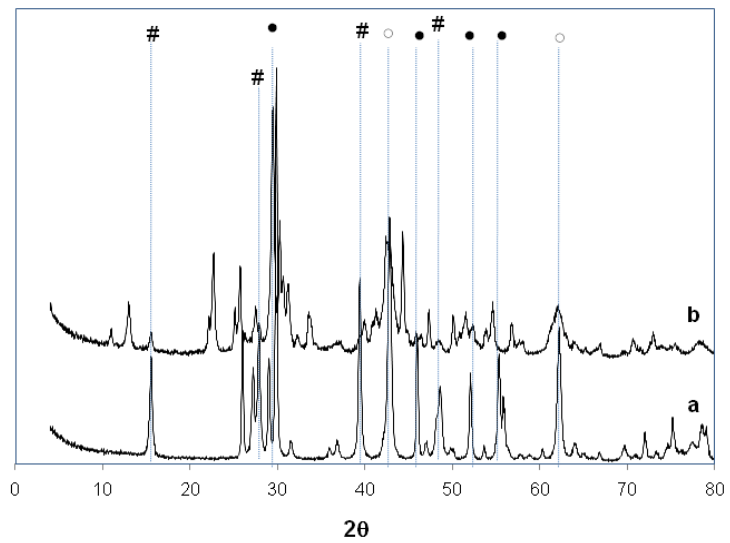
Figure 6. XRD patterns of Mg_9La_1 a) calcined at 773 K, b) calcined at 973 K. Identified species: MgO (●), La_2O_3 (○), and La_2MgO_x (**#**).
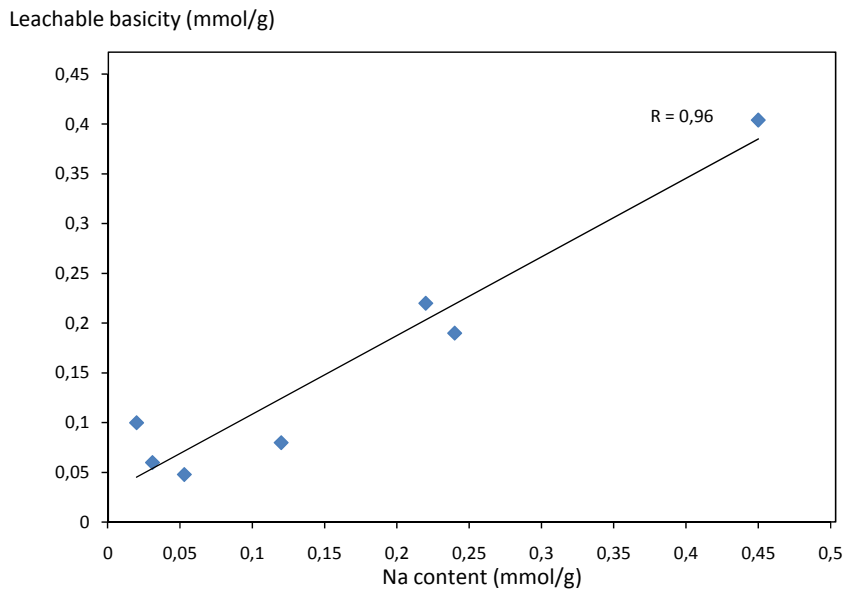
Leachable basicity (mmol/g)

Figure 7. Representation of leachable basicity *vs* Na content for $Mg_9M(III)_1$ solids.
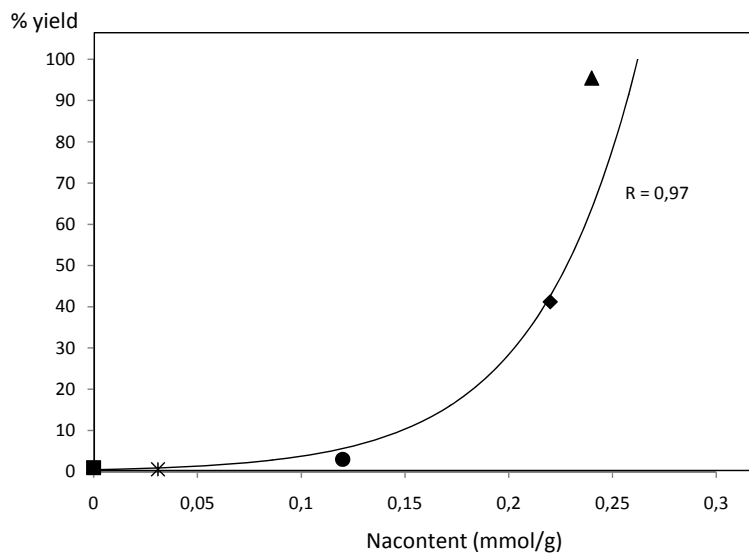
% yield

Figure 8. Representation of transesterification yields of methyl palmitate with isobutanol catalyzed by $Mg_9M(III)_1$ solids *vs* sodium content. (▲) Mg_9Al_1, (♦) Mg_9La_1, (●) Mg_9La_1 (thoroughly washed), (✳) Mg_9Ga_1, (■) $Mg_9La_1(NH_4)$.