11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Preparation of solid acid catalysts from brazilian *flint* kaolin.

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Abstract – This study assessed the production of a less aggressive heterogeneous catalyst to the environment. Flint kaolin sample was heated up at 850 and 950ºC and activated with H2SO4 4M and HNO3 4M forming four materials that were characterized by XRD, N2 physiosorption and SEM. The acid sites were evaluated by TGA and FT-IR spectroscopy of pyridine adsorbed. All the materials were tested as catalysts to acetic acid with methanol esterification and presented catalytic activity, with a maximum conversion of 94,85%.

The conventional methods of the esterification reaction use homogeneous catalysts, like sulphuric acid, which cause problems in the separation their after the reaction, besides waste generation and corrosivity [1]. The alternative to these catalysts could be the acid-activated clays, because they are efficient solid catalysts for processes in liquid phase, relatively inexpensive and possess strong acid sites [2]. The Capim region (Pará-Brazil) possesses a great layer of flint kaolin considered sterile for present high percentage of iron, that represents an additional cost to the kaolin industry [3]. These factors motivated the production of new solid acid catalysts by thermal treatment and acid activation from the amazon flint kaolin.

The flint kaolin was purified and submitted to thermal treatment at 850 and 950ºC, forming the metakaolins MF8 and MF9 that were activated by 1 hour with H2SO4 and HNO3 4M, forming the compounds MF8S4, MF8N4, MF9S4 and MF9N4. These compounds were characterized by XRD, SEM and N2 physisorption.

The SEM micrograph (Figure 1) shows that the flint kaolin is formed of flaky particles relatively stacked with pseudo-hexagonal morphology. The acid-activated metakaolins present well-bonded particles agglomerates and spaces that should be responsible for the microporous behavior of these materials observed by the N2 physisorption. The acid leaching increased the acid-activated metakaolin superficial area values (120-406 $m^2.g^{-1}$) compared with flint kaolin (24 $m^2.g^{-1}$) due to the amorphous SiO_2 phase formed. The materials acidity was analyzed by TGA and to FT-IR spectroscopy of piridina adsorbed. All compounds shown both Brönsted and Lewis acid sites, and the sample MF9S4 presented the largest density of acid sites (147 μmol $Py.g^{-1}$).

The leached metakaolins were tested as catalysts to the esterification reaction (acetic acid with methanol) using about 200 mg of catalyst in a reaction of 2 hours at 200ºC with molar ratio 1:4 (0,2 mols acid:0,8 mols alcohol). In these conditions, the compound MF9S4 presented the largest catalytic activity for this reaction, obtaining 94.85% of conversion. According these results, the objective of producing a new heterogeneous catalyst, less aggressive to the environment, from the caulim amazon flint was reached.

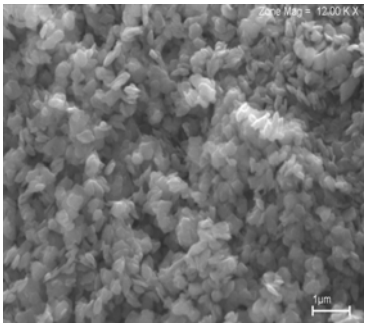

Figure 1. SEM image of the *flint* kaolin sample.

Table 1. MF9S4 and MF9N4 samples data.

Sample	Specific surface area (m^2/g)	Number of acid sites (μmol Py/g)	Conversion (%)
MF9S4	406	147	94.85
MF9N4	247	98	86.36
MF8S4	341	123	79.45
MF8N4	120	69	74.87

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