Chemical routes to materials

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Potassium-containing hydroxylated hydrotalcite as efficient catalyst for the transesterification of sunflower oil

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ABSTRACT

Different hydrotalcite-based materials were evaluated as heterogeneous catalysts for the transesterification of sunflower oil with methanol. A set of compounds based on magnesia-alumina structures (MgAl hydrotalcites) were synthesized. To carry out the initial co-precipitation, salts and bases of either sodium or potassium were chosen. The products obtained were afterward submitted to calcination and dehydration/rehydration treatments in order to induce layered restoration. The intermediate and final solids obtained were characterized by XRD, FTIR, SEM and EDX analyses. The catalytic activity of the rehydrated samples was tested in the transesterification reaction of sunflower oil with methanol for biodiesel production. The effectiveness of these materials as heterogeneous catalysts was evaluated in terms of time for maximum conversion and reusability. All the products were identified as hydrotalcite-like materials being accompanied by small percentages of crystalline Mg phases when potassium ions were used for providing the alkaline synthesis medium. Improved conversion levels were obtained by using K-containing MgAl hydrotalcites submitted to calcination at 500 °C and subsequently rehydrated under controlled conditions. The presence of residual sodium or potassium was detected in the rehydrated samples, in concordance with the corresponding cation used for the starting synthesis formulation. Both materials were catalytically active, the better results being those reached with the potassium-containing samples. Conversion as high as 80% of biodiesel was obtained at a

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methanol/oil mass ratio of 3:10, a catalyst concentration of 3% w/w referred to the oil mass and 65 $\pm$ 1 °C for 180 min of reaction time. After reactivation, the catalyst was reused giving 40% oil conversion after 300 min of reaction time.

Introduction

Nowadays, most of the world's fuel demand is covered by fossil fuels. These nonrenewable fuels are rapidly depleting and causing serious environmental problems. Biofuels look like a current solution to reduce the exhaustion of traditional fuels.

Biodiesel derived from vegetable oils is one of the most widely used biofuels. In addition to being renewable, it has low toxicity and it is biodegradable. It is usually produced by transesterification of triglycerides with methanol in the presence of a catalyst, to give a mixture of methyl esters of fatty acids and glycerin as product [1–4].

Nowadays, the industrial production of biodiesel uses homogeneous catalysts. Among them, the most widespread is sodium methoxide, which can be obtained from sodium and methanol [3–5]. Sodium methoxide is a simple and efficient catalyst, but its use presents some difficulties associated with the formation of water and soaps during the reaction, which increases catalyst consumption and leads to side effects, such as the formation of emulsions and long settlement times that affect the product quality. Additional washing steps of biodiesel would also be needed, increasing the production cost [5–9].

Several compounds have been studied as heterogeneous catalysts for the synthesis of biodiesel, alkaline and alkaline earth metal oxides, hydroxides and salts being the most widely tested materials [7–14]. Among them, the double-layered hydroxide materials, which are also known as hydrotalcites, have attracted much attention during the development of new environmentally friendly catalysts [15–19]. Hydrotalcites are characterized by basic properties, but they are not frequently used in catalysis as pristine hydrotalcites because their catalytic sites are not of easy accessibility, unlike the active mixed oxides resulting from hydrotalcite calcination [20]. In some cases, the basic activity of hydrotalcites can be significantly improved by reconstructing the structure with hydroxides in the interlayer spaces and then, being able to be used in transesterification reactions to produce biodiesel. Furthermore, the deposition of nanoparticles of sodium or potassium salts or hydroxides, which are effective catalysts for the mentioned reaction, on the hydrotalcite surface could increase even more the hydroxylated hydrotalcite activity [16, 21].

In the present paper, catalyst materials derived from MgAl hydrotalcites were studied. The starting hydrotalcites were obtained by the conventional synthesis method, i.e., co-precipitation of mineral salts in alkaline aqueous medium, followed by the hydrothermal treatment of the obtained gels. The aim of this work was to use potassium instead of sodium salts in the initial co-precipitation mixture and to determine the influence of potassium presence on the structure, textural properties and catalytic activity of the derived catalysts obtained. On this basis, here we present the synthesis, characterization and catalytic performance of the prepared solids in the transesterification reaction of sunflower oil and methanol for biodiesel production.

Experimental

Materials

The chemicals used in this study include aluminum nitrate (Al(NO$_3$)$_3$ 9H$_2$O, Biopack Art. 9996.06), magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O, Biopack, Art. 9597.07), sodium carbonate (Na$_2$CO$_3$, Anedra, Art. 7165), potassium carbonate (K$_2$CO$_3$, Cicarelli, Art. 233), sodium hydroxide (NaOH, Anedra, Art. 6482), potassium hydroxide (KOH, Cicarelli, Art. 1055), refined sunflower oil (Cañuelas) and methanol (Biopack, Art. 6197P1).

Catalyst preparation

Two Mg–Al hydrotalcite-like compounds were prepared by the co-precipitation method [16, 20, 22]. For this purpose, an aqueous solution of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O was prepared as the source of Mg and Al. Two alkaline solutions of the following compositions were also prepared: (1) 2.34 M NaOH

and 0.6 M Na_2CO_3, and (2) 2.34 M KOH and 0.6 M K_2CO_3, using deionized water as the solvent.

The solution containing Al and Mg was treated independently with one of the two alkaline solutions, giving rise to the corresponding hydrotalcite-type material. The process was carried out as follows: 50 mL of Al–Mg solution and 50 mL of the selected alkaline solution were slowly and simultaneously added dropwise under vigorous stirring in an Erlenmeyer flask for 1 h. The chemical composition obtained corresponded to a Mg/Al molar ratio of 5. The temperature was maintained around 25 °C, and the pH was controlled during the addition. The resulting mixture was aged in an oven at 65 °C for 24 h. After cooling, the solids were recovered by filtration, washed with distilled water and dried overnight in an oven at 100 °C. The solids obtained using solutions numbered (1) and (2) were named HT_{Na} and HT_K, respectively.

After characterization, samples HT_{Na} and HT_K were calcined at 500 °C for 6 h (HTC_{Na} and HTC_K). Finally, the samples were dispersed in boiling deionized water for 30 min. In each experiment, the solid fraction was separated from the liquid by filtration, and the solid was dried in a vacuum oven (25 mm Hg) at 65 °C until constant weight. The obtained samples were named $HTCR_{Na}$ and $HTCR_K$.

Catalyst characterization

The structural characterization of crystalline materials was performed by X-ray diffraction (XRD). The diffraction patterns were obtained in PANalytical X´Pert PRO 3373/00 equipment (40 kV, 40 mA, Cu Kα by Ni filter, step width 0.02°). The Rietveld method [23] and the program "FullProf" [24] were used for estimating the percentage of different crystalline phases and the crystalline parameters of the hydrotalcite materials.

Shimadzu IR Affinity-1 Fourier transform infrared equipment, pellets in KBr and a measuring range of 4000–400 cm^{-1} were used to obtain the FTIR spectra. The samples were placed directly into the chamber, and 48 scans were used for each spectrum.

The alkalinity of the solids was evaluated by CO_2-temperature programmed desorption (TPD). Approximately 10 mg of catalyst, sandwiched by quartz wool, was loaded in a quartz tube. The CO_2 adsorption was performed at room temperature over the fresh material for 1 h. Then, pure nitrogen was

flowed, the temperature was increased up to 100 °C, and this temperature was maintained until no physically adsorbed CO_2 was detected. The TPD experiment was carried out by heating at 12 °C min^{-1} in nitrogen flow from 100 to 750 °C. The CO_2 coming out of the sample cell passed through a methanation reactor. To this reactor a H_2 stream was also fed, quantitatively converting CO_2 to CH_4, using a Ni catalyst. The CH_4 was continuously measured by a FID detector. The equipment was calibrated by sending pulses of CO_2 diluted in He. A blank experiment (without CO_2 adsorption) was also performed. In this case, the fresh sample was heated in N_2 flow, performing the TPD under the same conditions.

The morphology of the samples was obtained by scanning electron microscopy (SEM) using a Philips 505 microscope. The semiquantitative chemical composition was obtained by energy-dispersive X-ray (EDX) using an electron microprobe coupled to the scanning electron microscope.

The adsorption–desorption nitrogen isotherms were measured for the synthesized samples using Micromeritics ASAP 2020 apparatus at the temperature of liquid nitrogen (− 196 °C), in the relative pressure range 0.01–0.99. Before adsorption, the samples were outgassed by heating at 100 °C in vacuum, with a pressure lower than 3×10^{-2} mm Hg for 12 h. The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area.

Transesterification reaction

The catalytic evaluation of the prepared solids was performed using sunflower oil and methanol. Transesterification reactions were carried out in a closed glass reactor, at 65 °C, with a methanol/oil mass ratio of 3:10 and a catalyst concentration of 3% w/w referred to the oil mass. Temperature was controlled with a thermostatic water bath. The mixture was stirred by a magnetic bar at 200 rpm.

Sunflower oil was preheated in the glass reactor. A suspension of the catalyst and methanol was added once the oil temperature was 65 °C.
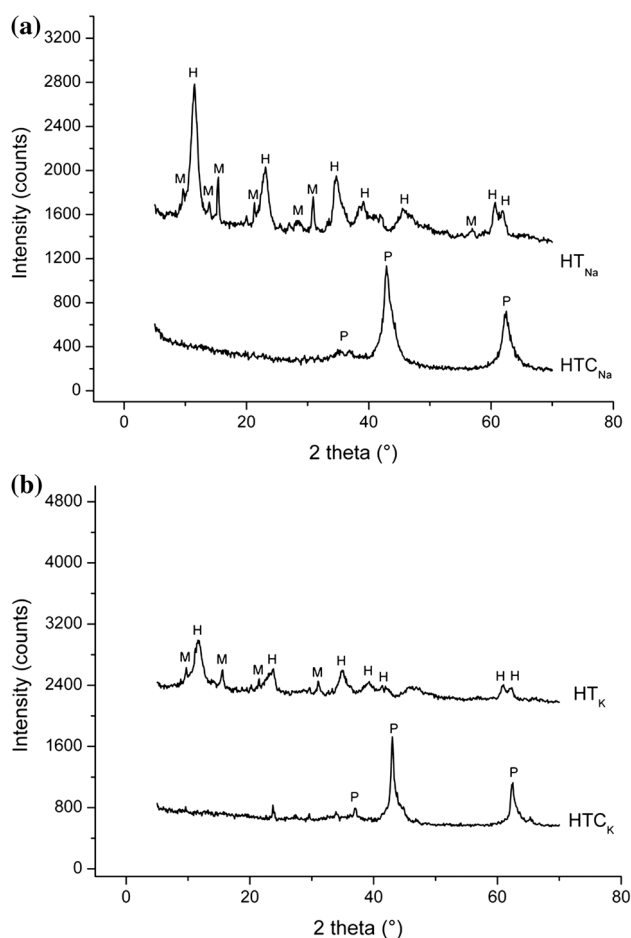
The reaction progress was controlled by thin-layer chromatography (TLC). Samples were taken with a syringe through a septum at different reaction times. The final conversion was determined by gas chromatography.

Results and discussion

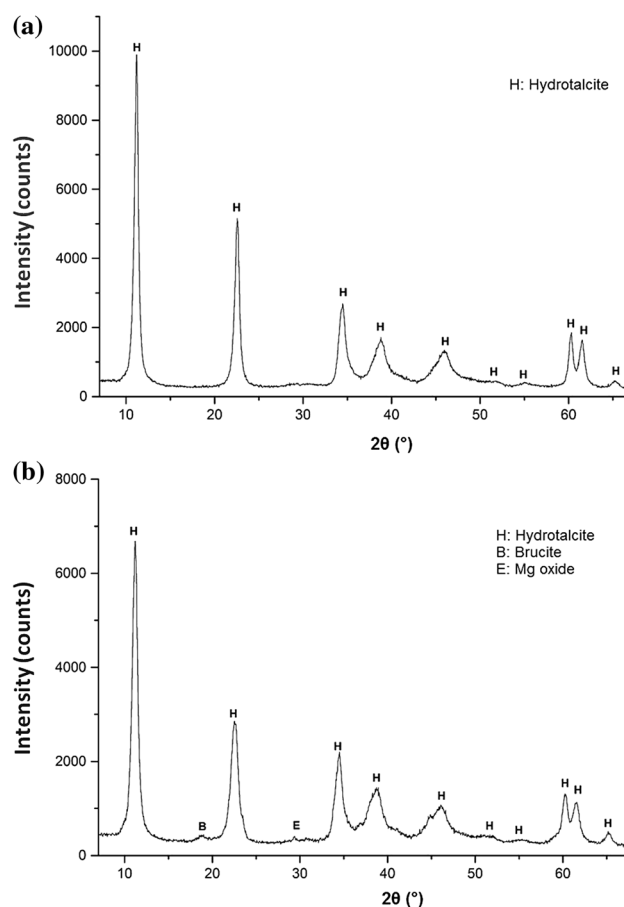### Catalyst characterization

X-ray diffraction

In Fig. 1 the original solids and their calcination products are compared. Figure 1a shows the XRD patterns corresponding to HT_{Na} and HTC_{Na}, and Fig. 1b those corresponding to HT_K and HTC_K. The two samples showed characteristic peaks corresponding to the crystallographic planes (003), (006), (009), (012), (110) and (113), ascribed to carbonated Mg–Al hydrotalcite (H) (JCPDS card 14-0191). The crystallization of a small percentage of carbonate hydroxide $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O$ (M) was also observed (JCPDS card 08-0179). These peaks disappear in the diffraction pattern of the calcined samples (HTC_{Na} and HTC_K) where peaks corresponding to

mixed oxides of Mg(Al) can be observed at $2\theta = 42.9°$ and $62.5°$.

Figure 2 shows the diffraction patterns of the samples $HTCR_{Na}$ and $HTCR_K$. The regeneration of the original structures is observed after rehydration. The two samples showed the characteristic peaks corresponding to the crystallographic planes (003), (006), (009), (012), (110) and (113), which were present in the as-synthesized samples and were lost after calcination. These peaks were, as before, ascribed to carbonated MgAl hydrotalcite, named as H phase in Figs. 1 and 2. The $HTCR_{Na}$ sample showed reflection peaks with higher intensities than those present in $HTCR_K$, indicating a crystallinity in the order $HTCR_{Na} > HTCR_K$. In $HTCR_{Na}$, diffraction peaks were ascribed to a pure, well-crystallized hydrotalcite phase H. In $HTCR_K$, the major phase was also the H phase, but minor fractions of brucite (B) and a spinel-type MgO (E) were also present. The alteration of the symmetry of the H peak situated at $2\theta = 23°$ could be

Figure 1 XRD of the original hydrotalcites and their corresponding calcination products: **a** sodium-containing samples; **b** potassium-containing samples.

Figure 2 XRD patterns corresponding to samples **a** $HTCR_{Na}$ and **b** $HTCR_K$.

attributed to traces of quintinite $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$, not shown in Fig. 2.

To estimate the structural parameters of the hydrotalcites, the diffraction peaks were indexed to a hexagonal lattice with rhombohedral 3R symmetry. It is known that the parameter a ($a = 2 \times d_{110}$) varies according to the metal–metal distance within the layers, and the parameter c ($c = 3 \times d_{003}$) depends on the metal cation nature, the water content and the size of the charge-compensating anions present in the interlayer region [25]. For the prepared samples, the value of the lattice parameter a is almost constant, $a \approx 3.06$ Å, revealing that the average intermetallic spaces of the obtained layered matrices are identical. Additionally, the c parameter, related to the interlayer distance, is ≈ 7.7 Å, indicating that OH^- ions are present in the interlayer space [26]. Rehydration after calcination results in the formation of meixnerite, a hydrotalcite in which hydroxides are the compensating anions present in the interlayer space [20]. Furthermore, in the diffraction patterns of the reconstructed samples no peaks were observed for sodium or potassium compounds, indicating that these compounds are present in the form of very small particles not detected by this technique. It can be considered then that the hydrotalcite reconstructions from mixed oxides in aqueous medium promote the reaction of the oxides with water to form, on the one hand, the meixnerite-like hydrotalcite and, on the other, NaOH and KOH nanoparticles, which are deposited on the hydrotalcite crystal surfaces.

Chemical composition

Table 1 shows the local chemical composition of the samples obtained by EDX.

For the initial HT samples the Mg/Al ratio of the solids did not seem to be significantly altered by the inclusion of K^+. Regarding the Mg concentration, it is

worthwhile to note that in the K-containing samples this bulk value comprises the Mg^{2+} participating in the hydrotalcite structure and also in the other crystalline phases detected by XRD (Fig. 2). The high K level in HTK, HTCK and HTCRK could be related to the presence of insoluble amorphous phases containing this cation and/or also to K^+ ions situated inside the layer sheets, near the interlayer region. This last hypothesis was based on previous work, where the author suggested that K could be included in the octahedral voids of hydrotalcites, generating a lack of crystallinity by deformation of the ordered layers [27].

FTIR spectroscopy

The FTIR spectra of the rehydrated materials $HTCR_{Na}$ and $HTCR_K$ are shown in Fig. 3.

The FTIR spectra of the two rehydrated hydrotalcites are similar. The bands corresponding to OH^- group vibrations are present at 3500 cm^{-1}, being mainly attributed to the hydroxyl groups of the hydrotalcite layers, to interlaminar water molecules and to OH^- stretching. The 1650 cm^{-1} bands are assigned to the water confined between hydrotalcite layers [28]. Vibrations located at 1380 cm^1, associated with interlayered carbonates (CO_3^{2-}), clearly appear in $HTCR_{Na}$ and $HTCR_K$. Then, the FTIR analysis indicates the presence of OH^- and CO_3^{2-} in the interlayer zone as counterbalancing charged species. The bands appearing between 400 and 900 cm^{-1} are

Table 1 Chemical analysis obtained by EDX (% w/w)

Sample	Na$_2$O	K$_2$O	MgO	Al$_2$O$_3$	MgO/Al$_2$O$_3$ ratio
HT$_{Na}$	0.92	0	61.78	37.3	1.66
HTC$_{Na}$	0.78	0	66.2	33.02	2.00
HTCR$_{Na}$	0.97	0	62.61	36.42	1.72
HT$_K$	0	17.27	51.81	29.77	1.74
HTC$_K$	0	15.46	53.68	30.86	1.74
HTCR$_K$	0	15.77	53.27	30.96	1.72
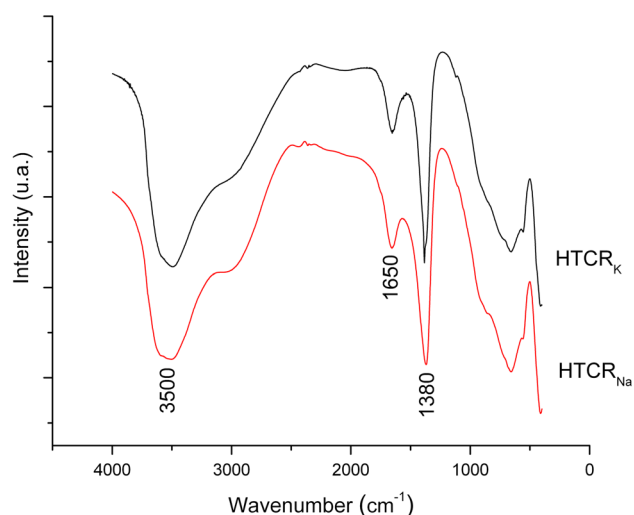
Figure 3 FTIR patterns of the rehydrated samples $HTCR_{Na}$ and $HTCR_K$.

related to the presence of M^{2+} and M^{3+} cations [25, 28, 29].

CO_2-TPD analyses

As is shown in Fig. 4 the CO_2-TPD profiles of the obtained materials show a single broad desorption peak between 350 and 500 °C (Fig. 4). The latter accounts for high CO_2 retention sites, given that the basicity strength is proportional to the desorption temperature of CO_2 molecules. The position of the desorption peak maxima in the CO_2-TPD patterns slightly increases in the order $HTCR_K > HTCR_{Na}$, and the CO_2 retention, calculated from the TPD pattern, increases in the order $HTCR_K < HTCR_{Na}$. It can be seen that better catalytic results were obtained for $HTCR_K$. These results could be explained on the basis of the active sites accessibility. It is known that in hydrotalcite-like materials, small cations like Mg could lie in the octahedral voids of hydrotalcite layers, the water molecules and anions being located between the layers. This localization of small cations gives rise to a molecular sieve effect that could modify the catalytic site accessibility. Besides, as described in [27] the eventual inclusion of larger cations such as Na^+ and K^+ could produce a distortion of the layered structure. Recently, other authors have analyzed this opposite trend in terms of limited CO_2 accessibility [30].

Scanning electron microscopy

The SEM micrographs in Fig. 5 correspond to the hydrotalcite-like materials $HTCR_{Na}$ (Fig. 5a, b) and $HTCR_K$ (Fig. 5c, d). In both samples, particles with an irregular size distribution, between 2 and 30 μm, are observed. An aggregation of the characteristic platelets detected in the as-synthesized samples (not shown) seemed to occur in the rehydrated samples. Nevertheless, some laminar structures could still be observed.

Surface area analysis

The BET surface areas of prepared hydrotalcites and their corresponding calcined and rehydrated samples are shown in Table 2.

In general, no big changes were noted in the BET area values after the different post-synthesis treatments. The surface areas of the original hydrotalcites were 8.27 m^2/g for HT_{Na} and 5.61 m^2/g for HT_K. While the surface areas of the samples increased slightly after calcination, Table 2 shows that the surface areas of the rehydrated samples decreased with respect to the calcined ones. The higher surface area of the calcined samples can be associated with the release of interlayer water molecules and carbon dioxide from carbonate anions. The mixed oxide phase is reconstructed after the rehydration process in the water solution, presenting surface areas of 6.71 and 5.22 m^2/g for $HTCR_{Na}$ and $HTCR_K$, respectively.
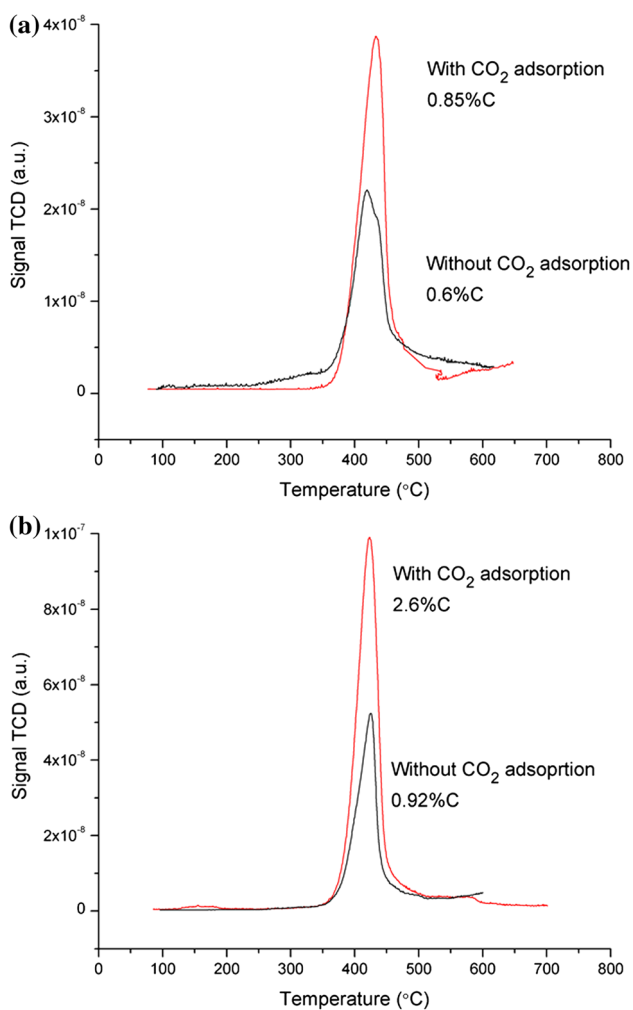
Figure 4 CO_2-TPD corresponding to **a** $HTCR_K$ and **b** $HTCR_{Na}$.
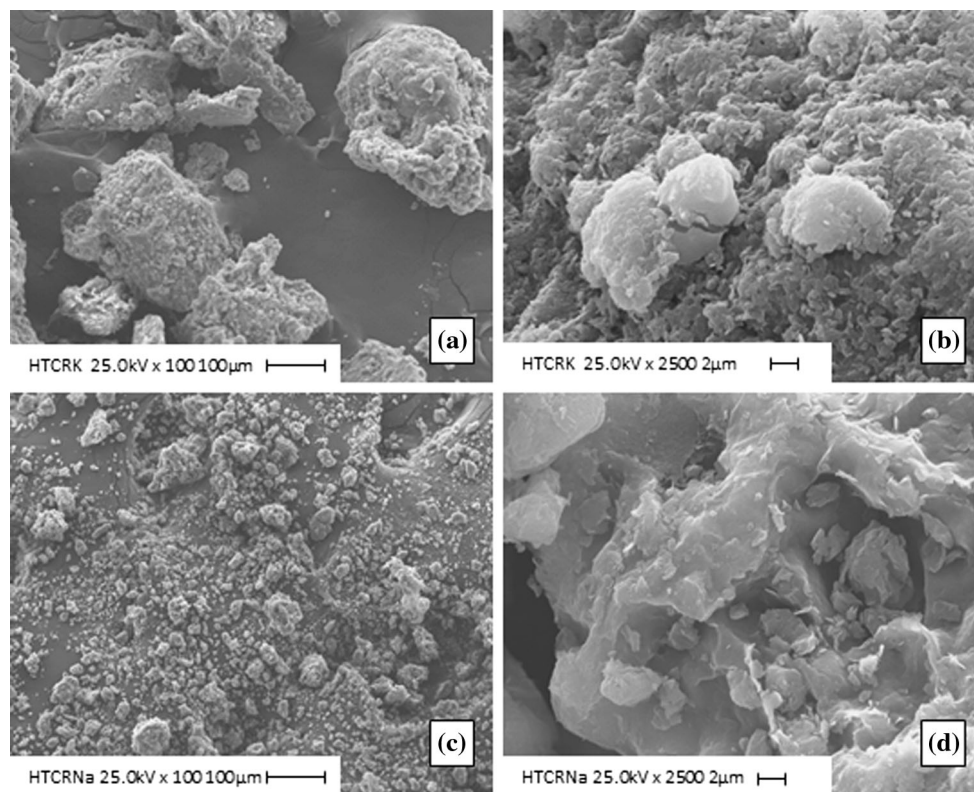
**Figure 5** SEM images of HTCRK (**a**, **b**) and HTCRNa (**c**, **d**) samples.

Table 2 BET surface area

Sample	BET surface (m^2/g)
HT$_{Na}$	8.27
HT$_K$	5.61
HTC$_{Na}$	9.56
HTC$_K$	7.64
HTCR$_{Na}$	6.71
HTCR$_K$	5.22

Catalytic performance

Catalytic test

The original HT$_{Na}$, HT$_K$ synthesized materials and their reconstructed products HTCR$_{Na}$ and HTCR$_K$ were tested as catalysts for the synthesis of biodiesel under mild reaction conditions (temperatures not higher than 65 °C). The results obtained are shown in Fig. 6 and Table 3. The transesterification reaction was followed by thin-layer chromatography. The conversion values given in Table 3 were obtained by gas chromatography.
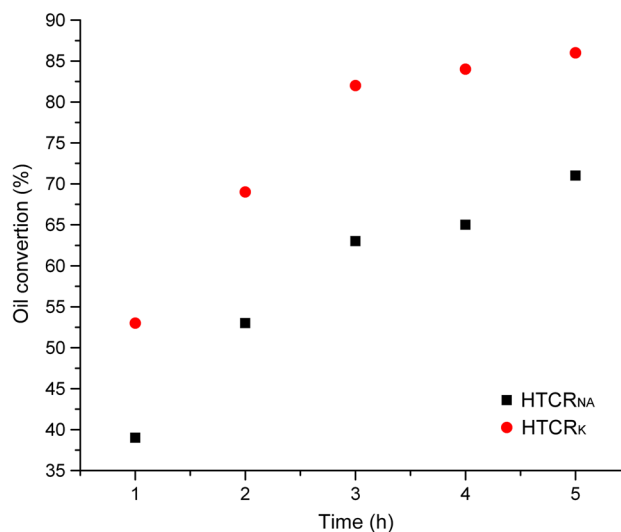
Figure 6 Evolution of sunflower oil conversion with reaction time for HTCR$_{Na}$ and HTCR$_K$ catalysts.

The initial hydrotalcite samples, as expected, were not active for the studied reaction, indicating that the hydroxide anions present in the hydrotalcite layers are situated in structural voids or positions that are not accessible to the reactant and then, catalytically inactive [16]. Instead, in the reconstructed samples,

Table 3 Time and values recorded for maximum conversion in biodiesel using the different synthesized samples

Sample	Reaction time (h)	Conversion (%)
HT_{Na}	20	–
HTC_K	20	–
$HTCR_{Na}$	8	> 70
$HTCR_K$	3	> 80

the interlayered hydroxide anions act as Brønsted sites, exhibiting a strong basic character [31], and are active for the studied reaction. It should be noted that the CO_2-TPD results seem not to be in agreement with the performance of the catalysts (Table 3). Furthermore, a clear reduction in the time needed for getting high conversion values was observed when $HTCR_K$ was used as catalyst. Percentage values for maximum conversion higher than 80 at a reaction time as short as 3 h were recorded for the K-containing sample. Undoubtedly, the presence of potassium instead of sodium compounds in the first step of hydrotalcite preparation induces the generation of solid products that retain appreciable quantities of K that consist of a crystalline mixture of MgAl hydrotalcite accompanied by a low content of other Mg ordered structures. Nevertheless, the high K content reflected by EDX analysis should be present forming hydroxide compounds spread over the crystalline surfaces in sizes not detectable by XRD.

Reuse

$HTCR_K$ samples were selected to study their reusability capacity. After the transesterification reaction, the catalyst was recovered from the product by centrifugation. The used catalyst was embedded in the remaining glycerol that could block the catalyst active sites, so the mixture was washed with tetrahydrofuran and recovered by centrifugation. This procedure was repeated four times, and then the sample was filtered and dried. After reactivation, the catalyst was reused giving 40% oil conversion after 300 min of reaction time. Xie et al. [32] reported the transesterification of soybean oil with methanol catalyzed by NaX zeolites loaded with KOH. They found a good initial activity, but a very fast decrease when reusing the catalyst due to potassium hydroxide lixiviation from the zeolite surface. It seems that in the present work, the potassium compounds are accessible and strongly retained on the hydrotalcite structure, as shown by the high conversion of 40% obtained after reuse.

Conclusions

All the synthesized solids mainly consist of MgAl hydrotalcites, regardless of the synthesis medium. After being thermally treated, the solids lose their ordered structure and present the characteristics of mixed magnesium and aluminum oxides. In agreement with previous works found in the literature, the samples regenerate their structure after being subjected to an easy rehydration process, containing interlayered OH^- after rehydration. The regenerated hydroxylated hydrotalcite in addition to potassium hydroxide homogeneously dispersed on the hydrotalcite surface results in a material with high activity in the heterogeneous transesterification reaction of sunflower oil for obtaining biodiesel fuels.

Acknowledgements

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