# Acidified and pillared clays for production of dimethyl ether fuel

<u>Francielle C.F. Marcos<sup>1</sup></u>, Thaisa M. de Matos<sup>1</sup>, José M. Assaf<sup>2</sup>,Elisabete M. Assaf<sup>1</sup> <sup>1</sup>University of São Paulo, São Carlos-SP/Avenue Trabalhador São\_carlense 400-12560-970 <sup>2</sup>Federal University of São Carlos, Rod. W. Luiz, km 235 Brazil \* eassaf@igsc.usp.br

#### Introduction

Dimethyl ether (DME) is an important chemical, being used as an intermediate for production of methyl acetate, dimethyl sulfate and light olefins. However, the main focus has been in its use as a fuel, either for diesel engines or a substitute for liquefied petroleum gas. DME can be obtained from natural gas, coal and agricultural residues. Its application as an alternative to the traditional diesel fuel has been proposed because of its lower NOx emission and near-zero smoke evolution [2].

The selective dehydration of methanol to produce DME is conditioned by the properties of the acid-solid catalysts. Currently, pillared clays (PILC's) and acidified clay has been studied as acid catalysts due their performance and low cost [3;4]. The introduction of aluminum polycations in the clay and acidic treatment with  $H_2SO_4$  leads to a significant increase in its acidity. The acidity increases due to two factors: (a) increase in the specific area and (b) appearance of new acid sites in the pillars molecular introduced and the binding sites between the pillars and the lamellae [5].

The aim of this study was to compare the activity of aluminum-pillared clay and acid activation clay to produce DME from the dehydration of methanol reaction.

## Materials and Methods

The clay used was a Volclay (region Wyoming (EUA)) montmorillonite. The synthesis of the aluminum-pillared clay was carried out from a pillaring agent, which was prepared from the hydrolysis of an AlCl<sub>3</sub>•6H<sub>2</sub>O 1M solution with NaOH 0.4 M (OH<sup>-</sup>/Al<sup>3+</sup> = 2.0). NaOH was added dropwise on the aluminum chloride solution under stirring. This mixture was stirred overnight to obtain the pillaring agent (Al<sub>13</sub> Keggin ion). A montmorillonite aqueous suspension of 2 % (w/v) was prepared and stirred for 3h. The pillaring agent was added dropwise while stirring, then this mixture was stirred for 3h. The pillaring agent was added dropwise while stirring, then this mixture was stirred for further 3 h and left to settle for 24h. The solid was filtered and washed with deionized water until no chloride, dried at 60 °C and calcined at 500 °C/2h at a heating rate of 2 °C.min<sup>-1</sup>, obtaining the Volclay-Al PILC.

The clay was treated with  $H_2SO_4$  4M, during 6h/50°C. The solid/liquid ratio was 1g of solid to 30 mL of solution. The acidified clay was washed until the pH = 5, and it was dried at 95°C for 12 h and calcined at 500 °C/2h at a heating of 2°C.min<sup>-1</sup>, obtaining the Volclay-H<sup>+</sup>.

These materials were analyzed by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and  $N_2$  adsorption/desorption isotherms. The acidity studies were performed using TG/DTG and FTIR after pyridine adsorption. The tests in the reactions of methanol dehydration were carried out using 400 mg of catalyst and a feed of methanol flowing at 0.7 mL.h<sup>-1</sup> at temperature of 500 °C for 5 h under atmospheric pressure.

### **Results and Discussion**

The analysis by EDS for natural montmorillonites showed the presence of the elements Si, Al, O, K, Ti, Fe, Ca, Mg and Na as constituents of the structure of the natural clay, with Si,

Al, Fe, Na and O as the major elements. After the pillaring process and acid activation for Volcaly-Al PILC and Volcaly-H<sup>+</sup>, a significant decrease in the amount of Na and Ca were evident, which is indicative that the exchange of these ions for the Al<sub>13</sub> and (H<sub>3</sub>O<sup>+</sup>) were performed satisfactorily during the intercalation and acid treatments of the clay [3;5].

The XRD patterns for Volclay showed an intense reflection for the basal spacing  $d_{001}$ = 12.9Å, related to montmorillonite, and other peaks related quartz were also observed. The XRD profile of Volclay-Al PILC indicated that the pillaring procedure was successful due the increase of the basal spacing ( $d_{001}$ = 16.7Å). After acid treatment, the  $d_{001}$  value to Volclay-H<sup>+</sup> changed to 9.45 Å. It indicates a decrease of the interlayer region.

Results of textural characterization, acidity and catalytic tests are shown in Table 1. The gaseous products identified in catalytic tests were DME and ethylene. It was observed that the  $A_{13}$  pillaring process and acid treatment favored the increasing of the specific surface area, and increasing of Lewis and Brønsted acidity [3;6]. According to the analysis of acidity was verified that natural clay exhibit a weak acid character. PILC and acid clays showed bands in the regions 1550, 1490 and 1437 cm<sup>-1</sup> related to Brønsted, Lewis-Brønsted interacted and Lewis sites, respectively. The increase of the acidity improved the activity for methanol dehydration reaction to DME.

SAMPLE	$S_{\rm BET}$ m <sup>2</sup> .g <sup>-1</sup>	Acid sites (mmol py/g)	Yield of DME	Yield of Eteno
Volclay	26	0,00646	0,19	0,003
Volclay-Al PILC	245	0,42746	0,48	0,007
Volclay- H <sup>+</sup>	76	0,33989	0,13	0,004
DME maximum yield theoretical: 0,50				

Table 1. BET area; Quantity of acid sites; Yield (mol produced of i/ mol of methanol fed).

### Significance

The presence of aluminum pillars in clay produced materials with higher basal spacing, specific surface area and acidity, which provided a higher activity for the methanol dehydration reaction to produce dimethyl ether. Volclay-Al PILC clay showed the best yield to DME.

### References

- J. H. Flores.; D. P.B. Peixoto.; L. G. Appil.; R., R. de Avilez.; M. I. Pais da Silva. Catalysis Today 2011,172, 218.
- L, Bieseki.; F, Betella.; H, Treichel.; F.G Penha.; S.B.C Pergher. Materials Research 2013, 16, 1122.
- 3. A. Romero-Pérez.; E. Roca Jali.;, K. Sapag. Catalysis Today 2012,187, 88.
- T.J. Pinnavaia.; Ming-Shin, Tzou.; S.D. Landan,.; R.H. Raythatha. Journal Molecular Catalysis 1984, 27, 195.
- 5. I.P. Okoye.; C. Obi. Research Journal of Applied Sciences 2011, 6, 447.