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

Al_2O_3 support was prepared by hydrolysis of $Al(OC_3H_7)_3$ 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 NH_4VO_3, 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 N_2 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 V_2O_5 (2-theta = 20.5, 26.1, 31.2) is evident in the case of V15 e V20 samples. This is in according with the observed decrease in the surface area with increasing of the vanadia loading (**Table 1**).

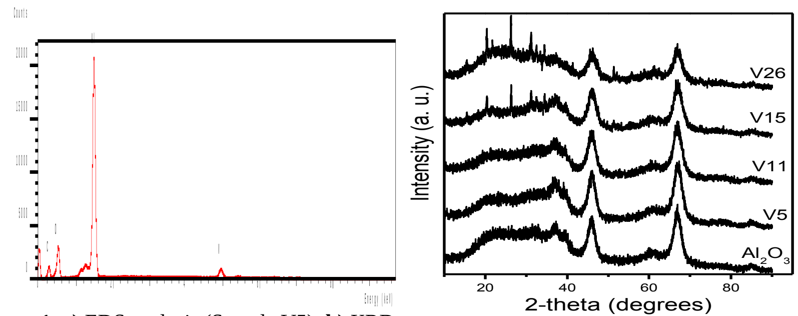

Figura 1. a) EDS analysis (Sample V5); **b)** XRD patterns.

Table 1 also shows the results of total acidities of the catalysts, it can be observed that the total acidity increased by adding vanadia to alumina for the samples with an amount of 5.3 and 11.7. The catalysts V15 and V26 showed decrease of the acidity, however, by adding vanadia occurs the increase of strong acid sites [3]. In the FTIR spectrum after pyridine adsorption appears bands relatives to Brønsted and Lewis acids sites, more apparent in V26.

Table 1. BET surface area, acidity and yield (mol produced/ mol of methanol fed).

Catalyst	S_{BET} $m^2.g^{-1}$	Acidity (mmol py/g)	DME yield	Olefin yield
Al_2O_3	263	0.15	0.11	0.02
V5	247	0.27	0.10	0,01
V11	207	0.19	0.11	-
V15	191	0.14	0.10	-
V26	144	0.10	0.12	-

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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