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Influence of concentration and order of aggregation of the active phases in V–Mo–O catalysts in the oxidative dehydrogenation of propane

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Abstract

The activation of alkanes by oxidative route is an alternative way to obtain products with greater added value. The mixed catalysts obtained by impregnation of Mo and V on different supports conform a potentially attractive system to achieve dehydrogenation of propane. The activity and selectivity depend on the Mo/V ratio used. In this work, we have studied the effect of the concentration and the order of incorporation of the active phases on the catalytic behavior and the nature of the acid sites on the catalyst surface for this reaction. Catalysts with weight contents of 1.4 and 2.8% of vanadium and/or 4 and 8% of molybdenum were prepared. The results show that for solids with low vanadium load the order of aggregation of the active phases does not modify the catalytic behavior. When vanadium load increases, greater conversion is observed when molybdenum is incorporated in the first place. This behavior can be related to the formation of Mo–V–O species. The catalytic properties are also influenced by the nature and strength of the acid sites on the surface.

Keywords: Vanadium–molybdenum catalyst; Oxidative dehydrogenation; Propane

1. Introduction

Selective oxidation reactions have been the subject of several studies to obtain derivatives which can be used in petrochemical industries. Among the reactions which have not yet been industrially developed, dehydrogenation of light paraffin could be an interesting choice, due to its many possible operative and economic advantages, in contrast with conventional dehydrogenation traditional processes. Unfortunately, the addition of oxygen also allows for competing combustion reaction of alkanes and alkenes to carbon oxides. Therefore, current research is focused primarily on the development of an active ODH catalyst exhibiting high olefin selectivity.

Previous studies have been focused on the behavior of vanadium oxide catalysts supported on silica and alumina [1] and molybdenum oxide supported on silica, alumina and titania [2] in the oxidative dehydrogenation of *n*-butane. The results obtained have shown that, although molybdenum oxides are selective in the olefins formation, they are less active than vanadium catalysts supported on alumina.

According to such results, it is possible to argue that interaction between these oxides constitute an efficient system for this reaction. Other studies reported show that the catalytic behavior depends on the used Mo/V ratio in supported molybdena–vanadia mixed oxide [3–9]. The catalytic properties of these materials may also be influenced by the type and strength of the acid sites on the surface [8].

In this work, we have studied the influence of both the concentration and order of molybdenum or vanadium precursors addition on the catalytic behavior and the nature of the acid sites on the catalyst in the oxidative dehydrogenation of propane.

2. Experimental

For the preparation of mixed oxides, γ-Al_2O_3 (Aldrich, $S_0 = 132\ m^2/g$) previously calcined at 550 °C, is impregnated with a dissolution of ammonium heptamolybdate to obtain 4 or 8% of Mo. After drying, it is impregnated with an ammonium

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metavanadate dissolution to obtain a load of 1.4 or 2.8% of vanadium.

The catalysts obtained are denominated Mo_xV_y/Al_2O_3.The same process can be applied to obtain V_yMo_x/Al_2O_3 solids, by inverting the order of impregnation.

The solids are dried at 120 °C during 4 h, with a heating velocity of 2 °C/min, and calcined for 16 h at 550 °C, at a heating velocity of 10 °C/min.

The specific surface area of catalysts is measured by means of a Micromeritics Flow Sorb II 2003. The samples are previously degassed for 2 h at 200 °C. Studies of XRD are carried out in a Powder Diffractometer Rigaku Model Dmax-IIC, using CuKα radiation. Studies of surface acidity are carried out through FTIR spectroscopy of adsorbed pyridine, using a Bruker IFS 88 spectrophotometer. Studies are made with self-supported thin wafers of 20 mg. Pretreatment is done in vacuum for 30 min at 250 °C. Once the reference spectrum has been registered, a pyridine pulse is adsorbed at room temperature. Then, it is evacuated for 30 min to 80 °C; 30 min at 150 °C, and 30 min at 200 °C, and the corresponding spectrum is registered in each case. Thermogravimetrical and thermodifferential DTA-TG analyses are carried out in a Rigaku TAS 1000 unit. Experiments are done using 20 mg of sample in a static air atmosphere, with a limit temperature of 1000 °C, and a heating velocity of 10 °C/min. The solids are also characterized by Raman spectroscopy, using a Bruker RFS 100 spectrophotometer equipped with He–Ne (λ = 632.8 nm) laser with an OLYMPUS DX-40 microscope. Resolution of spectra is 7 cm^{-1}, and their acquisition consists of a 30 s accumulation for each sample. Measures of catalytic activity are performed with a fixed bed microreactor. The dimensions of the catalytic bed high are set at 2 cm, and 25/30 mesh quartz is used as an upper and lower counter-bed. The mass of catalyst used is 0.4 g. Measures are taken by varying the total flow between 150 and 250 mL/min, and the temperature of reaction between 450 and 550 °C. Molar compositions of feed used in this work are $C_3H_8/O_2/N_2$:20/15/65 and $C_3H_8/O_2/N_2$:4/8/88. The analyses of the products in the reaction are carried out using two gas chromatographers connected in series. Light substances are analyzed in a Shimadzu GC-3BT chromatographer, and heavy substances in a Varian 3700 chromatographer.

3. Results and discussion

Specific surface of solids is shown in Table 1.

It can be observed that the order of aggregation of the oxides does not modify the specific surface area of the resulting catalyst; while for a fixed concentration of the first oxide, the load increase of the second one leads to a slight decrease of this property.

XRD patterns of calcined catalyst showed that all the solids are amorphous. No crystalline phases of molybdenum or vanadium can be detected, within the technical sensitiveness. These results show that a good dispersion of the oxides on the γ-Al_2O_3 surface take place.

All samples present a similar DTA profile, with a wide exothermic event associated with a monotonous weight loss ranging from 4 to 4.5% between 90 and 900 °C, which coincides with the observed behavior of the support. Between 820 and 900 °C, there appears a slight exothermic peak, related with the initial weight loss attributed to evaporation of the molybdenum oxide.

Table 1
Specific surface of γ-Al_2O_3, and catalysts

Sample	S_0 (m^2/g)
γ-Al_2O_3	132
$V_{1.4}/Al_2O_3$	133
$V_{1.4}Mo_4/Al_2O_3$	109
$V_{1.4}Mo_8/Al_2O_3$	105
$V_{2.8}Mo_4/Al_2O_3$	96
$V_{2.8}Mo_8/Al_2O_3$	94
$Mo_8V_{1.4}/Al_2O_3$	104
$Mo_8V_{2.8}/Al_2O_3$	92
Mo_4/Al_2O_3	130

Studies of pyridine adsorption show that on $V_{1.4}/Al_2O_3$ and $V_{2.8}/Al_2O_3$ solids, only acid sites of a Lewis type are present, which are characteristic of the γ-Al_2O_3 support. Fig. 1 shows the spectra of adsorbed pyridine on $V_{1.4}/Al_2O_3$. The bands observed at 1453, 1493, 1577 and 1622 cm^{-1} correspond to pyridine attached to Lewis acid sites [10,11].

As it can be observed, the more the temperature of evacuation increases, the significantly lower the intensity of absorption becomes. The intensity of 1616 cm^{-1} band is not significantly altered, but the position of the maximum is shifted toward higher frequencies. This could be related with two different types of Lewis acid sites on the catalyst surface [12].

Figs. 2 and 3 show the spectra of FTIR of Py adsorbed on the $V_{1.4}Mo_x/Al_2O_3$ solids, after evacuation during 30 min at 80 °C (a), 150 °C (b), and 250 °C (c).

Pyridine-related to Lewis centers bands are observed. The band located at 1540 cm^{-1}, associated with adsorbed pyridine on Brönsted acid sites, can also be detected for both $V_{1.4}Mo_4/Al_2O_3$ and $V_{1.4}Mo_8/Al_2O_3$. For $V_{1.4}Mo_8/Al_2O_3$ catalyst this band shows the highest intensity when the temperature of evacuation is 80 °C [13]. This band vanishes after the evacuation at 150 °C for $V_{1.4}Mo_4/Al_2O_3$, which indicates that these are relatively weak acid sites. For $V_{1.4}Mo_8/Al_2O_3$, greater acid strength is evident due to a permanence of this characteristic band after evacuation at the same temperature.

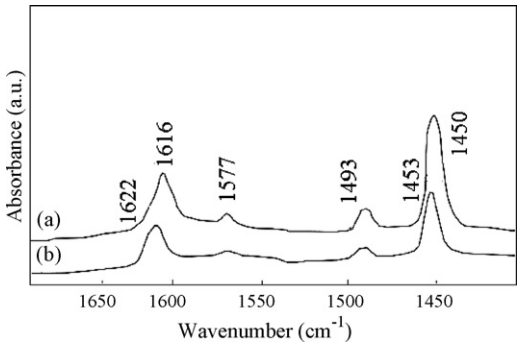

Fig. 1. FTIR spectra of pyridine adsorbed on $V_{1.4}/Al_2O_3$ after evacuation during 30 min at: (a) 80 °C and (b) 150 °C.