Vanadia-modified Alumina for Dimethyl Ether Production

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Introduction
Dimethyl ether (DME) is a promising energetic alternative to petroleum derivatives, being a potential fuel for diesel cycle engines and substitute of LPG. The advantages of DME are no emissions of particulates and nitrogen oxides. DME can be obtained from a variety of materials, such as natural gas, coal, biomass in general. The direct production of DME from syngas using a bifunctional solid catalysts provides a synthesis in one step, this form of production is considered more thermodynamically and economically favorable [1].

The direct synthesis of DME requires two kinds of active sites, one is for methanol formation and the other for methanol dehydration. Methanol synthesis is performed on CuZnAl catalysts with high activity and selectivity, while the dehydration of alcohols occurs in acidic catalysts, γ-alumina is the traditional catalyst. Oxides of elements with valence five or higher present very strong Brønsted acidity which make them good candidates as acid catalysts, such as vanadia [2].

In this study, the performance of supported vanadium oxide on alumina was evaluated in DME production.

Materials and Methods
Al₂O₃ support was prepared by hydrolysis of Al(OH)₃ at 95 °C for 24 h, the solution was dried at 100°C for 12 h and then the solid obtained was calcined at 550 °C for 3 h. Alumina supported vanadium oxide catalysts were prepared by the incipient wetness impregnation method with aqueous NH₄VO₃, the samples were dried at 100 °C and calcined at 500 °C for 2 h. The catalysts were characterized by X-Ray diffraction (XRD), energy dispersive spectroscopy (EDS) and N₂ adsorption/desorption isotherms. The study of acidity was performed by gas adsorption of pyridine, using the techniques of TG/DTG and FTIR.

Catalytic tests of methanol dehydration were performed in fixed bed reactor under atmospheric pressure using 400 mg of catalyst and a methanol feed of 0.7 mL·h⁻¹ at 300 °C for 5 h, the gaseous products were identified by gas chromatography.

Results and Discussion
The vanadium oxide contents of the catalysts, quantified by EDS, were 5.3, 11.7, 15.4 and 26.12 wt.%. The catalysts were designated according to the measured amount of vanadium V₅, V₁₁, V₁₅ and V₂₆, respectively. Figure 1a shows the presence of vanadium by EDS analysis for the sample V₅.

The XRD patterns of the alumina support (Figure 1b) showed only broad lines corresponding to γ-alumina (2-theta = 37.2, 46.0, 66.9). For the V₅ and V₁₁ catalysts the patterns were similar to the one for the alumina support, suggesting that vanadia is relatively well dispersed on the alumina support. Crystalline V₂O₅ (2-theta = 20.5, 26.1, 31.2) is evident in the case of V₁₅ e V₂₀ samples. This is in agreement with the observed decrease in the surface area with increasing of the vanadia loading (Table 1).

In the studied conditions of methanol dehydration, the DME maximum yield theoretical is 0.50. From the results of yield, it is possible to observe that the alumina modified with vanadium catalysts showed a better performance for DME. The V₅ catalyst produced a lower quantity of olefins with respect to the alumina, and in the reactions using the catalysts with higher vanadium content (V₁₁, V₁₅ and V₂₆) was not detected olefin production. The improved performance can be attributed to the presence of strong acid sites. The change in acidity is important since the dehydration occurs by two mechanisms of reaction [1].

Significance
The impregnation of vanadium oxide on alumina promoted a better performance in dehydration reaction of methanol for dimethyl ether production due to changes in acidity.

References
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