

KINETIC STUDY OF METHANOL DEHYDRATION OVER ZrO₂ SUPPORTED-ACTIVATED CARBONS

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Introduction

The growing concerns about climate change and energy consumption have been the driving force in seeking for alternative fuels such as DME, mainly produced via methanol dehydration over a solid acid catalyst. The use of activated carbons for this aim has been little studied up to date. Only a few studies can be found in the literature, reporting all of them materials with a low thermal stability of acid surface groups¹, which results into a fast deactivation of the catalyst.

In this work, the preparation of activated carbons via chemical activation with phosphoric acid, their surface modification with different ZrO₂ concentrations, and their application as methanol dehydration catalysts have been studied.

Materials and Methods

Activated carbon was prepared by chemical activation with phosphoric acid, by using olive stones (OS) as precursor. Firstly, olive stone was impregnated with H₃PO₄ 85% (w/w) at room temperature and dried for 24 h at 60°C in a vacuum dryer. The impregnation ratio (H₃PO₄/OS mass ratio) was 2:1. The impregnated substrate was then activated under continuous N₂ flow (150 cm³ STP/min) at 800°C for 2 h. The activated sample was then washed with distilled water at 60°C until constant pH and vacuum-dried for 24 h at the same temperature. This activated carbon presented a yield of 39% and was denoted as AC. The activated carbon was loaded with different amounts of ZrO(NO₃)₂ via incipient wetness impregnation, dried at 120°C for 24h, and calcined in air at 250°C for 2h, obtaining final ZrO₂ load ranging from 0 to 10 % (wt/wt).

The porous texture of the samples was characterized by N₂ adsorption-desorption at -196 °C. Surface chemistry of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) and ICP-MS. The total acidity and acid strength distribution of the prepared catalysts have been determined by temperature programmed desorption of ammonia (NH₃-TPD). Methanol dehydration reactions were performed at atmospheric pressure in a fixed bed reactor, at different space times, methanol partial pressures, and temperatures.

Results and Discussion

The prepared activated carbon shows a well-developed porous structure, with a specific surface area of 1280 m²/g. A slight decrease in the apparent surface area is observed after ZrO₂ loading (1143 m²/g with a zirconia loading of 7% (wt/wt)). XPS analyses revealed the presence of phosphorus species on the carbon support, which mainly appear in form of C-PO₃ and C-O-PO₃ surface groups². Zirconium phosphate groups are formed after the addition of the zirconia, as revealed by XPS. NH₃-TPD analyses show that most of the ammonia desorption takes place below 250 °C, associated to weakly adsorbed ammonia on the C-O-P and P-O-Zr groups present on the carbon surface.

Figure 1 presents the methanol conversion and selectivity towards DME as a function of the zirconia loading. As can be observed, the activated carbon loaded with a 7 % (wt) of ZrO_2 (ACZR7) showed the best methanol conversion and selectivity towards DME. This catalyst exhibits high steady state methanol conversion values even at temperatures as high as 400 °C ($X_{CH_3OH} = 70\%$, $0.1 \text{ g}\cdot\text{s}/\mu\text{mol}$, $P_{CH_3OH} = 0.02 \text{ atm}$ in helium), keeping a selectivity to DME higher than 96%.

A kinetic study of the methanol dehydration over this catalyst has been carried out. The active centers of the catalyst seem to be the P-O-Zr groups, present on the surface of the activated carbon. In the proposed reaction pathway, two methanol molecules are adsorbed on a P-O-Zr. Both molecules then react leading the formation of dimethyl ether and water, regenerating the active site. For the interpretation of the experimental data, the reactor was considered as a plug flow integral reactor, operating at steady-state conditions, and checking that the diffusional limitations were negligible. To this purpose the reactor mass balance equation was numerically integrated to calculate the exit conversion of methanol and DME yield.

Figure 2 illustrates the yield towards DME at different space times and a constant methanol partial pressure. The results predicted by the model are shown in solid lines for comparison purposes. It can be noted the good agreement between the experimental and the estimated values.

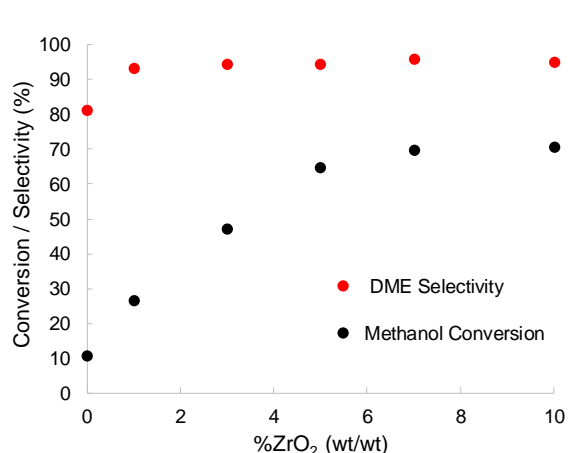


Figure 1. Methanol conversion and DME selectivity as a function of the ZrO_2 loading ($W/F_{MeOH} = 0.1 \text{ g}\cdot\text{s}/\mu\text{mol}$, $T = 400 \text{ °C}$, $P_{CH_3OH} = 0.02 \text{ atm}$).

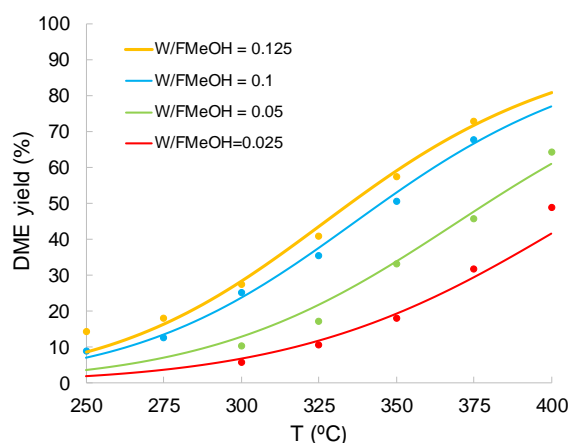


Figure 2. Experimental and simulated DME yield as a function of reaction temperature at different spaces times (W/F_{MeOH}). $P_{CH_3OH} = 0.04 \text{ atm}$.

Conclusions

An activated carbon prepared via chemical activation with H_3PO_4 and modified with ZrO_2 has been used as catalyst for methanol dehydration. The catalyst with 7% ZrO_2 exhibits high steady state methanol conversion values even at temperatures as high as 400 °C, keeping selectivity to DME higher than 96%. A kinetic study has been carried out on the catalyst that exhibits the best yield towards DME. The proposed model shows a good agreement with the experimental data.

Acknowledgment

We gratefully thank MINECO (Project CTQ2015-68654-R) for financial support. J.P. thanks MECED for a FPU fellowship (FPU13/02413).

References

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