Methanol dehydration over ZrO2 supported-activated carbons

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SUMMARY:

DME is playing an important role due to its potential use as an alternative fuel in diesel engines. The use of this fuel produces lower NO_x emissions, and less engine noise compared to traditional diesel fuels. Moreover, this compound is used as building block for many value-added chemicals such as lower olefins. DME is usually produced via catalytic dehydration of methanol over a solid acid.

The use of activated carbons in catalytic processes, acting directly as catalyst and as catalyst support, is focussing much attention. They can be obtained from different types of lignocellulosic waste, producing not only an environmental but an economical profit. In this sense, the preparation of activated carbons with phosphoric acid produces catalytic supports with certain surface acidity, which have shown high activity for alcohol dehydration. In this study, ZrO_2 supported activated carbons were prepared from an industrial byproduct as lignin for the methanol dehydration to DME.

The activated carbon was prepared by chemical activation with H_3PO_4, using Alcell® lignin as precursor. The impregnation ratio value (H_3PO_4/lignin) used was 3. The impregnated sample was activated under N_2 flow at 500 ºC for 2h, washed and dried. The activated carbon was loaded with different amounts of $ZrO(NO_3)_2$, dried at 120ºC for 24h, and calcined in air at 250ºC for 2h, obtaining ZrO_2 loadings of 5 and 10%, respectively. For the sake of comparison, pure ZrO_2 was also used. Catalytic tests were performed at atmospheric pressure in a fixed bed reactor, at different space times and partial pressures.

The activated carbon (ACP) prepared shows a well-developed porous structure, with an apparent surface area higher than 2000 m_2/g, and a high contribution of mesoporosity. After metal loading, a maximum decrease of 20% in all structural parameters of the ACP was observed.

The results show that ZrO_2 loading produces an enhancing in the catalytic activity of the carbon materials compared to the parent activated carbon (0.1 g·s/µmol, P_{CH3OH}= 0.02 atm in helium and 350 ºC). In this sense, a methanol conversion of 25% was observed with the addition of 10% w/w ZrO_2 (ACP-10Zr), at steady state conditions (Figure 1). ACP shows negligible conversion, at the same conditions and for pure ZrO_2 the methanol conversion was of 10%. Very high selectivity to DME (~100%) was found at temperatures lower than 350 ºC.

The methanol conversion increases with temperature, reaching a value of 67% at 475ºC, but a slight decrease in DME selectivity is observed, resulting in a higher production of light hydrocarbons, mainly CH_4.

The results suggest that the addition of only a 10% of ZrO_2 over an activated carbon prepared by chemical activation with H_3PO_4 enhances significantly the performance of the catalyst, compared to pure ZrO_2.

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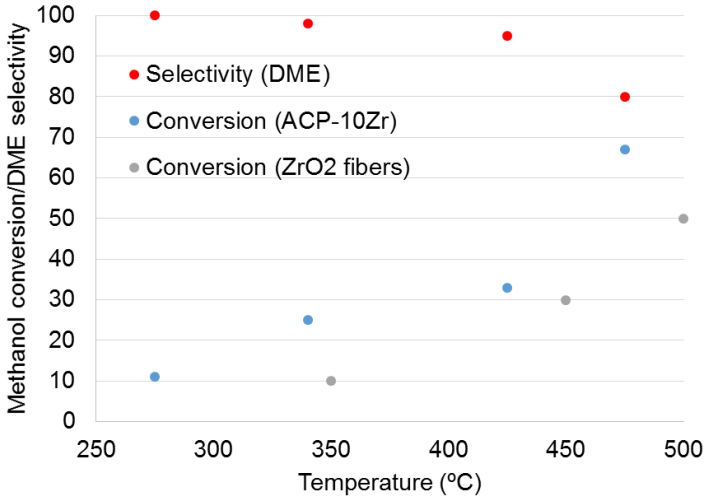

Figure 1. Steady state methanol conversion and DME selectivity for ACP-10Zr, and pure ZrO_2 at the following conditions: space time=0.1 g·s/µmol, P_{CH3OH}= 0.02 atm in helium and 350 ºC.