

Transesterification of Soybean Oil with Ethanol Using Heterogeneous Catalysts Based on Hydrotalcites

Evelyn Alves Nunes Simonetti¹ & Gilberto Garcia Cortez¹

¹ Escola de Engenharia de Lorena, University of São Paulo, Lorena, São Paulo, Brazil

Correspondence: Evelyn Alves Nunes Simonetti, Escola de Engenharia de Lorena, University of São Paulo, Lorena, São Paulo. E-mail: evelyn@dequi.eel.usp.br

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Abstract

This work evaluated the potential of hydrotalcites based in Ca-Al on transesterification of soybean oil with ethanol. The reaction was carried out at 78.5 °C with ethanol:oil molar ratio of 30 and 10 wt% of catalyst. The 2Ca-Al showed better performance than 3Ca-Al catalyst achieving conversion of 94%. The catalyst were characterized with XRD, BET and activity was evaluated on isopropanol decomposition reaction.

Keywords: biodiesel, ethanol, transesterification, hydrotalcite, soybean oil

1. Introduction

The search for renewable sources has opened a new field to fuels development and the biodiesel has stood out due to its same properties of conventional diesel and for the facility of being used directly in diesel engines or in mixtures. These properties are possible by the presence of mono-alkyl esters of long chain fatty acids on biodiesel structure. Another important fact is the biodiesel combustion, it has low emission of harmful gas such as sulfur oxide which is a great advantage to the environmental system (Gerogogianni et al., 2009; Helwani et al., 2009). Transesterification is the cheaper and easy route of biodiesel synthesis and it consists in a reaction between vegetable oil or animal fat with alcohol (methanol or ethanol) to form ester and glycerol. The stoichiometry is 3:1 (alcohol: triglycerides) and it is common to use an excess of alcohol to improve the yield (Enweremadu & Mbarawa, 2009). Transesterification is often applied as a homogeneous reaction using acid and basic catalysts, such as sulfuric and hydrochloric acids, KOH and NaOH (Meher et al., 2006; Demirbas, 2009). The advantages of these catalysts are low reaction time and high yields. Although there are many disadvantages such formation of soap, elevated ratio alcohol:oil, impossibility of reuse the catalyst and difficulty in separating the catalyst from the azeotropic system. To avoid these problems countless studies have been published to develop new heterogeneous catalysts - such like metal hydroxides, oxides, zeolites, supported catalysts and hydrotalcites (Lee & Saka, 2010; Semwal et al., 2011). Among these catalysts the hydrotalcites (LDHs) has opened a new source in heterogeneous catalysis due to its innumerable composition and applications. The layered double hydroxides or hydrotalcites (LDHs) can be represented by the following general formula: $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^x A^{m-}_{x/m} nH_2O$. The structure of hydrotalcites is based upon layered double hydroxides with brucite like (Mg(OH)₂) hydroxide layers containing octahedrally coordinated M²⁺ and M³⁺ cations (Crepaldi & Valim, 1998). The thermal processing of HDL promotes the formation of metastable crystalline phases, such as the spinel phase and/or mixed oxides, forming acid and/or basic sites (Vaccari, 1998; Goh & Lim, 2008). Studies developed identified four different types of active sites identified in calcined HDL samples: isolated O²⁻ ions, pairs of Mg²⁺O²⁻ and OH⁻ groups and acid sites (Al³⁺) (Di Cosimo et al., 1998). Many researches have been done on transesterification catalyzed by LDH. The most common hydrotalcite applied is the Mg-Al using methanol and vegetable oil as triglyceride source. It was achieved yields between 67-90.5% (Siano et al., 2006; Xie et al., 2006; Zeng et al., 2008). Another types of hydrotalcite can be used on transesterification such like MgCoAl-LDH. In this particular study was used canola oil and ethanol, the results showed elevated yields at high ethanol:oil ratio (Li et al., 2009).

The objective of this study is to evaluate the catalytic performance of hydrotalcite in the transesterification reaction using Ca-Al hydrotalcite obtained by continuous precipitation. It was evaluated the catalytic activity of the compounds with different molar ratio of Ca/Al.

2. Materials and Methods

2.1 Catalysis Synthesis

The hydrotalcite precursors were prepared from aqueous solutions containing $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The atomic ratio, $y = \text{Ca}^{2+}/\text{Al}^{3+}$, was equal to 2 and 3. An aqueous solution of 1.5 mol/L of K_2CO_3 was used as precipitating agent. These two solutions were maintained at 55 °C and mixed in a reactor keeping pH of 10.0 ± 0.4 during all process. The precipitate was kept at 40 °C for 24 hours under slow agitation. Then, it was separated by vacuum filtration and washed with deionized water up to neutral pH. The catalysts were calcined at 450 °C and named as 2Ca-Al calcined and 3Ca-Al calcined.

2.2 Surface Area and Pore Volume

Samples were treated at 300 °C for 3 hours in order to remove chemicals adsorbed. The surface area and pore volume were analyzed in an equipment BET, model Belsorp II, using nitrogen adsorption at 196 °C and relative pressures (P/P_0) ranging from 0.05 to 0.35. The pore distribution was determined using the BJH method from the adsorption/desorption isotherms and the specific area by BET method.

2.3 X-ray Diffraction (XRD)

X-ray diffraction were performed using the powder method an SEISERT equipment, model 1001, radiation $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) and nickel filter. Crystalline phases were identified using JCPDS (Joint Committee of Powder Diffraction Standards, 1983).

2.4 Isopropanol Decomposition Reaction

The catalytic performance was evaluated through the decomposition of isopropanol, using a fixed bed reactor (quartz), with a continuous flow of reagents at atmospheric pressure. The activation of the catalyst was performed in situ at 200 °C for 2 h at oxygen (AGA, 99.9999%) atmosphere. The reactor was fed with isopropanol (99.7%, Merck) using a pump Thermo Separation Products, Model Spectra P100, at 0.05 mL of flow, diluted in a mixture of He and O_2 (molar ratio 3/1) at a flow rate of $74 \text{ mL} \cdot \text{min}^{-1}$. The reaction was carried out at a range of 170 °C to 310 °C, using catalyst mass of 100 mg and a residence time factor (W/F_{A0}) equal to $2.4 \text{ g} \cdot \text{h} / \text{mol}_{\text{isop}}$. Gases released by the catalyzed reaction were analyzed on line by a chromatograph Varian GC-3350, equipped with a thermal conductivity detector (TCD) and provided with a column packed Carbowax 20M, operating with a heating temperature between 30 and 150 °C. Helium was used as carrier gas in the column.

The conversion (X_A), selectivity (S_p) and specific activity (mols of converted products) were calculated using Equations 1-3 and they were based on the input and output concentration and assuming a differential reactor:

$$X_A(\%) = \left(\frac{n_I}{n_{I0}} \right) 100 \quad (1)$$

$$S_p(\%) = \left(\frac{n_p}{n_I} \right) \left(\frac{N_{CP}}{N_{CI}} \right) 100 \quad (2)$$

$$\text{SpecificActivity} = \frac{F_{A0} X_A S_p}{W_A S_g} \quad (3)$$

Where:

n_I : mols of isopropanol consumed;

n_{I0} : mols of isopropanol fed;

N_{CP} : mols of carbon atoms formed;

N_{CI} : mols of carbon atoms in isopropanol;

F_{A0} : mols of isopropanol fed per minute;

W_A : catalyst mass;

S_g : catalyst specific area (m^2/g).

2.5 Transesterification with Ethanol

The catalysts were activated in an oven at 200 °C for 24 h and the transesterification reactions were conducted in a spherical reactor (500 mL) equipped with a mechanical stirring. The amount of catalyst used in each experiment was 10% relative in mass of soybean oil. The experiments were performed in fixed conditions of temperature (78.5 °C) and molar ratio of 1 to 30 (oil/alcohol). In many works it is common to use a molar ratio up to 15:1 (alcohol:oil). Although, this proportion is more usually in reactions with methanol. In this work we

use ethanol as alcohol font which is less reactive than methanol, so it was required a higher molar ratio. After the reaction the catalyst was separated by vacuum filtration. Then, distilled water was added to filtrate and homogenate. The upper phase was separated and washed twice with distilled water. Then, the sample was centrifuged and trace of methanol and ethanol were removed by distillation. The biodiesel was finally dried with anhydrous sodium sulfate and stored at 4 °C for further analysis.

2.6 Proton Nuclear Magnetic Resonance (^1H NMR)

The biodiesel samples were diluted in deuterated chloroform (CDCl_3 , Aldrich) and analyzed in a spectrometer model Varian MERCURY 300 MHz operating in the region from 4.4 to 4.0 ppm. The absorption signals of chloroform were used as internal reference for the standard scale. The values of chemical shifts are expressed in units (ppm), coupling constants (J) and Hertz (Hz).

The conversion in ethyl ester was evaluated based on the signals present in the region of 4.05 to 4.35 ppm of ^1H NMR spectrum. In the ^1H NMR spectrum of soybean oil, this region represents the methylene hydrogens of triglyceril (Garcia, 2006). According to Equation 4 the resonance peak of the etoxyl hydrogen atoms of the ethyl esters split into a quartet. The area under the first and fourth peak is $A_t/8$ and that one under the second and third is $3A_t/8$, where A_t is the sum of areas under the four peaks. The fourth component (A_{c4}) of the quartet of ethyl esters (range 4.07 to 4.08 ppm) is a single peak that does not suffer overlap from any other peak, so that component was used to calculate the conversion of ethanolsis vegetable oils.

$$EE(\%) = \left(\frac{8A_{c4}}{A_{dd+ee}} \right) 100 \quad (4)$$

Where:

A_{c4} = area of the component fourth peak;

A_{dd+ee} = area of all signals between 4.35 and 4.05 ppm;

EE(%) = percentage of ethyl esters in vegetable oils.

3. Results and Discussion

3.1 X-ray Diffraction (XRD)

Figure 1 shows the X-ray diffraction (XRD) profiles of the 2Ca-Al not calcined, 2Ca-Al calcined, 3Ca-Al not calcined and 3Ca-Al calcined samples. It can be observed that the samples 2Ca-Al not calcined and 3Ca-Al not calcined showed small peaks at 15°, 18°, 20°, 23° which are associated to layered structure. These peaks exhibit low intensity when compared to the conventional hydrotalcite Mg-Al. There are also the peaks related to the formation of CaCO_3 crystals (calcite) in 29°, 47° and 48° (JCPDS 72-1652). After the calcination process the peaks related to layered structure disappear in 2Ca-Al and 3Ca-Al calcined samples. The elevated temperature of drying and calcination increases the rate of water and carbon dioxide released. This phenomenon damages the solid structure leading to a loss of the lamellar arrangement. Besides, the preparation method not ensure the uniform mixing of the Ca^{2+} and Al^{3+} and the Ca^{2+} cations can agglomerate, favoring the formation of CaCO_3 crystals (Frost et al., 2009; Yu et al., 2011; Gao, 2010).

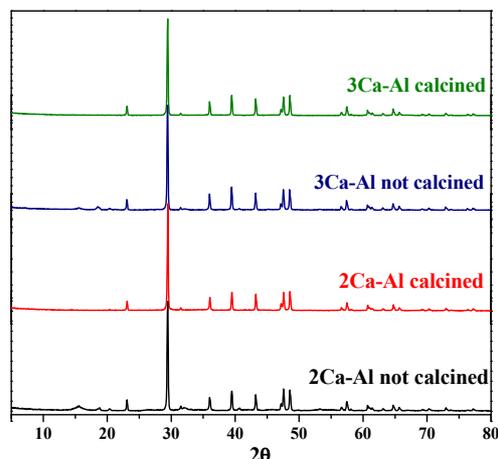


Figure 1. XRD patterns of samples 2Ca-Al uncalcined, 3Ca-Al uncalcined, 2Ca-Al calcined at 450 °C and 3Ca-Al calcined at 450 °C

3.2 Surface Area and Pore Volumes/Adsorption-Desorption

Figure 2 shows the nitrogen adsorption/desorption isotherms measured at $-196\text{ }^{\circ}\text{C}$ on 2Ca-Al calcined and 3Ca-Al calcined. Table 1 shows the characteristic parameters of the porosity of these catalysts, such as specific surface areas (S_{BET}) and total pore volumes (V_{p}). The isotherms can be classified as type III (IUPAC classification – International Union of Pure and Applied Chemistry). The shape of these isotherms is characteristic of non-porous or macroporous particles which interact very weakly with the adsorbent molecules. It also related to system with adsorption heat virtually nil and related to small gas volume - this can be observed in the sintered samples with surface area less than $5\text{ m}^2/\text{g}$ (Sing et al., 1982; Santilli & Pulcinelli, 1993). The hysteresis type is H3 and there are mainly two cases in which this type can be formed: very wide capillaries having narrow openings and an interstice between the parallel plates. It is also found in adsorption isotherms of many crystalline metal oxide aggregates of sheet-like shape. The slit width increase during adsorption and decreases irreversibly during desorption (Kaneko, 1994). Figure 2 also shows that the sample 2Ca-Al decreases the amount adsorbed as well the values of surface area and specific pore volume when compared to 3Ca-Al as showed in Table 1. Despite the smaller specific surface area the sample 2Ca-Al has a larger average pore diameter in accordance with Table 1. This may suggest that the 2Ca-Al catalyst has pores wider than those in 3Ca-Al catalyst and also has a smaller number of pores (Teixeira et al., 2001).

Table 1. Values of specific surface area (S_{BET}) and specific pore volume (V_{p}) of the samples 2Ca-Al calcined and 3Ca-Al calcined

Catalyst	S_{BET} (m^2/g) (BET)	V_{p} (cm^3/g) (BJH)	Pore Diameter (nm)
2Ca-Al calcined	6.60	0.07	45.10
3Ca-Al calcined	13.7	0.11	32.18

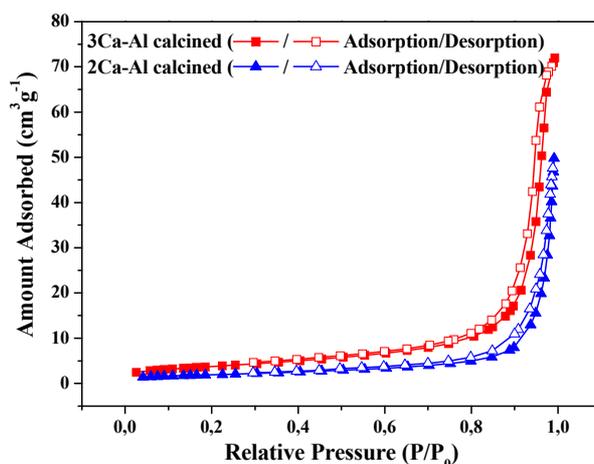


Figure 2. Nitrogen adsorption/desorption isotherms at $-196\text{ }^{\circ}\text{C}$ of samples 2Ca-Al calcined and 3Ca-Al calcined

3.3 Pore Size Distribution

Figure 3 shows the pore size distribution (estimated by N_2 adsorption) of the 2Ca-Al calcined and 3Ca-Al calcined catalysts. It can be noted that the porous structure of 2Ca-Al calcined and 3Ca-Al calcined are basically composed of pore in the mesoporous region ($2\text{ nm} < w < 50\text{ nm}$) with multimodal distribution indicating heterogeneity in the samples. In this region can be observed the presence of two peaks in about 10 nm for the 2Ca-Al calcined and 50 nm for the 3Ca-Al calcined sample.

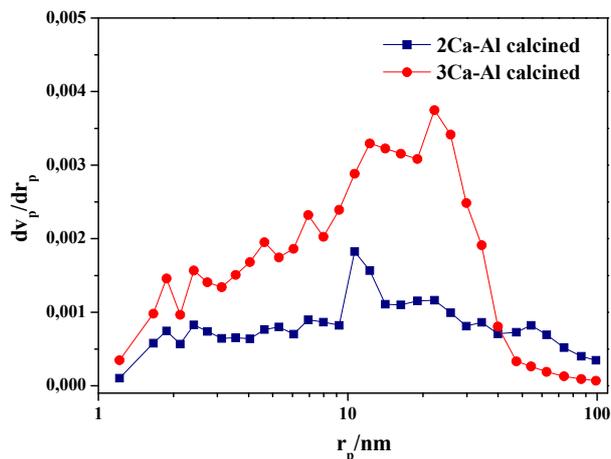


Figure 3. Pore size distribution of the samples 2Ca-Al calcined and 3Ca-Al calcined

3.4 Isopropanol Decomposition Reaction

Table 2 shows the results of specific catalytic activity of the catalysts evaluated in isopropanol decomposition reaction at 250 °C, 280 °C and 300 °C. The main products were propylene and diisopropyl ether in both catalysts. The 2Ca-Al calcined sample showed higher specific catalytic activity at different temperatures when compared to the 3Ca-Al calcined for both products, propylene and diisopropyl ether according to Table 2. Isopropanol conversion is often applied as catalytic test to obtain the effective catalytic properties of acid and base sites. Thus, the formation of propylene (from dehydration of isopropanol) or acetone (from dehydrogenation) provides information about the presence of acid and basic (or redox) centers, respectively (Gervasini et al., 1997). It can be observed that all samples showed the formation of propylene and diisopropyl ether. These products are related to dehydration of isopropanol using acid sites of the catalyst (Gervasini et al., 1997). The main reason to the acid sites are associated with great amount of aluminum ions represented to the high density of $\text{Al}^{3+}\text{O}^{2-}$ groups on the surface. However the basic groups are provided by MgO groups on the surface of the conventional hydrotalcites (Diez et al., 2003; Aramendia et al., 1996). The absence of basic represented by $\text{Ca}^{2+}\text{O}^{2-}$ groups is related to the bond between the calcium and carbonate. Both mechanism of propylene and diisopropyl formation are correlated to the abstraction of the alcohol molecule on catalysts surface by the acid site. This abstraction promotes the formation of carbanions and then olefins and ether (Robles-Medina et al., 2009). At 250 °C the diisopropyl formation was more intense with 3Ca-Al catalyst however at 280 °C and 300 °C the formation was much more intense with 2Ca-Al. The mechanism of ether and propylene formation can be represented below, where A represents an acid site and B a basic site.

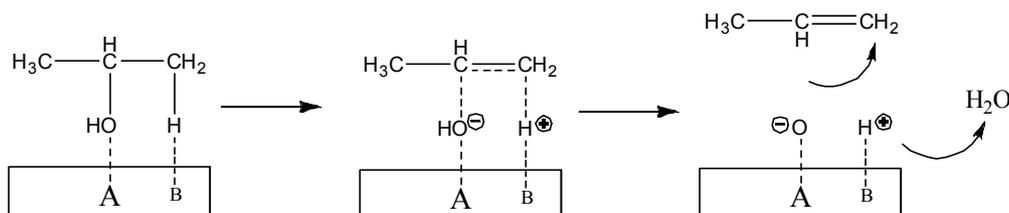


Figure 4. Mechanism of propylene formation on decomposition of isopropanol

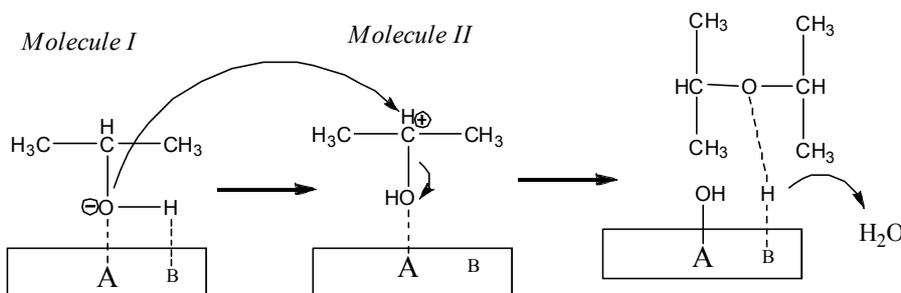


Figure 5. Mechanism of ether formation on decomposition of isopropanol

Table 2. Specific catalytic activity of samples 2Ca-Al calcined and 3Ca-Al calcined

Catalyst	Specific Catalytic Activity (10^{-4} mol m $^{-2}$ min $^{-1}$)					
	Propylene			Diisopropyl Ether		
	250 °C	280 °C	300 °C	250 °C	280 °C	300 °C
2Ca-Al calcined	0.110	0.440	1.400	0.002	0.140	0.660
3Ca-Al calcined	0.044	0.234	0.564	0.044	0.085	0.239

3.5 Transesterification Reaction

^1H NMR technique was used to characterize and quantify the ethyl ester formation by the transesterification reaction of soybean oil. The technique used to evaluate the conversion of triglycerides in ethyl esters is based on the signals presents in the region of 4.05 to 4.35 ppm of ^1H NMR spectrum (Garcia, 2006). This region represents the methylene hydrogens of triglycerides molecules of soybean. After transesterification reaction the signals of etoxyl hydrogen of ester molecules takes place. The Figure 4 shows the spectra of the reactions catalyzed by 2Ca-Al, 3Ca-Al calcined and soybean oil. It can be observed that the transesterification catalyzed by 2Ca-Al calcined showed the typical spectra etoxyl hydrogen of ethyl ester molecule. When compared with the soybean spectra it can be observed that there is no overlap with the signals of the triglyceride molecules indicating high conversion in ethyl esters. Table 3 shows the integration values of signals between 4.06 and 4.35 ppm where conversion with 2Ca-Al calcined reached 94%. The spectra of the reaction catalyzed by 3Ca-Al calcined showed an overlap of signals between the methylene hydrogens of triglycerides and the signals of etoxyl hydrogen of ethyl ester molecule. It can be observed that the 3Ca-Al calcined spectra approaches to the soybean spectra indicating low conversion. The table 3 shows that the reaction catalyzed by 3Ca-Al reached only 31% of conversion.

Table 3. Integration peaks and the conversion percentage determined by ^1H NMR

Catalyst	Area A_{c4}	Area A_{dd+ee}	Conversion (%)
2Ca-Al calcined	1.06	7.58	94
3Ca-Al calcined	0.04	0.99	31

The addition of calcium in the 3Ca-Al catalyst was expected to enhance the conversion of ethanolsis due to the creation of basic sites which are more active than acid sites, but the effect was the opposite. The carbonate present in the samples displays no particular catalytic activity on the reaction. This function belongs to the mixed oxides after calcination (Xie et al., 2006). The Al^{3+} cations occupy the octahedral sites in hydrotalcites before calcination and the structure rearranges at high temperature in a tetrahedral form combined with Ca^{2+} cations. A positive charge is generated by this rearrangement and it is compensated by the formation of two types of defects: cationic vacancies and/or inclusion of interstitial oxygen which promotes the formation of sites like $\text{Al}^{3+}\text{O}^{2-}$ or $\text{Ca}^{2+}\text{O}^{2-}$ (Xie et al., 2006). In this study the main site formed was related to $\text{Al}^{3+}\text{O}^{2-}$ as evidenced in isopropanol decomposition reaction and the calcium content promotes the formation of carbonate. Adding more calcium in structure enhances the formation of carbonate and decreases the aluminum sites. With less active site available the access to the bulky triglyceride molecules decreases and then the conversion in ethyl esters is lower. Another important factor are the wider pores present in the 2Ca-Al catalyst which provides more contact with the triglyceride molecules and then increase the conversion in ethyl esters. Despite the higher surface area of 3Ca-Al catalysts it does not contributed to the elevation of conversion. The amount of carbonate formed occupies a large extension of catalyst inhibiting the action of the active sites and blocking contact with the triglyceride molecules.

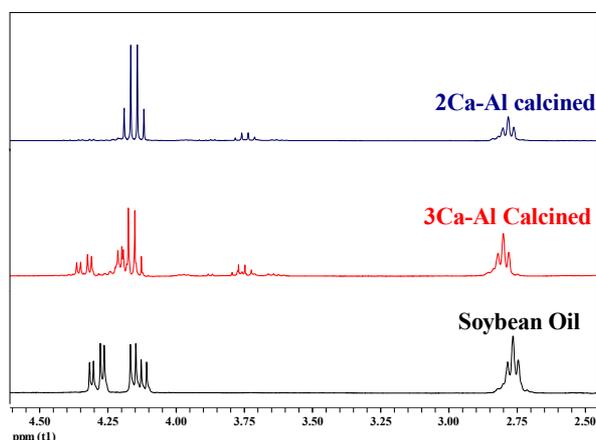


Figure 6. ^1H NMR spectra of soybean oil and ethyl ester catalyzed

4. Conclusion

In this work was proposed the use of heterogeneous catalysts using hydrotalcites in soybean oil ethanolysis. The Ca-Al LDHs were prepared by the co-precipitation method using Ca/Al ratio of 2 and 3. The XRD spectrum showed the appearance of peaks related to CaCO_3 crystals in all samples – that can be the elevated temperature of drying and calcination used in this work. The isotherms were classified as type III characteristic of non-porous or macroporous particles which interact very weakly with the adsorbent molecules. The surface area of the catalyst increased with the addition of calcium content as also the pore volume. The 2Ca-Al showed higher specific catalytic activity than 3Ca-Al. The acid sites formed were probably related to the aluminum content. The calcium addition inhibits these acid sites decreasing the production of propylene and ether in the isopropanol decomposition reaction. The transesterification of soybean oil reached the conversion of 94% with 2Ca-Al catalyst and 31% with 3Ca-Al. The main reason for the difference in reaction yields is related to higher amount of active sites in the catalyst 2Ca-Al. The larger surface area of the catalyst 3Ca-Al did not transform in higher yields.

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