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VPO CATALYSTS USING ACTIVATED CARBONS AS A TEMPLATE. ODH OF PROPANE

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SUMMARY:

Vanadium phosphates is one of the most studied heterogeneous catalytic systems due to its properties to activate alkanes. In fact, they are used commercially for the oxidation of n-butane to maleic anhydride and experimental studies have shown that vanadium phosphates are also effective catalysts for propane and pentane partial oxidation. The most active phase of VPO catalysts is made up of a well-crystallized $(VO)_2P_2O_7$, which is considered to possess unique structural and surface features to allow the activation of alkanes. This phase is generally generated by calcination of the precursor $VOHPO_4 \cdot 0.5H_2O$. A new strategy to obtain this precursor has been analyzed in this study. The proposed methodology is simple and low cost and implies the use of a carbon material as a template to obtain the mixed oxide with a developed porous structure.

Several VPO catalysts were prepared by using different activated carbons, which were obtained from lignocellulosic waste, as template. The carbonaceous materials were obtained by chemical activation with phosphoric acid of olive stones and by liquid phase impregnation of zeolite templates with lignin solution. Both porous carbons were impregnated with a solution containing the dissolved vanadium phosphate precursor. This solution was prepared by mixing water with ammonium metavanadate, phosphoric acid and oxalic acid in the precise amounts to obtain a V/P atomic ratio of 1. Finally, in order to remove the carbonaceous matrix and to obtain the active phase $(VO)_2P_2O_7$, the impregnated samples were calcined in air at 500 °C for 6 h.

The presence of the desired active phase $(VO)_2P_2O_7$ was confirmed by using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffraction (XRD). The porous structure was characterized by N_2 adsorption-desorption at -196 °C. Catalytic tests were performed in a fixed bed microreactor under a gas flow mixture ($W/F = 0,075 \text{ g} \cdot \text{s} \cdot \text{mL}^{-1}$) containing propane, oxygen and helium (45.7/11.4/42.9 vol. %). The reaction was studied at different temperatures from 500 to 575 °C.

The use of a carbon as a template results in VPO catalysts with relatively high development of the porous structure (apparent surface area of 40 m^2/g), compared to those reported in the literature. These catalysts

present propane conversions up to 22 % with selectivities to propylene as high as 60 %. It is noteworthy that selectivities to ethylene about 25% were also observed, which is a highly valued product in the chemical industry. These results are comparable to those reported in the literature for supported vanadium oxides at higher space times.

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