Chemical modification of the surface of alumina with alkaline earth metal oxides using the polymeric precursor method for catalysis application

(Modificação química da superfície de alumina com óxidos de metais alcalino-terrosos usando o método do precursor polimérico para aplicação em catálise)

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Abstract

In this study, modifications of alumina surface with of alkaline earth metal oxides were studied, using the polymeric precursor method. The modified compounds were characterized by X-ray diffraction, nitrogen adsorption-desorption and scanning electron microscopy. The catalytical properties of these new catalysts were evaluated for the transesterification reaction of babassu oil. It is observed that the transesterification reaction of babassu oil with methanol was successfully carried out using the modified alumina samples.

Keywords: surface modification, alumina, alkaline earth metal oxides.

Resumo

Neste trabalho foram estudadas modificações da superfície de alumina com óxidos de metais alcalino-terrosos, usando o método dos precursores poliméricos. Os compostos modificados foram caracterizados por difração de raios X, adsorção-dessorção de nitrogênio e microscopia eletrônica de varredura. As propriedades catalíticas desses novos catalisadores foram avaliadas para a reação de transesterificação de óleo de babaçu. Foi observado que a reação de transesterificação de óleo de babaçu com metanol ocorreu com sucesso na presença das aluminas modificadas.

Palavras-chave*: modificação de superfície, alumina, óxidos de metais alcalino-terrosos.*

INTRODUCTION

Nowadays, many studies have been undertaken aiming at obtaining new solid-state materials displaying physical and chemical properties that are suitable for useful technological applications. It is well known that alumina is one of these materials, once unmodified and modified alumina have been studied for various applications.

The Bayer process, starting from bauxite, is the most common route for the production of alumina. However, there are several methods for preparing this material. For example, Ibrahim and Abu-Ayana [1] used the sol–gel polymeric route for synthesizing ultrathin alumina. Recently, alumina has been applied as soft replica molding for large area UV-nanoinprint lithography [2] and nitric oxide sensors [3]. Among many other applications, it can be used as substrate for superconducting materials [4], packing material for the reversed-stationary phase of HPLC columns [5] support for various active phases [6-8], in heterogeneous catalysis. Chen and co-workers [9] prepared a series of alumina-supported alkaline earth metal oxides by impregnation and studied the basicities of these materials by temperature-programmed desorption of carbon dioxide. However, the surface of solids can be modified by using other physical and chemical techniques. Maciel and co-workers [10, 11] modified the surface of alumina with lanthanum oxide nanocoats, using the polymeric precursor method, a sol-gel like method. In this study, the authors coated the water-dispersed alumina particles, with a polymeric precursor. The modified alumina shows, at high temperatures, significant modifications in the grain morphology and microstructure.

Thus, in the present work we report the results on the investigation of surface modifications of commercial alumina with alkaline earth metals, using the polymeric precursor method and we report results on the catalytic activity of these materials. The catalytic properties of new materials were appraised for biodiesel from the transesterification reaction of the babassu oil into methanol. Babassu oil is obtained from the seeds of the babassu tree (native Brazilian palm) that contains a high percentage of saturated fatty acids.

MATERIALS AND METHODS

The samples of commercial alumina with the surface modified by alkaline earth metal oxides were prepared using the following starting materials: barium nitrate (Aldrich, purity >99.9%), calcium nitrate (CQA, purity >99.5%), magnesium nitrate (CQA, purity >99.5%), commercial alumina (ALUMAR, Brazil, purity >99%), citric acid (Merck, purity >99.9%) and ethylene glycol (Mallinckrodt Baker, purity >99.9%).

Polymeric precursors from alkaline earth metal oxides were used to modify the alumina surface. These precursors were obtained from alkaline earth metal nitrates and citric acid. Ethylene glycol was added to promote the polymerization reaction. The aqueous solutions of such polymeric precursor method were prepared with appropriate reagents in distilled water. These polymeric precursors were added to the alumina aqueous suspension, previously dispersed in distillated water, using an ultra-sonic probe [11]. Adequate amounts of polymeric precursors of alkaline earth metal oxides were added in order to achieve exactly 5% molar concentrations of the different alkaline earth metals in relation to alumina. Following, water was slowly evaporated at 80 ºC. The dried materials were decomposed for 4 h at 350 ºC to remove the organic matter. Finally, these materials were heat treated for 2 h at 700 ºC. Fig. 1 displays the main steps required for preparing commercial alumina modified with alkaline earth metal oxides by the polymeric precursor method.

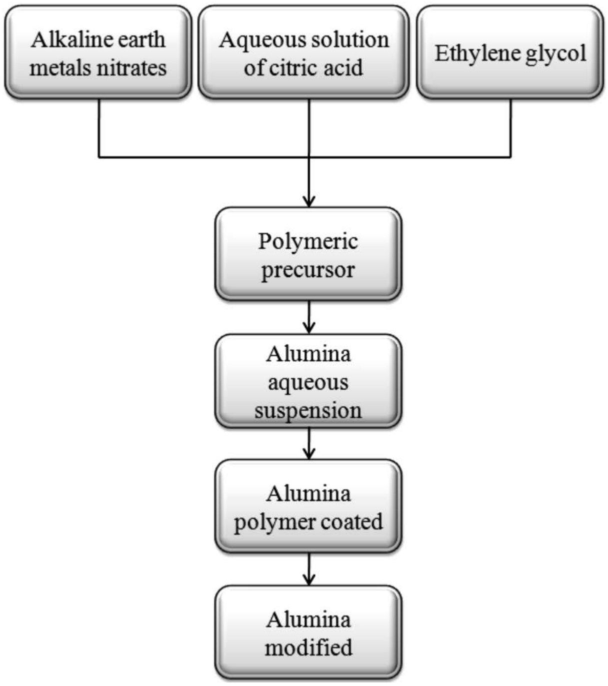

Figure 1: The main steps for preparing alumina modified with alkaline earth metal oxides by the polymeric precursor method.
[Figura 1: Principais etapas para preparação da alumina modificada com óxidos de metais alcalino-terrosos pelo método dos precursores poliméricos.]

The materials were structurally characterized by X-ray diffraction (XRD) using a Rigaku-DMax/2500PC, Japan, diffractometer with Cukα radiation ($\lambda = 1.5406$ Å) in the 2θ range from 20º to 75º, with angular step 0.05º/s.

The BET and BJH methods were applied for the determination of the specific surface area, and porous structure, respectively. The nitrogen adsorption–desorption isotherms were measured by means of a Micromeritics ASAP 2000 system at -196 °C. Before the measurement, the samples were dried at 100 °C and evacuated until that a degassing pressure lower than 6 μmHg was attained.

The sample morphologies were verified using scanning electron microscopy (FEG-SEM), Carl Zeiss Supra 35-VP. All measurements were performed at room temperature.

Semi-refined babassu oil, obtained from Empresa Oleaginosas do Maranhão (OLEAMA, S. Luís, MA, Brazil) and methanol (Quimex, PA) were utilized. These reagents were used as received.

The transesterification reactions were carried out in a Parr reactor series 4561 with Parr 4842 controller. The reactions occurred at 180 ºC for 16 h. The babassu methyl esters obtained were analyzed by gas chromatography (GC) in a Varian 3800 Chromatograph with a flame ionization detector and 5% phenyl 95% polydimethylsiloxane column (30 m x 0.25 mm). The temperatures of the injector and detector were set at 290 and 300 °C, respectively.

RESULTS AND DISCUSSION

Fig. 2 displays the obtained X-ray diffraction patterns for commercial alumina, (a) unmodified, (b) modified with 5% calcium oxide and (c) modified with 5% magnesium oxide. The XRD pattern for alumina modified with 5% barium is shown in Fig. 3.

In Fig. 2, the XRD patterns of unmodified alumina and alumina modified with calcium and magnesium oxides only display two characteristic phases: corundum (rhombohedral) and aluminum oxide (monoclinic), according to the corresponding JCPDS files 46-1212 and 23-1009, respectively.

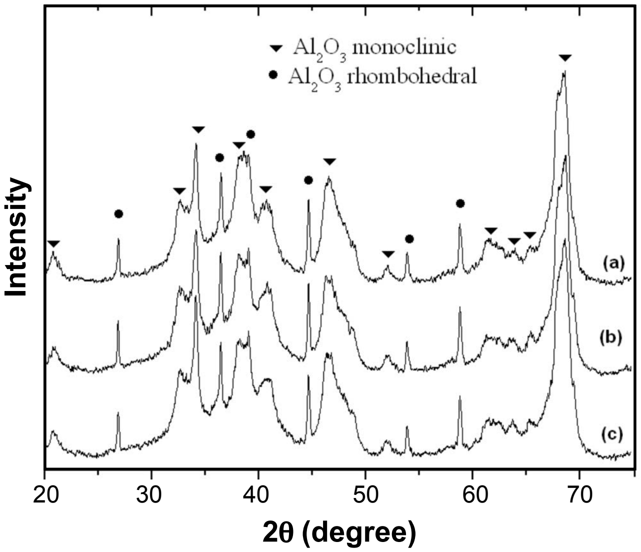

Figure 2: XRD patterns, (a) for unmodified alumina, (b) for alumina modified with 5% calcium oxide and (c) for alumina modified with 5% magnesium oxide.
[Figura 2: Padrões de DRX, (a) para alumina não modificada, (b) para alumina modificada com 5% de óxido de cálcio e (c) para alumina modificada com 5% de óxido de magnésio.]

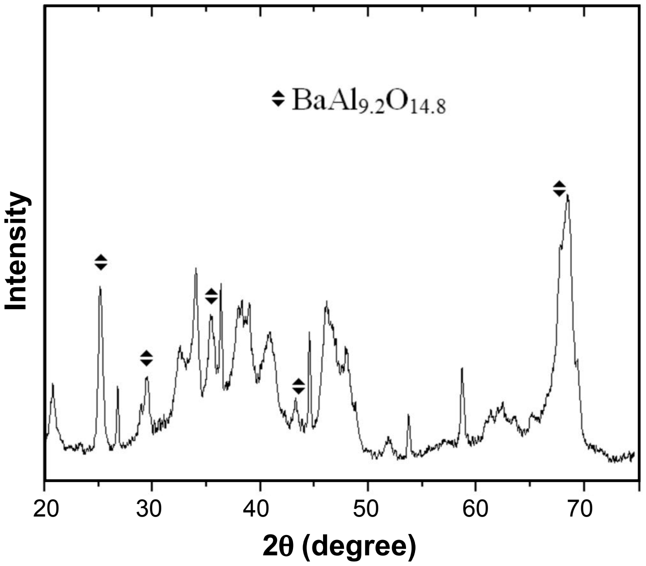

Figure 3: XRD pattern for alumina modified with 5% barium oxide.
[Figura 3: Padrão de DRX para alumina modificada com 5% de óxido de bário.]

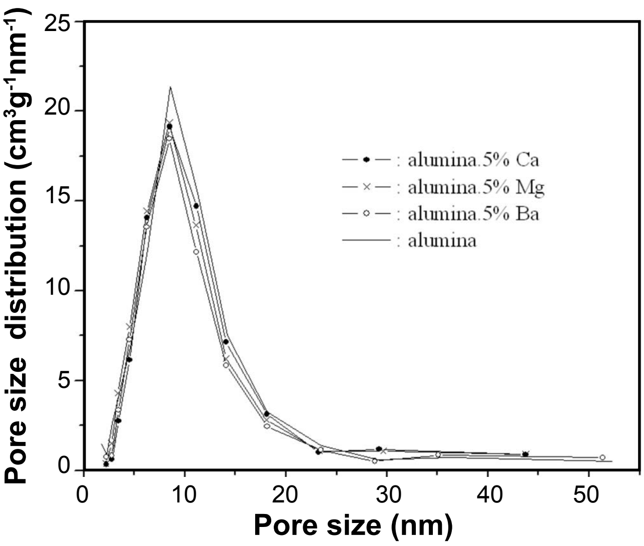

Figure 4: Information on the pore structure of the unmodified and modified alumina samples heat treated at 700 °C. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions.
[Figura 4: Informações sobre a estrutura de poros de amostras de alumina não modificada e modificadas tratadas termicamente a 700 °C. (a) Isotermas de adsorção-dessorção de N_2 *e (b) distribuição de tamanho de poros.]*

However, for the sample modified with barium oxide, occurs the formation of a new crystalline phase, see Fig. 3. It is observed that, in this case, the new structure obtained on the surface of the commercial alumina modified by barium oxide, using the sol-gel method, is related to the stoichiometry $BaAl_{9.2}O_{14.8}$ (JCPDS file 33-0129). A large number of non-stoichiometric barium aluminates are known, in which the phase formation is related to the molar ratio between barium oxide and alumina [12-14]. Nevertheless, $BaAl_{9.2}O_{14.8}$ is not a common aluminate phase. The formation of $BaAl_{9.2}O_{14.8}$ can be justified by the new route synthesis, in which, initially the barium polymeric precursor is attached on the alumina surface. Subsequently the material undergoes a heat treatment. The alumina surface atoms easily react with barium oxide giving rise to the aluminate phase on surface of the alumina. The X-ray patterns for unmodified alumina and alumina modified with barium oxide are very similar, except that the latter presents the peaks of the new phase. This similarity indicates that the bulk alumina support is not modified in the process. This suggests that only the surface

Table I - Textural properties of the unmodified alumina and alumina modified with Ba, Ca, Mg.
[Tabela I - Propriedades texturais da alumina não modificada e modificadas com Ba, Ca, Mg.]

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
BET surface area, m^2/g	58.20	45.20	49.32	48.25
BJH surface area of pores, m^2/g	85.46	67.85	71.05	73.65
Micropore area, m^2/g	-5.22	-3.07	-0.56	-1.78
Micropore Volume, cm^3/g	-0.0034	-0.0023	-0.0010	-0.0016
Average pore diameter (BJH), nm	9.14	9.69	9.96	9.42

Sample 1: Unmodified alumina; Sample 2: Alumina.5% Ba; Sample 3: Alumina.5% Ca; Sample 4: Alumina.5% Mg

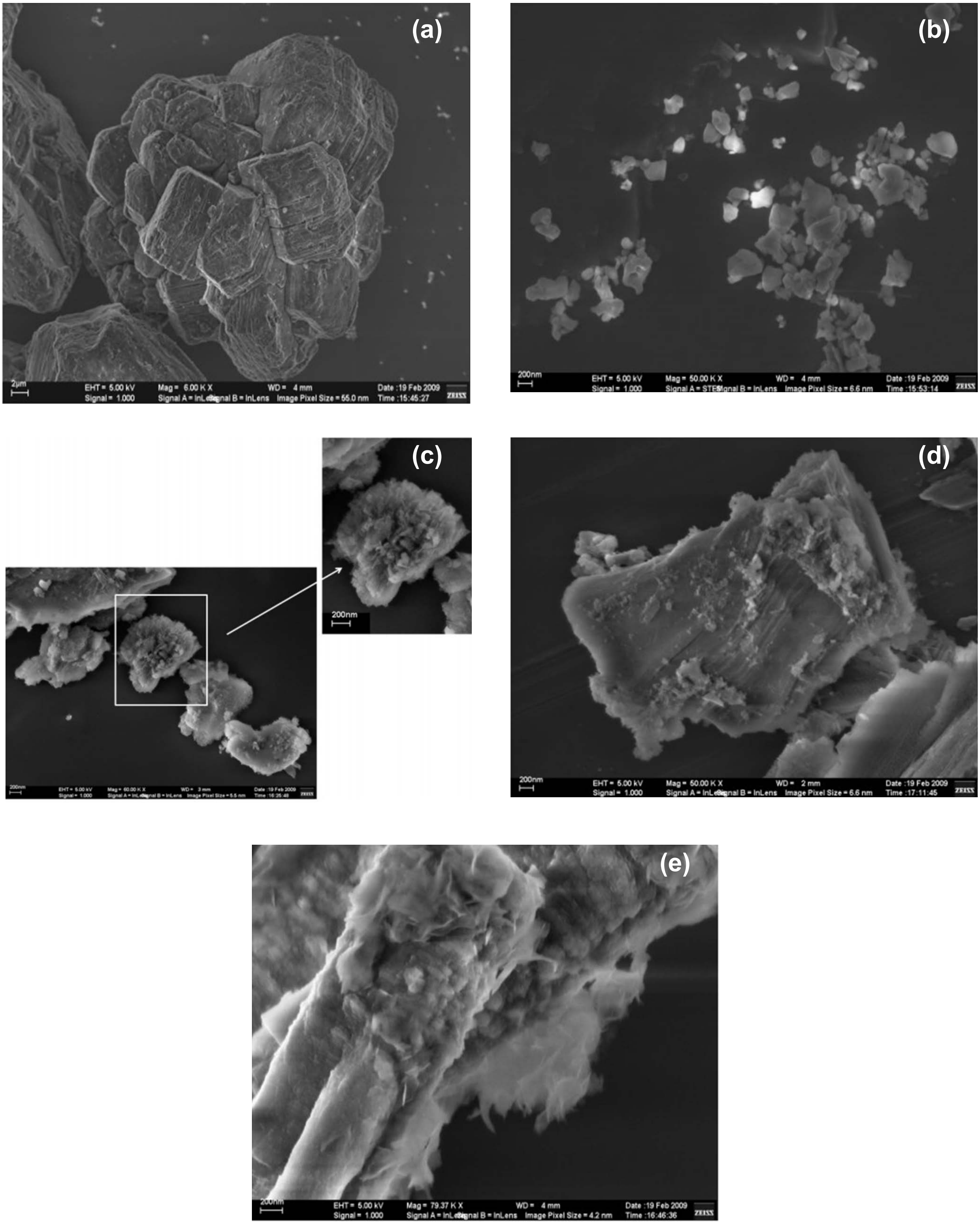

Figure 5: SEM micrographs. (a, b) unmodified alumina, (c) alumina modified with 5% barium oxide (d) alumina modified with 5% calcium and (e) alumina modified with 5% magnesium oxide.

[Figura 5: Micrografias de MEV. (a, b) alumina não modificada, (c) alumina modificada com 5% de óxido de bário e (d) alumina modificada com 5% de óxido de cálcio e (e) alumina modificada com 5% de óxido de magnésio.]

layers of the alumina react with barium oxide.

The unmodified alumina (raw material) shows a surface area of 62.70 m^2/g. After a heat treatment at 700 °C for 2 h, its surface area decreases to 58.20 m^2/g (Table I). Commonly, increasing the heat treatment temperature, occurs the formation of a sintered alumina phase, such as α-Al_2O_3, with the consequent grain growth; and this process progressively reduces the surface area of the material. This behavior was also observed for the BJH cumulative desorption surface area of pores, see Table I. A negative volume and area of micropores can be an indication of the absence of micropores in the samples [15]. The sample of alumina modified with barium oxide was the one that presented the greatest modifications in surface and pore structures, as compared with the unmodified alumina sample. Probably, this is due the formation of a new crystalline phase of barium aluminate on the surface of alumina.

Fig. 4 shows the surface and pore properties of the samples analyzed by nitrogen adsorption-desorption measurements. Fig. 4 (a) shows that all isotherms behave similarly, as typical type IV sorption with H2 hysteresis loop. This behavior is characteristic of mesoporous structures (2-50 nm). The pore size distribution obtained by the BJH method for the samples shows narrow monomodal distributions in the region between 2 and 50 nm, see Fig. 4(b). Significant changes were not observed in the average pore diameters of the samples, which were kept at around 9 nm. These results suggest that uniform pore structures were maintained even after the modification of the alumina surface.

In Figs. 5 a-b, it can be observed that particles of the commercial alumina show bimodal grain size distribution. The coarser part of the sample is formed by agglomerates with average size of 40 μm. In these agglomerates there are large grains with average size about 10 μm, see Fig. 5 a. These large particles probably present corundum phase [16]. Fig. 5 b displays the finer part of the commercial alumina, which shows an average size of about 200 nm. These fine particles could be related to aluminum oxide (monoclinic) phase.

Fig. 5 c shows the morphology of the sample of alumina modified with barium oxide, displaying particles of about 1 μm, it can be noticed that such morphology is similar to the mesocrystal structure reported [17]. In the particle enlarged, the aluminate phase, displaying the stoichiometry $BaAl_{9.2}O_{14.8}$, is clearly observed on the surface of the alumina. The aluminate phase is formed by agglomerated nanometric particles with 50 nm of average size. In the SEM micrographs of the samples of alumina modified with calcium oxide, Fig. 5d, and magnesium oxide, Fig. 5e, new phases were observed on the surface of the alumina particles. These phases were not observed by XRD analysis, and then these compounds formed on the surface present non-crystalline phases. In the scientific literature, various vitreous phases of calcium and magnesium aluminates are reported [18]. Fig. 5d shows small areas of the new non-crystalline phase on the alumina surface for the samples of alumina modified with calcium oxide. These small areas present an average size smaller than 50 nm. In Fig. 5e, representing the sample of alumina modified with magnesium oxide, nanometric flake-like structures can be observed on the surface of alumina. These flakes presented an average thickness of around 30 nm and average length of about 500 nm.

Fig. 6 shows that the catalysts based on alumina modified with alkaline earth metal oxides were efficient for transesterification reaction of babassu oil. No significant reaction was noticed with unmodified alumina. It can be seen in Fig. 6 that the catalyst with 5% magnesium oxide presented the best methyl ester yield. This is due to the fact that magnesium oxide addition leads to a number of alkaline sites higher than does the addition of calcium and barium oxides [19].

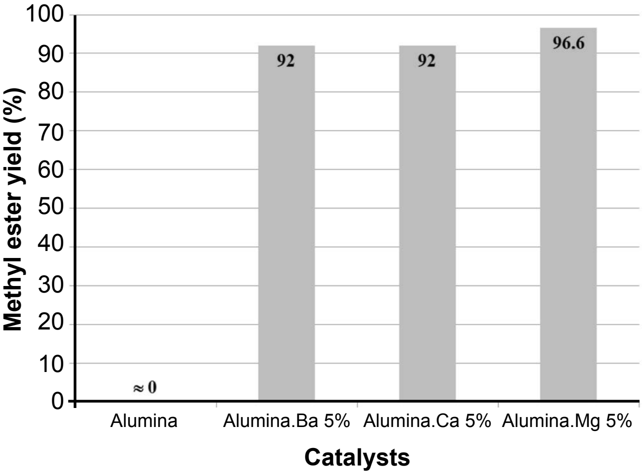

Figure 6: Methyl esters yields obtained for the transesterification of babassu oil using alumina modified with alkaline earth metal oxides as catalysts.

[Figura 6: Rendimentos de ésteres metílicos obtidos para a transesterificação do óleo de babaçu usando alumina modificada com óxidos de metais alcalino-terrosos como catalisadores.]

CONCLUSIONS

This work describes the synthesis, by the polymeric precursor method, and the properties of surface modifications of alumina with alkaline earth metal oxides. The results suggest that bulk alumina support was not modified in the process; only the surface layers of alumina reacted with alkaline earth metal oxides. The formation of the barium aluminate crystalline phase on the alumina surface is an indicative of the success of this new route for obtaining this kind of material. The isotherms obtained for all samples by nitrogen adsorption–desorption measurements present the same behavior, as typical type IV sorption with H2 hysteresis loop, which is characteristic of mesoporous structures (2-50 nm). The results suggest that uniform pore structures were maintained even after the modification of the alumina surface. Alumina modified with alkaline earth metal oxides (Ba, Ca and Mg) was shown to be efficient heterogeneous catalysts for the transesterification reaction of babassu oil.

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