

## DEACTIVATION OF ZIRCONIUM-PHOSPHORUS ACTIVATED CARBON ON THE DEHYDRATION OF METHANOL TO DIMETHYL ETHER

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### Introduction

Dimethyl ether (DME) can be used for energy purpose instead of GLP and diesel or as a feedstock for fuel cells. Moreover, DME is a platform and an attractive alternative as a clean propellant or as a hydrogen vector<sup>1</sup>.

At the moment, DME is produced by two different routes: direct synthesis, in which syngas is directly converted to DME; and indirect synthesis, in which syngas is, in a first stage, transformed into methanol and then dehydrated to DME. This syngas could be obtained from biomass gasification, generating a sustainable source for DME synthesis. For this reason, DME is being deeply studied as a potential renewable substitute for petroleum derivative. Many research studies have been devoted to study the effect of operating conditions on the performance of different catalysts in this reaction. However, addressing catalyst deactivation is also an issue of great interest for the development of this process. Our work focuses on this point, given that the knowledge of deactivation details will allow us optimizing the catalyst synthesis for the best DME production process conditions.

### Materials and Methods

Physical (AC) and chemical activated carbon (ACP) were prepared from olive stone and studied as catalysts and catalyst supports for methanol to DME reaction. AC was produced in two steps: firstly, olive stone was heated at 800°C for 2 hours in N<sub>2</sub> flow (150 cm<sup>3</sup> STP/min). Then it was gasified at 800°C for 6 hours in CO<sub>2</sub> flow (150 cm<sup>3</sup> STP/min). On the other hand, to produce ACP, olive stone was initially impregnated with H<sub>3</sub>PO<sub>4</sub> 85% with an impregnation ratio (H<sub>3</sub>PO<sub>4</sub>/Olive Stone) of 2:1. The impregnated sample was activated at 800°C for 2 hours under N<sub>2</sub> flow (150 cm<sup>3</sup> STP/min). The sample is then washed until constant pH. Both AC and ACP were loaded with ZrO(NO<sub>3</sub>)<sub>2</sub> and thermal treated to get a 7% of ZrO<sub>2</sub> (wt/wt) on the carbons surface (AC-Zr and ACP-Zr). The methanol to DME reaction experiments were carried out in a laboratory fixed bed reactor at a partial pressure of 0.04 atm and at several space times (from 0.05 to 0.1 g·s/μm) and temperatures (from 300 to 600°C). These catalysts were characterized before and after being used in the reaction conditions by N<sub>2</sub> adsorption-desorption at 77 K and CO<sub>2</sub> adsorption at 273 K, temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS).

### Results and Discussion

AC shows no conversion of methanol to DME under any reaction condition studied. In contrast, AC-Zr shows some activity, but the highest conversion achieved is about 30% at 600 °C and deactivates very fast. Moreover, selectivity to DME at low temperatures is only 50%. In general, the conversion values for ACP and APC-Zr are considerably higher than those for AC and AC-Zr, and the products obtained (**Figure 1**) were mainly DME and methane, and in less extent, CO. Traces of CO<sub>2</sub>, ethane and ethylene were also detected (not shown). At low temperature, ACP shows an almost total selectivity to DME, but as temperature increases, selectivity to methane rises. At 500°C (and above) selectivity to methane is higher than DME. A different behaviour can be observed for ACP-Zr, in

which DME is always the main product (selectivity higher than 90% even at 500°C).

Conversion profiles of ACP and ACP-Zr show high initial conversion values of methanol (**Figure 2**). For both catalysts, as temperature increases, the initial conversion increases too, but the deactivation rate is very high in the case of ACP and only residual activity can be seen at all the studied temperature (<10%) after 100 minutes under reaction conditions. However, for ACP-Zr catalyst, even at the fastest deactivation temperature studied (600 °C), it is necessary to wait more than 600 minutes to reach a conversion below 10%.

According to TPD and XPS analyses, ACP presents different phosphorus surface groups, mainly in form of  $\text{CPO}_3$  and  $\text{COPO}_3$ , which are responsible of its relatively high acidity<sup>2</sup>. Furthermore, ACP-Zr shows the presence of zirconium phosphate surface species. The acidity of ACP is responsible for its high initial activity on methanol dehydration, but it also produces a fast deactivation due to coke deposition on phosphorus groups, but its activity remains practically the same at temperatures below 500 °C up to 600 min. Thus, zirconium phosphate species seem to be the responsible for this stable activity. Above 400°C, even those zirconium phosphate species seem to be also sensitive to coke deposition and activity gradually decays.

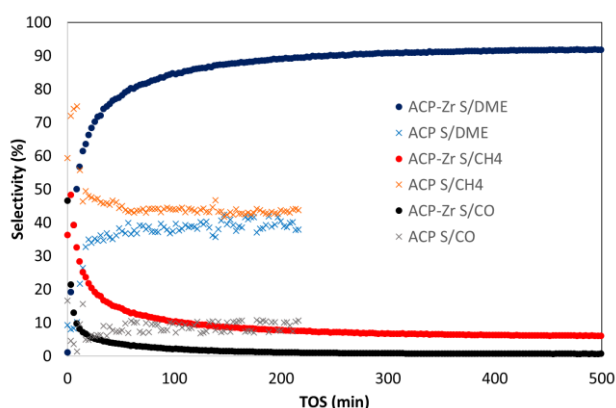


Figure 1. ACP and ACP-Zr selectivity profile at 500°C

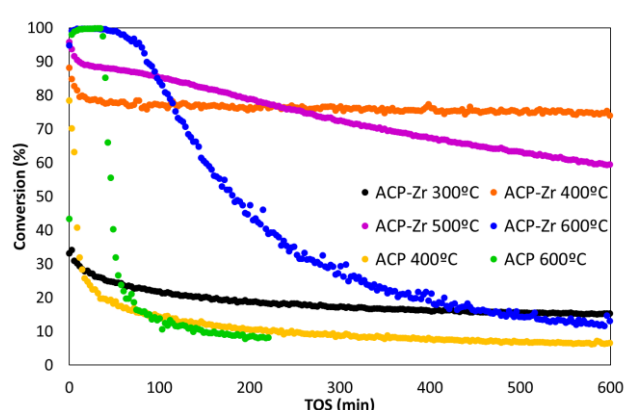


Figure 2. ACP and ACP-Zr conversion profile

## Conclusions

ACP-Zr has shown to be a highly active and selective catalyst for methanol dehydration to DME, but it deactivates at temperatures higher than 500 °C. Two kinds of active sites seems to be present on the catalyst, that related to phosphorus-carbon surface groups loses their activity very fast at any studied temperature, while the one associated to zirconium phosphate species, does not lose activity at temperatures lower than 500 °C.

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## References

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