

Synthesis and Characterization of Vanadium and Molybdenum Oxycarbides in the HDS of Thiophene.

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Introduction

Nitrides and carbides of transition metals have developed a great interest in the last few years in refining petroleum reactions, mainly in hydrotreatment due to their high resistances to catalytic poisons contained in the different charges. On the other hand, these materials have showed activity in the isomerization of light parafines⁽¹⁾ and butane reforming⁽²⁾. Nevertheless, the basic and acid properties have not been widely studied their influence in the performance of the catalysts.

Experimental.

The synthesis of these materials were carried out by means of a TPR technique using a metal oxide (V_2O_5) or precursor containing phosphorous $[(NH_4)_3 PMo_{12} O_{40}XH_2O]$. Carburation took place with a mixture of CH_4/H_2 (2:1) VC-a was obtained at 660 ml/min, VC-A and MoPC at 8 ml/min of the mixture of CH_4/H_2 . The catalysts were characterized by X-rays diffraction. To study to presence of acid and basic sites a potentiometer titration with n-butylamine⁽³⁾ and the dehydration of 2 propanol at 423 °K⁽⁴⁾ were used. The catalysts were used in the isomerization of n-hexane at 573 °K and n-heptane at 623 °K which was carried out and hydrogen atmosphere. The HDS of thiophene took place at 623 °K, a continuous flow microplant was used for three reactions at atmospheric pressure.

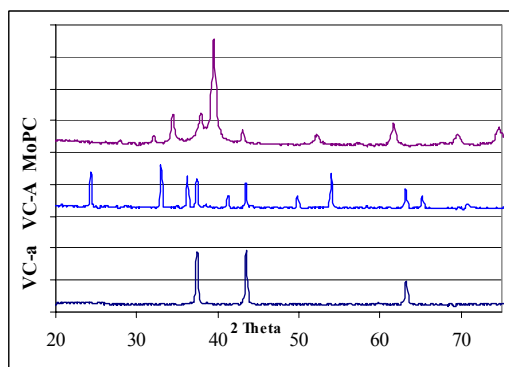


Figure 1. X-rays diffractograms Molybdenum and vanadium carbides

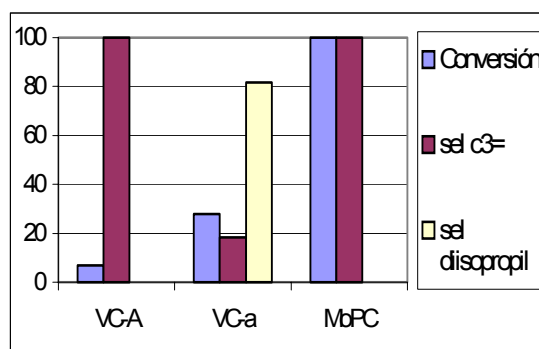


Figure 2. Dehydration of 2 propanol at 423 °K.

Results.

In figure 1, the X-rays diffractograms show the crystalline phases of carbides ⁽⁵⁾. Other phases were detected, too but probably these coincide with the precursor that is used as the source of the carbide. The potentiometric titration of the samples show the following order in streng acid: MoPC, 214 mV; VC-A, 14 mV; and VC-a, -114 mV.

The figure 2 show results of dehydration of 2 propanol with VC-a, VC-A and MoPC, the selectivity toward C_3^- indicate acid sites existence, whereas diisopropyl ether formation with VC-a catalysts correspond to site of moderate acidity when low temperatures are used ⁽⁶⁾.

A 6% conversion is attained in the isomerization of n-hexane using MoPC with a selectivity of 60% toward 2MP and 27% to 3MP for a 90 minute reaction time. The other two catalysts did not report a considerable activity. For the n-heptane isomerization reaction the MoPC show conversions of 25%.

The hydrodesulfurization of thiophene, show 30% conversion. The activity order of these materials for the reaction is as follows:

MoPC>>VC-a>VC-A.

Conclusions.

Vanadium carbides show acid properties and this property is maximun when low flow rate of the mixture CH_4/H_2 is used. The presence of phosphorous in the molybdenum carbide probably increases the acidity of the MoPC catalyst.

References.

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