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Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH

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Abstract

The activity and selectivity of a series of NaOH catalysts supported on alumina for the transesterification with methanol of refined sunflower oil have been investigated. The performance of the supported catalysts has been compared with that of homogeneous NaOH. The influence of the molar methanol/oil and catalyst/methanol ratios and of the NaOH loading of the supported catalysts has been considered. The results have shown that the transesterification rate largely depends on the catalyst/methanol ratio, whereas the reaction selectivity seems to be governed by the methanol/oil molar ratio. Calcination of the NaOH/γ-Al_2O_3 catalysts had a negative effect on their activity. On the other hand, the performance of the NaOH/alumina catalysts just dried at 393 K was not far of that of homogeneous NaOH. Measurements of sodium leached during the progress of the transesterification reactions have evidenced some lack of chemical stability of the supported NaOH catalysts under reaction conditions. Therefore, progress should be made to prepare more stable catalysts based on supported NaOH for this application.

Keywords: Biodiesel synthesis; Transesterification selectivity; Heterogeneous catalysts; Alumina

1. Introduction

Biodiesel is a fuel obtained from renewable biomass feedstocks that can be used in diesel engines as neat fuel or blended at various proportions with conventional fossil diesel fuel. It consists of mono-alkyl esters usually produced by transesterification with an alcohol (alcoholysis), most commonly methanol (methanolysis), of the triglycerides found in vegetable oils, animal fats or waste cooking oils [1–4]. However, production costs are high, which is due to the high vegetable oil prices and some technological issues. As a result, biodiesel produced in the European Union breaks even at petroleum prices around €60 per barrel [5].

Most of the commercial biodiesel is produced from plant oils (mainly colza, soybean and sunflower) using very effective homogeneous base catalysts such as NaOH or KOH, which are soluble in methanol. Nevertheless, these alkali compounds have some drawbacks: they must be neutralized giving rise to wastewaters and cannot be reutilized, they favour the formation of stable emulsions making separation of the methyl esters (biodiesel) difficult, glycerol is obtained as an aqueous solution of relatively low purity and the reaction becomes very sensitive to the presence of water and free fatty acids. These problems can be alleviated with the use of heterogeneous transesterification catalysts. Therefore, there is an increasing interest in the possibility of replacing the homogeneous alkaline hydroxides, carbonates or metal alkoxides by heterogeneous solid catalysts insoluble in methanol that could potentially lead to easier refining of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs [6]. As a matter of fact, Axens (Institut Français du Pétrole Group Technologies), commercializes the Esterfip-H^{TM} process, which is operated in the continuous mode and includes two successive fixed-bed reactors [6,7].

In recent years a considerable research effort is being devoted to the heterogeneously catalyzed methanolysis of vegetable oils. As a result, a great variety of catalysts such as alkaline-earth metals oxides and hydroxides [8–10], alkali metals (Na and K) hydroxides or salts supported on γ-alumina [11–13], zeolites [14], hydrotalcites [15] as well as some acid solids [16] have been checked to date at very different reaction conditions and with a variable degree of success. Nevertheless, it is generally

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recognized that their activity is significantly lower than that of the homogenous basic catalysts.

In this work, we report on the activity and selectivity of a series of basic solids consisting of NaOH supported on commercial alumina for the transesterification of sunflower oil with methanol at 323 K. A screening of the reaction conditions has been carried out by examining the effect of the concentration of catalyst and the initial methanol/oil and catalyst/methanol molar ratios. Simple catalysts formulations and method of preparation have been chosen with a view to a more direct possible transference of the results to the productive sector. Also in this regard, the performance of the heterogeneous catalysts has been compared with that of conventional homogeneous NaOH.

2. Experimental procedures

2.1. Catalysts preparation and characterization techniques

The catalysts were prepared by incipient wetness impregnation of the 212–300 μm size fraction of commercial alumina (Spheralite 505, Procatalyse). To this end, the required amounts of aqueous NaOH (Aldrich, 99.998%) solutions were slowly added to the support. The catalytic carrier was previously calcined in a muffle for 12 h at 773 K. After impregnation the catalysts were dried for 12 h at 393 K under reduced pressure (10 kPa). A portion of the dried catalysts was treated in a muffle at 673 K for 12 h. The nominal sodium hydroxide contents of the final solids were 10.7 and 19.3 wt.%; these catalysts will be referred to as 10-Al and 19-Al, respectively. Samples subjected to calcination will be designated as 10-Al-c and 19-Al-c.

The nitrogen adsorption–desorption isotherms at 77 K of the supports and the catalysts were measured by the static method in an automatic volumetric Micromeritics® ASAP 2020 adsorption analyzer. Prior to the measurements, samples were degassed at 353 K and 0.1 Pa. The BET equation was applied to five adsorption data taken at relative pressures below 0.2 in order to calculate the specific surface areas. The total specific pore volumes were estimated from the volume of nitrogen adsorbed at about 0.99 relative pressure. The mean pore diameters were derived from the pore volume distributions calculated by the BJH method [17].

The X-ray diffraction (XRD) patterns of selected samples were obtained with a Philips APD 1710 powder diffractometer. Nickel filtered Kα radiation of copper was employed covering 2θ angles of up to 80°; data were recorded in the step mode at 2θ increments of 0.05°. Samples subjected to analysis were ground previously in an agate mortar.

2.2. Transesterification reactions and chemical analyses

The experiments were carried out at 323 K and atmospheric pressure in two different experimental set-ups. When using the homogeneous NaOH catalyst, a 1 L jacketed glass reactor fitted with a sampling device, reflux condenser, a nitrogen inlet, a stainless steel agitator comprising a turbine (370 rpm), a thermocouple probe and a heated circulating water bath (PolyScience) was employed. Edible-grade sunflower oil (c. 300 g, Urzante, Navarra, Spain; acid value of 0.07 mg KOH/g) and some methanol (c. 40 g, Scharlau, HPLC grade) were initially charged into the reactor to reach the reaction temperature. The desired amount of NaOH catalyst (Aldrich, 99.998% pellets) was rapidly added into the reactor dissolved in the amount of methanol necessary to give overall alcohol/oil molar ratios of 6:1 or 12:1. The NaOH pellets were ground in an agate mortar prior to be dissolved in methanol at room temperature. A molecular weight of 879.5 was assumed for sunflower oil [18]. Samples (1–1.5 g) were withdrawn during the experiment at various intervals. The sampling device consisted of a polyamide tube connected to a stainless steel one-way compression-nut stopcock and a 10 mL polypropylene syringe. A recirculation loop comprising a PTFE tube, a diaphragm-type metering pump (ProMinent Gamma/L) working at 80 mL/min and a stainless steel three-way ball valve was also used for sampling purposes.

In the case of the heterogeneous catalysts a screening of the reaction conditions was carried out by performing series of five parallel reactions in closed glass flasks (60 mL) immersed in thermostatic water baths at 323 K with magnetic stirring. Twenty grams of sunflower oil, the required amount of supported catalysts and the volume of methanol required to reach alcohol/oil molar ratios of 6:1, 12:1, 24:1 or 48:1 were added into the flasks. Samples (about 0.5 g) were withdrawn at various intervals by means of a polyamide tube crossing the flask stoppers and connected to a stainless steel one-way compression-nut stopcock and a 2 mL polypropylene syringe. The samples were analyzed at room temperature by size exclusion chromatography (SEC) as described previously [19].

2.3. Leached sodium measurements

The chemical stability of the catalysts has been investigated by analysing the sodium content of the reaction mixture. To this end, some of the samples taken from the reactor were carefully filtered and then introduced in a rotary evaporator at room temperature. After evaporation, the dry fraction was treated with 50 mL of 0.1 N hydrochloric acid. The resulting solution was analysed by atomic absorption spectrophotometry (AAS, Perkin-Elmer 373) in order to determine the sodium concentration. Leached sodium was referred to the total sodium in the amount of catalyst in the sample withdrawn from the reactor.

3. Results and discussion

3.1. Performance of homogeneous NaOH

The aim of this work is to study the potential of NaOH/γ-Al_2O_3 catalysts for biodiesel synthesis by methanolysis of vegetable oils. Therefore, homogeneous NaOH is considered here as the reference catalyst and it is necessary to evaluate first its performance under the transesterification conditions of relevance to this work.

Fig. 1 depicts the evolution with reaction time of the sunflower oil conversion for a series of methanolysis reactions carried out at 323 K. Catalyst concentrations ranged from 0.05 to 0.2 wt.% referred to the amount of oil (c. 300 g) charged ini-

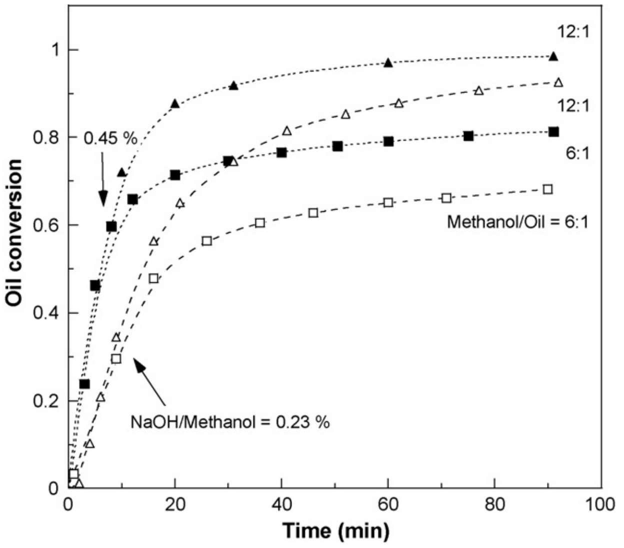

Fig. 1. Evolution with reaction time of the sunflower oil (c. 300 g) conversion for a series of transesterification reactions carried out at 323 K. Methanol/oil molar ratios and NaOH amounts were: 12:1 and 0.6 g (▲), 12:1 and 0.3 g (△), 6:1 and 0.3 g (■), 6:1 and 0.15 g (□).

tially into the reactor. The molar methanol/oil ratios considered were 6:1 and 12:1. The initial rate of transesterification is controlled by the catalyst/methanol ratio. Indeed, curves in Fig. 1 can be grouped in two categories according to the concentration of NaOH in the alcohol phase: 0.45 (0.3 g NaOH, methanol/oil 6:1 and 0.6 g NaOH, methanol/oil 12:1) or 0.23 wt.% (0.15 g NaOH, methanol/oil 6:1 and 0.3 g NaOH, methanol/oil 12:1). The experiments performed with the same catalyst/methanol ratio also exhibit the same initial rate of methanolysis. Moreover, the reaction rate increases with the concentration of NaOH in the alcohol phase. It should be noted that NaOH is soluble in methanol according to the following reaction leading to the formation of sodium methoxide, which is generally believed to be the active species [20,21]:

$$\mathrm{NaOH} + \mathrm{CH_3OH} \leftrightarrow \mathrm{NaOCH_3} + \mathrm{H_2O} \qquad (1)$$

The process of oil methanolysis involves three stepwise reversible reactions. First, the triglycerides (TG) present in the oil are converted to diglycerides (DG). The second step is the conversion of diglycerides to monoglycerides (MG), which are finally converted to glycerol (GLY). A molecule of methyl ester (ME) is produced from each acylglycerol (TG, DG or MG) at each step:

$$\mathrm{TG} + \mathrm{CH_3OH} \xleftrightarrow[k_2]{k_1} \mathrm{DG} + \mathrm{ME} \qquad (2)$$

$$\mathrm{DG} + \mathrm{CH_3OH} \xleftrightarrow[k_4]{k_3} \mathrm{MG} + \mathrm{ME} \qquad (3)$$

$$\mathrm{MG} + \mathrm{CH_3OH} \xleftrightarrow[k_6]{k_5} \mathrm{GLY} + \mathrm{ME} \qquad (4)$$

The reaction proceeds via the nucleophilic attack of the methoxide species on a carbon atom of the carbonyl groups of the acylglycerols resulting in the formation of a methyl ester. Taking into account that the methoxide species are formed from methanol and sodium hydroxide according to Eq. (1), this mechanism justifies the important role found for the NaOH concentration in determining the initial rate of transesterification.

However, reactions (2)–(4) are reversible. This fact implies that the final extent to which the oil is converted mainly depends on the methanol/oil ratio, that is, the amount of methanol used in excess with respect to the stoichiometric relation (3:1), which helps to shift the reaction towards the methyl esters formation. This is clearly shown in Fig. 1 for the two reactions conducted with a methanol/oil ratio of 12:1 since in spite of the different NaOH concentrations, the oil conversions achieved after 90 min are not very different, and close to the equilibrium conversion. A similar behaviour for the reactions carried out under a 6:1 methanol/oil ratio is not so clearly observed probably due to the very low catalyst concentration in the reaction conducted with only 0.15 g of NaOH.

Selectivities for the several products were calculated as previously described [19]. The selectivities of homogeneous NaOH for diglycerides and monoglycerides in the above-described series of reactions are plotted against the oil conversion in Fig. 2. The results are consistent with the reaction scheme given by Eqs. (2)–(4). Thus, diglycerides are the primary products of the

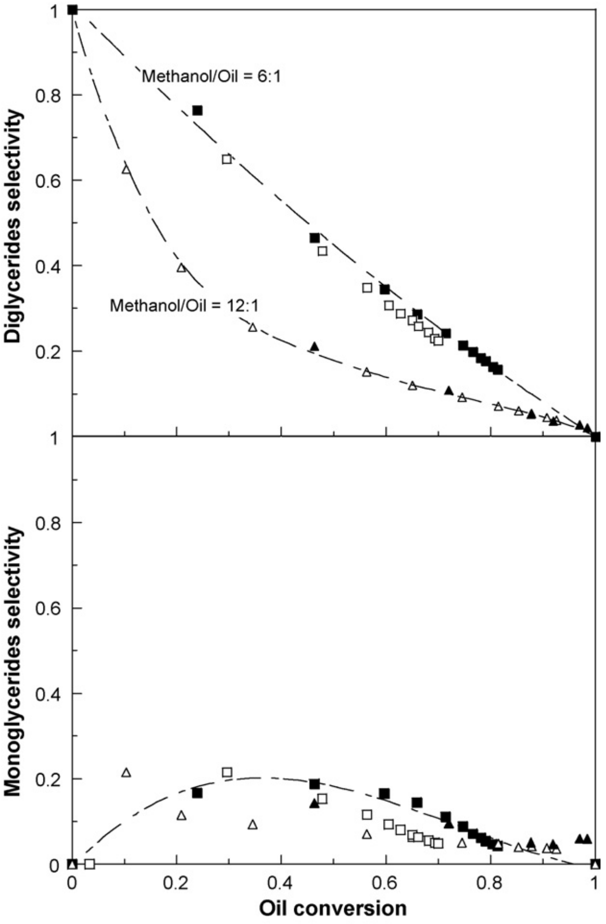

Fig. 2. Selectivities for diglycerides and monoglycerides as a function of sunflower oil (c. 300 g) conversion for a series of transesterification reactions carried out at 323 K. Methanol/oil molar ratios and NaOH amounts were: 12:1 and 0.6 g (▲), 6:1 and 0.3 g (△), 12:1 and 0.3 g (■), 6:1 and 0.15 g (□).

methanolysis reaction and, accordingly, selectivities for these products are close to 1 for very low oil conversions as it can be seen from Fig. 2. Interestingly, the curves can be grouped in two new categories, indicating that the reaction selectivity mainly depends on the methanol/oil ratio and seems to be unaffected by the catalyst concentration. Selectivities for diglycerides rapidly decrease, and those for glycerol and biodiesel increase, as the amount of methanol/oil ratio increases. This again illustrates the positive effect of using methanol in excess in the transesterification reactions. Regarding the selectivities for monoglycerides, the most relevant feature of the results is the low values reached. Selectivities do not surpass about 20% in the range of oil conversions between 10 and 30%, and then decrease as the reaction progresses. The lack of precision associated to these low selectivity values does not allow us to identify any clear influence of the reaction variables. Nevertheless, the lowest selectivities for monoglycerides correspond to the reaction carried out with a 12:1 methanol/oil ratio and 0.3 g of NaOH. These results indicate that monoglycerides are poorly stable intermediates under the usual reaction conditions and once formed are easily converted to glycerol and methyl ester. This view is supported by kinetic studies performed previously by others on the methanolysis of palm oil [22] and soybean oil [23]. For example, Noureddini and Zhu conducted the transesterification of soybean oil at 323 K and methanol/oil molar ratio of 6:1 catalyzed with NaOH at 0.2 wt.% [23]; it should be noted that these experimental conditions are very similar to the ones of this study on sunflower oil methanolysis. These authors found, with reference to the rate constants defined in Eqs. (2)–(4), the following ratios between the kinetic parameters: $k_1/k_2 = 0.45$ (TG $\leftrightarrows$ DG); $k_3/k_4 = 0.17$ (DG $\leftrightarrows$ MG); $k_5/k_6 = 35$ (MG $\leftrightarrows$ GLY). These values of the kinetic constants would lead obviously to very low concentrations of monoglycerides, in accordance with the results shown in Fig. 2.

3.2. *Texture and structure of the heterogeneous catalysts*

In Table 1 the specific surface areas (S_{BET}), total specific pore volumes (V_{p}), mean pore diameters (d_{BJH}) and nominal NaOH contents of both the as prepared catalysts as well as those calcined at 673 K are tabulated. As is made clear by these data, the introduction of NaOH damages the textural properties, with a remarkable decrease of the specific surface area and pore volume of the supports. This effect is more pronounced as the NaOH loading increases, and it seems to take place at the early stages of the catalysts preparation, namely impregnation and drying since calcination does not introduce additional effects.

Table 1
Textural properties of the catalysts indicated

Catalyst	S_{BET} (m^2/g)	V_{p}(cm^3/g)	d_{BJH} (Å)	NaOH (wt.%)
γ-Al_2O_3	211	0.40	75	–
10-Al	90	0.31	140	10.7
10-Al-c[a]	92	0.30	131	10.7
19-Al	51	0.20	158	19.3
19-Al-c[a]	44	0.19	175	19.3

[a] Samples calcined in a muffle at 673 K for 12 h.

From a qualitative point of view, these results are not surprising since in heterogeneous catalysis the reduction of the specific surface area of the support is a well documented consequence of the promotion of a catalyst with alkali metals [24–26]. Of course, the loss of surface area and pore volume is favoured by the high amount of sodium introduced, which blocks the pores. The possible interactions of the alkali metal compounds with the catalytic supports include formation of solid solutions, acid–base reactions, and formation of ternary compounds such as aluminates. As concerns the negative effect of the alkali metals on the texture, this is attributed to a cement effect, as explained by Perrichon and Durrupty [26].

XRD analyses of selected samples have been performed to obtain more information about the catalysts structure. Fig. 3 shows the XRD patterns of the as-prepared (impregnated and dried at 353 K) 19-Al catalyst and the sample calcined at 673 K. The patterns of the calcined and the as-prepared one are very similar. Several diffraction peaks are clearly visible showing the presence of NaOH and Na_2O_2, both as hydrated compounds, as well as sodium aluminate ($NaAlO_2$). These results indicate that NaOH has reacted with the support giving rise to the formation of aluminates. In general, these results are in accordance with previous studies on Na/alumina and silica [26], Na/alumina [12] and K/alumina [13] catalysts.

3.3. *Supported NaOH catalysts: screening of the reaction conditions*

Due to the lack of previous experience with these catalysts and the scarcity of information in the biodiesel literature, an exploratory study of the transesterification reaction was initially conducted at 323 K. The mass of supported catalysts used was fixed at 0.413 g in order to obtain NaOH concentrations relative to the oil mass (c. 20 g) four times (0.4%) the one used in a homogeneous NaOH-catalyzed reaction taken as reference (0.1%).

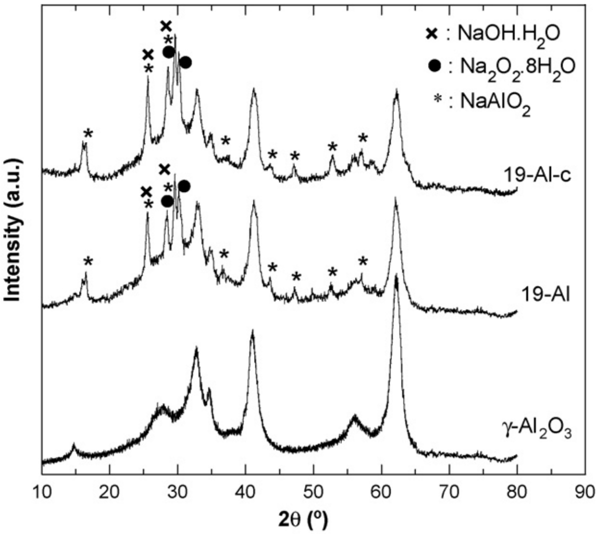

Fig. 3. XRD patterns of the support and the catalysts indicated.

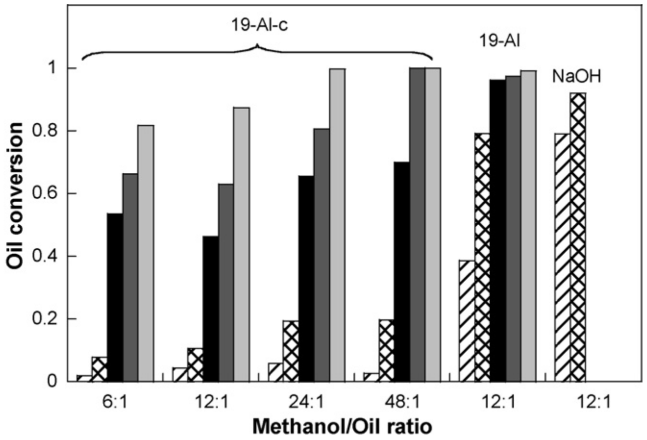

Fig. 4. Evolution with reaction time (0.5 h (▨), 1.5 h (☒), 4.5 h (■), 7.5 h (▩), 24 h (☐)) of the sunflower oil conversion for a series of transesterification reactions carried out at 323 K with the 19-Al-c catalyst at methanol/oil ratios from 6:1 to 48:1, and the 19-Al catalyst at 12:1 methanol/oil ratio. The results with homogeneous NaOH at 0.2 wt.% and 12:1 methanol/oil ratio are also included. The mass of supported catalysts used was equivalent to 0.4 wt.% NaOH.

The evolution of the oil conversion with reaction time for a series of transesterification reactions carried out with the calcined 19-Al catalyst and the following methanol/oil molar ratios: 6:1, 12:1, 24:1 and 48:1 is shown in Fig. 4. Also included in this Figure are the results for reactions conducted with the as-prepared catalysts and homogeneous NaOH under an intermediate methanol/oil molar ratio of 12:1. These screening experiments have provided very interesting information, namely:

i. The performance of the NaOH/γ-Al_2O_3 catalysts is very dependent on the methanol/oil molar ratio. An oil conversion as high as 82% is reached at only 6:1 methanol/oil ratio; it increases up to 88% at 12:1 and is almost complete at methanol/oil ratio of 24:1.

   It should be noted that in presence of heterogeneous catalysts the reaction mixture is a three-phase oil/methanol/catalyst system. The active methoxide species are formed upon adsorption of methanol on the catalyst surface and the methanolysis reaction becomes mass transfer-controlled [13]. There is a very limited knowledge of the kinetics of the heterogeneously-catalyzed methanolysis reactions. De Filippis et al. [27] do consider that in presence of solid-base catalysts the methanolysis reaction also involves the active participation of methoxide species, and then, the efficiency of a catalyst should be related with the rate of formation of sodium methoxide. In a recent study on the transesterification of ethyl acetate with methanol catalyzed by MgO, Dossin et al. [8] have found that the kinetic data were described by an Eley–Rideal type mechanism including the reaction between methanol adsorbed on a basic active site of the catalyst surface and ethyl acetate from the liquid phase. Methanol adsorption was the rate-determining step. A similar mechanism applied to the methanolysis of sunflower oil would be compatible with our experimental results since as the methanol/oil ratio increases the driving-force for methanol adsorption increases as well, thus favouring the transesterification reaction in spite of the lower catalyst/methanol ratio. This is in contrast with the use of methanol-soluble NaOH (see Fig. 1). In this case, the reaction mixture is a two-phase oil/methanol system where the amount of methanol has little effect on the formation of the methoxide species provided it is present in a quantity high enough. In this case the initial transesterification rate is determined by the concentration of NaOH in the methanol phase, that is, the NaOH/methanol ratio.

ii. The performance of the as prepared sample is better than that of the calcined catalysts. In the case of the 19-Al-c catalyst at 12:1 molar methanol/oil ratio, the oil conversion achieved after 24 h of reaction is about 86%, but increases up to 99% with the non calcined 19-Al sample.

   These results cannot be attributed to differences in specific surface area (see Table 1). Such behaviour contrasts strongly with that of other heterogeneous catalysts such as MgO [8] or KNO_3/Al_2O_3 [13] which just require activation by means of air calcination to remove adsorbed CO_2 and H_2O. Interestingly, Kim et al. [12], who also used NaOH as precursor of a series of alumina-supported catalysts, conducted the methanolysis of soybean oil with the fresh catalysts. As discussed in the preceding section, the alkali metals promote the vitrification of the catalysts surface upon heating. It is likely that such a surface became significantly inert and poorly active, which could be related with the lower activity of our calcined catalysts when compared with the as-prepared ones.

   In view of these results it was decided to continue the study considering only the samples impregnated and dried for 12 h at 393 K under reduced pressure (10 kPa).

iii. Homogeneous NaOH is clearly more active than the heterogeneous catalysts. This is, of course, a primary consequence of the fact that the solid catalysts are insoluble in methanol. As a result, whereas almost all pure NaOH added in the homogeneous process does react according to Eq. (1) to form sodium methoxide, the amount of active species formed in the heterogeneous reaction depends critically on the surface properties and texture of the solid catalysts. Nevertheless, it is worth mentioning that the performance of the as-prepared 19-Al catalysts is also excellent. In fact, after 1.5 h of reaction and 12:1 methanol/oil molar ratio, 0.1 wt.% homogeneous NaOH gives an oil conversion of 92%, whereas 19-Al at 0.4 wt.% NaOH yields a remarkably high value of 80%.

3.4. Supported NaOH catalysts: influence of the NaOH loading of the catalyst

The supported NaOH catalysts were prepared with two different NaOH loadings: 10.7 and 19.3 wt.%. Due to the relatively low pore volume of alumina, loadings above 19 wt.% could not be achieved with only one impregnation step and it was decided to limit the samples to the above cited catalysts.

Fig. 5 depicts the evolution with reaction time of the sunflower oil conversion for methanolysis reactions carried out at

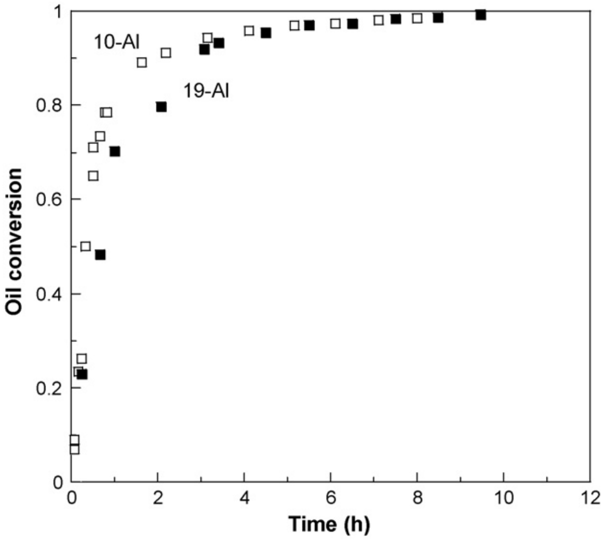

Fig. 5. Evolution with reaction time of the sunflower oil (c. 20 g) conversion for a series of transesterification reactions carried out at 323 K and 12:1 methanol/oil molar ratio. The catalysts were: 10-Al, 0.74 g (☐); 19-Al, 0.41 g (■).

323 K with the alumina-supported catalysts. The experiments were conducted under 12:1 molar methanol/oil ratio and a solid catalyst concentration equivalent to 0.4 wt.% NaOH referred to the oil mass (c. 20 g) charged into the reactor. To this end, the amount employed of each catalyst was adjusted taking into account its nominal NaOH loading. As it can be seen, both catalysts give similar results from the point of view of the final conversion. However, the slopes of the curves indicate that the initial transesterification rate is higher when using the 10-Al catalyst. These results can be interpreted in terms of the texture of the solids and the expected effect of these properties on the rate of formation of surface methoxide species. Indeed, as made clear by Fig. 5 and Table 1, a correlation can be established between the activity and the specific surface area of the catalysts: 10-Al (90 m^2/g) > 19-Al (51 m^2/g). Nevertheless, there is also the possibility that due to a lack of chemical stability of the catalysts in the reaction mixture, part of the NaOH turns out to be extracted from the solid and could act as homogeneous catalyst. In order to check this hypothesis, leached sodium measurements were performed as described in Section 2.3. It was found, that some sodium was extracted; however, the percentage was low (c. 5%), remained almost unchanged during the reaction and was not significantly different for both 10-Al and 19-Al catalysts. Therefore, differences of activity between these samples are not due to leached sodium. Nevertheless, this lack of stability is a drawback from the practical point of view since neutralization and washing of the resulting biodiesel and glycerol will be required as in the case of the homogeneous catalysts.

The selectivities for diglycerides, monoglycerides and glycerol in the above-described series of reactions conducted under 12:1 molar methanol/oil ratio and a solid catalyst concentration equivalent to 0.4 wt.% NaOH are included in Fig. 6. As it can be seen, the NaOH loading of the catalyst does not influence the reaction selectivity. The results are in accordance with the reaction scheme given by Eqs. (2)–(4). Ebiura et al. [28] have investigated the methanolysis of triolein over a variety of Li, Na and K salts supported on alumina. They found that the selectivities did no depend on the type of solid-base catalysts, which suggested that the basic strength of the catalysts does not influence the selectivity. Nevertheless, on comparing the results in Figs. 2 and 6 at a methanol/oil molar ratio of 12:1, it can be seen that the heterogeneous catalysts are less selective to diglycerides and monoglycerides, and hence, more selective for biodiesel production than homogeneous NaOH. This is as expected for reactions in series and the fact that the activity of the supported NaOH catalysts is significantly lower than that of homogeneous NaOH. As the two first steps lead to the formation of diglycerides and monoglycerides and these steps are the slower ones, the selectivity for these products decreases with decreasing catalyst activity.

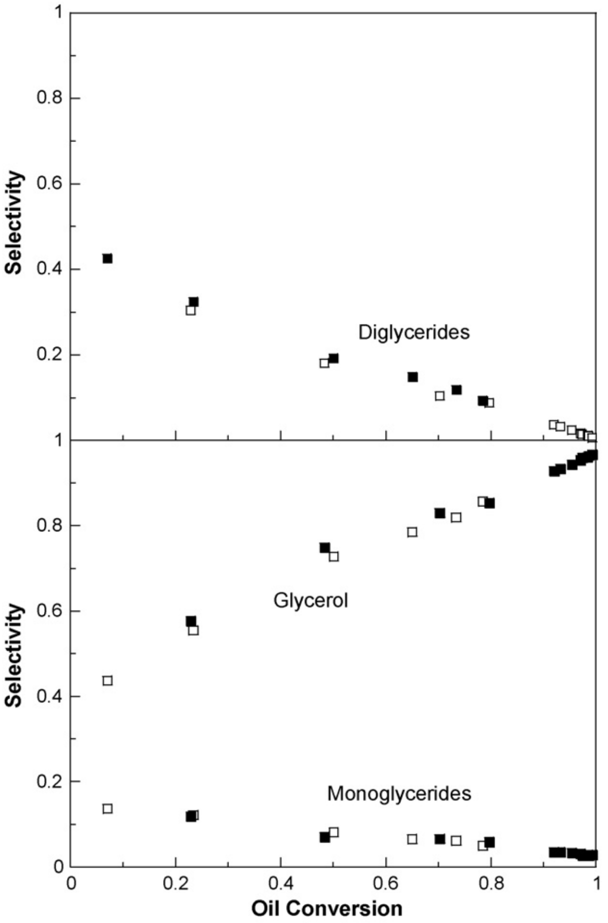

Fig. 6. Selectivities for diglycerides, monoglycerides and glycerol as a function of sunflower oil (c. 20 g) conversion for a series of transesterification reactions carried out at 323 K and 12:1 methanol/oil molar ratio. The catalysts were: 10-Al, 0.74 g (☐) and 19-Al, 0.41 g (■).

3.5. *Supported NaOH catalysts: influence of catalyst concentration and methanol/oil ratio*

A similar study to the one reported for homogeneous NaOH in Section 3.1 was conducted with 19-Al. Experiments were

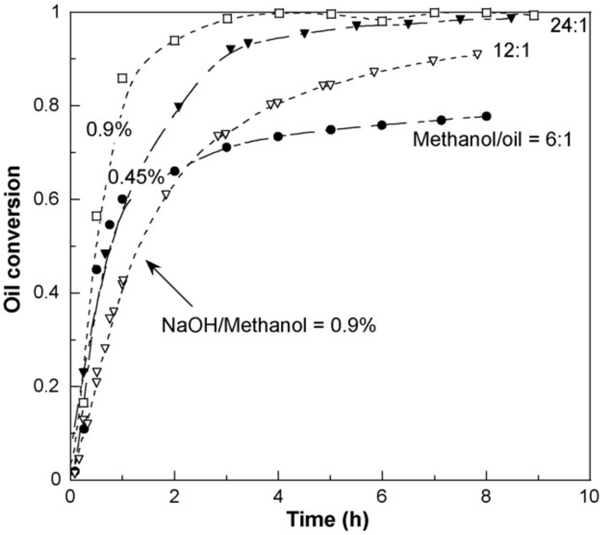

Fig. 7. Evolution with reaction time of the sunflower oil (c. 20 g) conversion for a series of transesterification reactions carried out with the 19-Al catalyst at 323 K. Methanol/oil molar ratios and catalyst amounts were: 24:1 and 0.40 g (□), 12:1 and 0.20 g (▽), 12:1 and 0.40 g (▼), 6:1 and 0.20 g (●).

carried out with amounts of supported catalysts equivalent to 0.2 or 0.4 wt.% homogeneous NaOH referred to the amount of oil charged into the reactor (c. 20 g). In addition, three molar methanol/oil ratios, 6:1, 12:1 and 24:1, were considered in order to simultaneously study the effect of this variable and that of the concentration of catalysts in the reaction mixture. The results are depicted in Fig. 7.

It can be seen that, as in the case of homogeneous NaOH (see Fig. 1), the curves in Fig. 7 can be grouped in two categories according to the NaOH equivalent concentration/methanol ratio: 0.9 wt.% (0.40 g 19-Al, methanol/oil 12:1 and 0.20 g 19-Al, methanol/oil 6:1) or 0.45 wt.% (0.40 g 19-Al, methanol/oil 24:1 and 0.20 g 19-Al, methanol/oil 12:1). The experiments performed with the same NaOH equivalent concentration/methanol ratio also exhibit the same initial rate of methanolysis, which obviously increases with the catalyst concentration. Assuming that the active methoxide species are formed upon adsorption of methanol on the catalyst surface, as the methanol/oil ratio increases the driving-force for methanol adsorption increases as well, thus favouring the transesterification reaction, in accordance with the results in Fig. 7.

As regards the transesterification selectivities the results obtained in the above described series of reactions are showed in Fig. 8. It can be seen that the molar methanol/oil ratio is the parameter that seems to govern the distribution of the reaction products. In fact, the selectivity for diglycerides decrease, and therefore, that for glycerol and methyl esters (biodiesel) increase as the amount of methanol in excess with respect to the stoichiometric value increases. This is likely due to the positive effect of the methanol concentration on the rate of the forward reactions leading to the conversion of triglycerides in diglycerides (Eq. (2)) and diglycerides in monoglycerides (Eq. (3)). Once formed, monoglycerides easily react to glycerol and methyl esters according to Eq. (4). As a matter of fact selectivities for monoglycerides are always very low (see Fig. 8), and they are relatively unaffected by the catalyst nature and methanol/oil molar ratio.

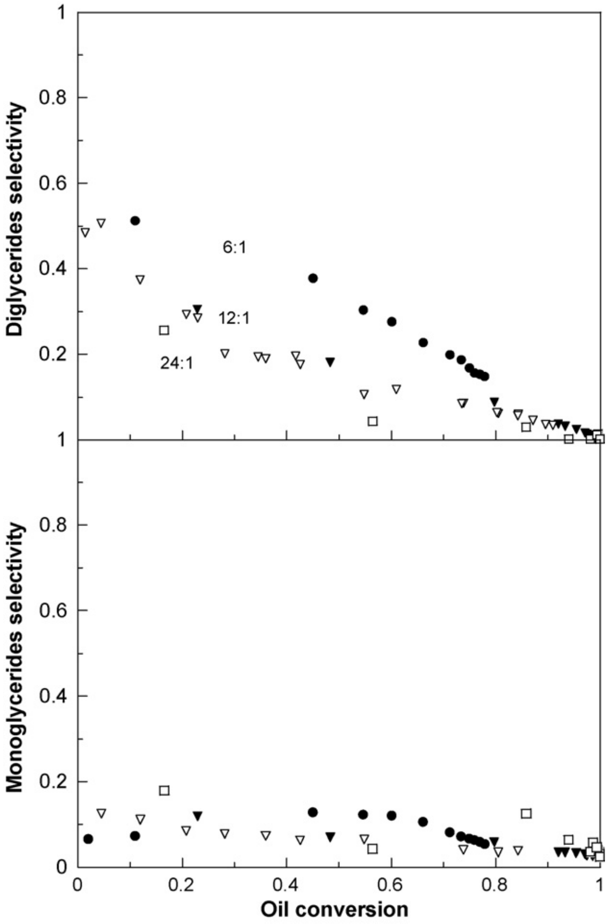

Fig. 8. Selectivities for diglycerides and monoglycerides as a function of sunflower oil (c. 20 g) conversion for a series of transesterification reactions carried out with the 19-Al catalyst at 323 K. Methanol/oil molar ratios and catalyst amounts were: 24:1 and 0.40 g (□), 12:1 and 0.20 g (▽), 12:1 and 0.40 g (▼), 6:1 and 0.20 g (●).

Chemical analyses of the refined biodiesel were not carried out in this study. However, selectivities for diglycerides and monoglycerides at oil conversions close to 1 are of the order of 0.2 and 2%, respectively (see Fig. 8). This allows estimating contents of diglycerides and monoglycerides of 0.14 and 0.80 wt.%, respectively, in the biodiesel, which are within the limits of the UNE-EN 14214 requirements [29] if the excess of methanol is sufficiently high.

4. Summary and conclusions

In the case of homogeneous NaOH, it has been found that the initial rate of transesterification is controlled by the catalyst/methanol ratio. NaOH is soluble in methanol and leads to the formation of sodium methoxide, which is considered the catalytically active species; therefore, the reaction rate increases with the concentration of NaOH in the alcohol phase. On the other hand, the selectivity of homogeneous NaOH for the several products mainly depends on the methanol/oil ratio and is unaffected by the concentration of catalyst.

As concerns the supported NaOH catalysts, it has been found that their performance is very dependent on the methanol/oil molar ratio. This behaviour can be interpreted in terms of a more favoured methoxide formation as the methanol/oil ratio increases due to an increased driving-force for methanol adsorption. This is in contrast with the use of NaOH since in this case the amount of methanol has little effect on the formation of the methoxide species provided it is present in a sufficiently high quantity.

In the range of NaOH loadings of the catalysts considered in this work, the alumina-supported catalysts gave similar results in experiments conducted at the same NaOH equivalent concentration. The NaOH loading did not influence the reaction selectivity that, as for the homogeneous NaOH catalyst, was governed by the molar methanol/oil ratio.

It has been found that part of the sodium initially deposited onto the catalyst is leached from the solids, which reveals a lack of chemical stability of the catalysts under reaction conditions. However, the percentage leached did not surpass 5% even after 9 h of reaction; therefore, the influence of the leached sodium on the overall performance of the NaOH/γ-Al_2O_3 catalysts is expected to be of little importance.

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References

[1] F. Ma, M.A. Hanna, Bioresour. Technol. 70 (1999) 1–15.
[2] A. Srivastava, R. Prasad, Renew. Sust. Energ. Rev. 4 (2000) 111–133.
[3] J. Van Gerpen, Fuel Process. Technol. 86 (2005) 1097–1107.
[4] L.C. Meher, D. Vidya Sagar, S.N. Naik, Renew. Sust. Energ. Rev. 10 (2006) 248–268.
[5] Commission of the European Communities. Communication from the Commission on An EU Strategy for Biofuels. COM (2006) 34. Brussels, 8.2.2006.
[6] L. Bournay, D. Casanave, B. Delfort, G. Hillion, J.A. Chodorge, Catal. Today 106 (2005) 190–192.
[7] http://www.axens.net/.
[8] T.F. Dossin, M.-F. Reyniers, G.B. Marin, Appl. Catal. B 61 (2006) 35–45.
[9] S. Gryglewicz, Bioresour. Technol. 70 (1999) 249–253.
[10] S. Gryglewicz, Appl. Catal. A 192 (2000) 23–28.
[11] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Chem. Eng. J. 116 (2006) 61–66.
[12] H.-J. Kim, B.-S. Kang, M.-J. Kim, Y.M. Park, D.-K. Kim, J.-S. Lee, K.-Y. Lee, Catal. Today 93–95 (2004) 315–320.
[13] W. Xie, H. Peng, L. Chen, Appl. Catal. A 300 (2006) 67–74.
[14] G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mandiky, M.J. Goff, Appl. Catal. A 257 (2004) 213–223.
[15] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, Appl. Catal. A 287 (2005) 183–190.
[16] S. Ramu, N. Lingaiah, B.L.A. Prabhavathi Devi, R.B.N. Prasad, I. Suryanarayana, P.S. Sai Prasad, Appl. Catal. A 276 (2004) 163–168.
[17] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1991.
[18] B. Freedman, E.H. Pryde, T.L. Mounts, J. Am. Oil Chem. Soc. 61 (1984) 1638–1643.
[19] G. Arzamendi, E. Arguiñarena, I. Campo, L.M. Gandía, Chem. Eng. J. 122 (2006) 31–40.
[20] G. Vicente, A. Coteron, M. Martinez, J. Aracil, Ind. Crop. Prod. 8 (1998) 29–35.
[21] D.G.B. Boocock, S.K. Konar, V. Mao, C. Lee, S. Buligan, J. Am. Oil Chem. Soc. 75 (1998) 1167–1172.
[22] D. Darnoko, M. Cheryan, J. Am. Oil Chem. Soc. 77 (2000) 1263–1267.
[23] H. Noureddini, D. Zhu, J. Am. Oil Chem. Soc. 74 (1997) 1457–1463.
[24] S. Szczepańska, S. Malinowski, J. Catal. 15 (1969) 68–82.
[25] W.-D. Mross, Catal. Rev. Sci. Eng. 25 (1983) 591–637.
[26] V. Perrichon, M.C. Durrupty, Appl. Catal. 42 (1988) 217–227.
[27] P. De Filippis, C. Borgianni, M. Paolucci, Energy Fuels 19 (2005) 2225–2228.
[28] T. Ebiura, T. Echizen, A. Ishikawa, K. Murai, T. Baba, Appl. Catal. A 283 (2005) 111–116.
[29] European Committee for Standardization, Automotive fuels. Fatty methyl esters (FAME) for diesel engines. Requirements and test methods, European Standard EN 14214:2003.