

## LIGNOCELLULOSIC BIOMASS WASTE AS PRECURSOR FOR THE PREPARATION OF ACTIVATED CARBON MONOLITHS FOR ALCOHOL DEHYDRATION

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### Introduction

DME is recognized as a clean diesel substitute and a key intermediate for other important chemicals, such as olefins, methyl acetate and dimethyl sulphate. DME can be obtained by methanol dehydration reactions using acid catalysts such as zeolite materials,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and acid modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In this sense, chemical activation with phosphoric acid is able to provide activated carbons with a high development of the porosity, relatively high oxidation resistance and a great presence of low-moderate acidic sites [1]. In this work, activated carbon monoliths (ACMs) from different lignocellulosic biomass waste have been prepared by the direct extrusion of the precursors with phosphoric acid, followed by activation under inert atmosphere, and washing with distilled water. These ACMs were used as catalysts for different alcohol dehydration reactions.

### Materials and Methods

Olive stone (OS), Alcell (AL) and Kraft lignin (KL) were used as precursors of the ACMs. These precursors were impregnated with H<sub>3</sub>PO<sub>4</sub> at different impregnation ratios, 1 and 2 (H<sub>3</sub>PO<sub>4</sub>/raw material mass ratio), and kept in a vacuum dryer for 24 hours, at 60 °C. The impregnated samples, without any kind of binder, were conformed by extrusion in a home-made extruder, using a cylindrical mould with an internal diameter of 2 cm, at room temperature and 80 MPa, obtaining monoliths with 25 channels/cm<sup>2</sup>. When both lignins were used as raw material, a stabilization step of the impregnated samples, previous to the extrusion, was necessary. This step consists of a thermal treatment at 250 °C, under air flow (150 cm<sup>3</sup>/min), for 1 h. Subsequently, the obtained monoliths were activated in a tubular furnace at 700 °C for 2 h, with a heating rate of 10 °C/min. Finally, carbon monoliths were washed with distilled water at 60 °C.

ACMs were characterized by adsorption-desorption of N<sub>2</sub> at 77 K, adsorption of CO<sub>2</sub> at 293 K, temperature programmed desorption (TPD), NH<sub>3</sub>-TPD, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) under air atmosphere and scanning electron microscopy (SEM). Gas phase decomposition of alcohols was studied in a fixed bed microreactor with an alcohol partial pressure of 0.03 atm, in inert or air atmosphere.

### Results and Discussion

Cylindrical ACMs were obtained with preparations yields ranging from 30 to 40 % (weight ACMs/weight raw material). Figure 1 shows a SEM micrograph of the ACM from olive stone, at an impregnation ratio of 1. ACMs show apparent surface area ranging from 700 to 1500 m<sup>2</sup>/g,

with phosphorus surface concentrations determined by XPS analyses between 2.1 and 4.5%. A more detailed description of the preparation and characterization of these ACMs can be found elsewhere [2].

2-propanol decomposition in inert atmosphere was used to characterize the acidity of the ACMs. The highest conversion for 2-propanol decomposition was obtained by the ACMs derived from olive stone. Selectivity to propylene was quite high at all the evaluated temperatures, being higher than 90% from 250 °C, for all the ACMs. The values for the apparent activation energies (supposing a first-order kinetic) are quite similar, ranging from 100 to 130 KJ/mol.

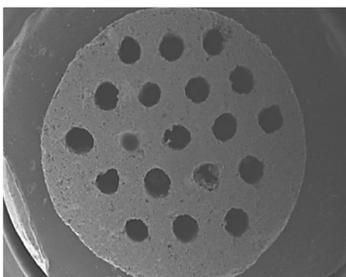


Figure 1. SEM micrograph of OS-ACM

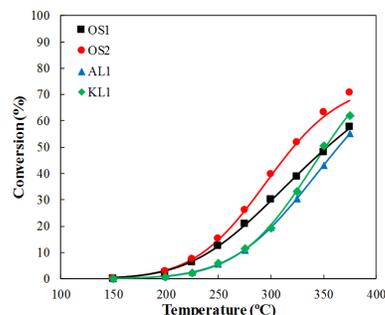


Figure 2. Methanol conversion vs  $T^a$  under air conditions.  $P_{MeOH} = 0.03$  atm,  $W/F_{MeOH} = 0.1$  g·s/ $\mu$ mol

Methanol decomposition reaction was analyzed under air atmosphere. As can be seen in Figure 2, the highest conversion obtained is approximately 70% at 375°C, being OS the most active ACM, followed by KL and AL catalyst. The main reaction product was DME, showing selectivity to DME higher than 90% for all the ACMs. At higher temperatures than 375 °C, the burn-off of ACMs was considerable and the methanol dehydration was not evaluated. The possible influence of the monolithic conformation was also analyzed by comparing to powder activated carbon with the same physico-chemical properties. Furthermore, several kinetic models were evaluated to predict the methanol conversions, taking also into account the competitive influence of water. In this sense, Langmuir-Hinshelwood mechanism with competitive water adsorption provides the best model predictions for the methanol conversion, represented as lines in Figure 2.

## Conclusions

ACMs prepared from direct extrusion of biomass waste with phosphoric acid were successfully tested as catalyst for methanol dehydration, showing high activity, stability and selectivity to DME larger than 90% at the experimental condition evaluated.

## Acknowledgment

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## References

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