

# 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.

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**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,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich,  $S_0 = 132 \text{ m}^2/\text{g}$ ) 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  $\text{Mo}_x\text{V}_y/\text{Al}_2\text{O}_3$ . The same process can be applied to obtain  $\text{V}_y\text{Mo}_x/\text{Al}_2\text{O}_3$  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  $\text{CuK}\alpha$  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. Thermogravimetical 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 ( $\lambda = 632.8$  nm) laser with an OLYMPUS DX-40 microscope. Resolution of spectra is 7  $\text{cm}^{-1}$ , 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  $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2:20/15/65$  and  $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2:4/8/88$ . 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  $\gamma\text{-Al}_2\text{O}_3$  surface take place.

All samples present a similar DTA profile, with a wide exothermic event associated with a monotonous weight loss

Table 1  
Specific surface of  $\gamma\text{-Al}_2\text{O}_3$ , and catalysts

Sample	$S_0$ ( $\text{m}^2/\text{g}$ )
$\gamma\text{-Al}_2\text{O}_3$	132
$\text{V}_{1.4}/\text{Al}_2\text{O}_3$	133
$\text{V}_{1.4}\text{Mo}_4/\text{Al}_2\text{O}_3$	109
$\text{V}_{1.4}\text{Mo}_8/\text{Al}_2\text{O}_3$	105
$\text{V}_{2.8}\text{Mo}_4/\text{Al}_2\text{O}_3$	96
$\text{V}_{2.8}\text{Mo}_8/\text{Al}_2\text{O}_3$	94
$\text{Mo}_8\text{V}_{1.4}/\text{Al}_2\text{O}_3$	104
$\text{Mo}_8\text{V}_{2.8}/\text{Al}_2\text{O}_3$	92
$\text{Mo}_4/\text{Al}_2\text{O}_3$	130

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.

Studies of pyridine adsorption show that on  $\text{V}_{1.4}/\text{Al}_2\text{O}_3$  and  $\text{V}_{2.8}/\text{Al}_2\text{O}_3$  solids, only acid sites of a Lewis type are present, which are characteristic of the  $\gamma\text{-Al}_2\text{O}_3$  support. Fig. 1 shows the spectra of adsorbed pyridine on  $\text{V}_{1.4}/\text{Al}_2\text{O}_3$ . The bands observed at 1453, 1493, 1577 and 1622  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\text{V}_{1.4}\text{Mo}_x/\text{Al}_2\text{O}_3$  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  $\text{cm}^{-1}$ , associated with adsorbed pyridine on Brönsted acid sites, can also be detected for both  $\text{V}_{1.4}\text{Mo}_4/\text{Al}_2\text{O}_3$  and  $\text{V}_{1.4}\text{Mo}_8/\text{Al}_2\text{O}_3$ . For  $\text{V}_{1.4}\text{Mo}_8/\text{Al}_2\text{O}_3$  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  $\text{V}_{1.4}\text{Mo}_4/\text{Al}_2\text{O}_3$ , which indicates that these are relatively weak acid sites. For  $\text{V}_{1.4}\text{Mo}_8/\text{Al}_2\text{O}_3$ , greater acid strength is evident due to a permanence of this characteristic band after evacuation at the same temperature.

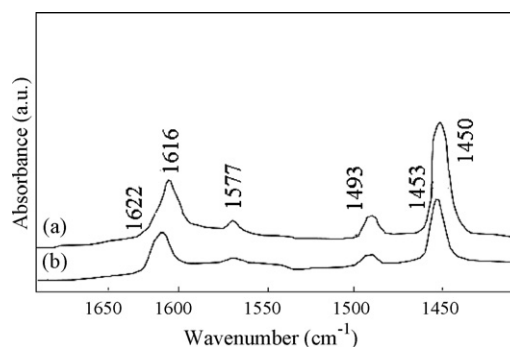


Fig. 1. FTIR spectra of pyridine adsorbed on  $\text{V}_{1.4}/\text{Al}_2\text{O}_3$  after evacuation during 30 min at: (a) 80 °C and (b) 150 °C.

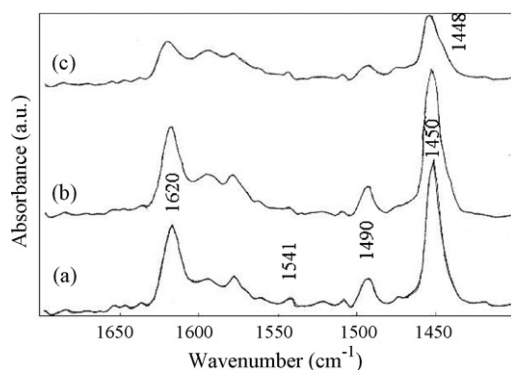


Fig. 2. FTIR spectra after pyridine adsorption for  $V_{1.4}/Al_2O_3$  after evacuation during 30 min at: (a) 80 °C, (b) 150 °C and (c) 250 °C.

Pyridine studies show that the order of aggregation of the oxide does not modify the acidity properties of the studied catalyst.

Fig. 4 shows the Raman spectra for  $V_{1.4}Mo_x$ .

The band centered near at  $1033\text{ cm}^{-1}$ , spectrum (a), is assigned to the symmetrical stretching mode of the terminal bond  $V=O$  of isolated monomer groups [3,5,14].

The spectrum for  $V_{1.4}Mo_4/Al_2O_3$  shows a wide, asymmetric band, with a maximum intensity at  $939\text{ cm}^{-1}$ . This band is attributed to the stretching mode of bridges  $M-O-M$  bonds in polymeric surface species of molybdenum or vanadium oxides [3,5]. In the spectrum (c), the band at  $847\text{ cm}^{-1}$  is attributed to antisymmetrical stretching modes of  $Mo-O-Mo$  bonds of superficial molybdenum oxides in different configurations (dimers and oligomers).

Bibliographic references show that the bands located at  $1000\text{ cm}^{-1}$  are related with the antisymmetrical stretching of terminal groups  $M=O$  of monomeric and polymeric surface species of vanadium and molybdenum [3,5,8,14]. The fact that this band is shifted at  $956\text{ cm}^{-1}$  may involve an additional distortion of the species of molybdenum superficial oxides which result from the interaction with vanadium cations [3].

Fig. 5 shows the Raman spectra obtained for  $Mo_4V_x/Al_2O_3$ . The band located at  $1039$  and  $911\text{ cm}^{-1}$ , spectrum (a), corresponds to the vibration modes of  $Mo=O$  and  $Mo-O-Mo$ , respectively.

The spectrum for  $Mo_4V_{1.4}/Al_2O_3$  shows a wide band at  $934\text{ cm}^{-1}$ . This band presents greater definition as the

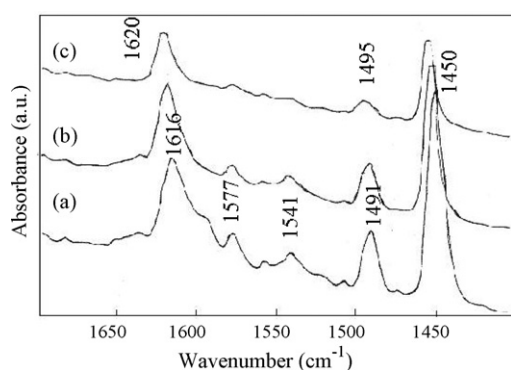


Fig. 3. FTIR spectra of pyridine adsorbed on  $V_{1.4}Mo_8/Al_2O_3$  after evacuation during 30 min at: (a) 80 °C, (b) 150 °C and (c) 250 °C.

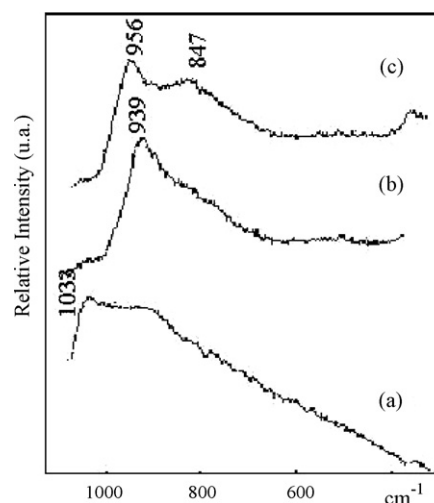


Fig. 4. Raman spectra for (a)  $V_{1.4}Mo_0/Al_2O_3$ , (b)  $V_{1.4}Mo_4/Al_2O_3$  and (c)  $V_{1.4}Mo_8/Al_2O_3$ .

concentration of vanadium increases, and a splitting can be observed with maxima at  $939$  and  $830\text{ cm}^{-1}$ . The presence of a band at  $770\text{ cm}^{-1}$  could be attributed to  $V-O-Mo$  vibrations. This band corresponds to polymolybdovanadate species, which shows that there is direct interaction of supported species when molybdenum is incorporated in the first instance [3,5].

Catalytic results show that an increase in the total flow leads to an extremely low decrease on propane conversion.

The results observed in both of the feed ratios used show that, under higher oxidizing conditions  $C_3H_8/O_2/N_2:4/8/88$ , the solids present greater conversions. Consequently, a decrease can be observed in the selectivity of the dehydrogenation products.

Tables 2 and 3 present the results obtained for  $C_3H_8/O_2/N_2:20/15/65$  feed ratio and 200 mL/min total flow. For this feed ratio an increase in propene selectivity is observed due to the less oxidative atmosphere used. This also contributes to avoid the formation of hot spots in the reactor. In ODH reactions the enthalpy of  $CO_2$  production corresponds to about  $-520\text{ kcal/mol}$  at  $500\text{ °C}$  while for propene production is about  $-37\text{ kcal/mol}$  at the same temperature. Then, if  $CO_2$  formation is decreased, the risk of reactor run-away is minimized.

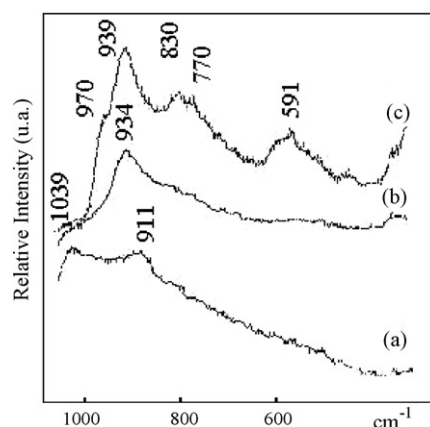


Fig. 5. Raman spectra for: (a)  $Mo_4V_0/Al_2O_3$ , (b)  $Mo_4V_{1.4}/Al_2O_3$  and (c)  $Mo_4V_{2.8}/Al_2O_3$ .

Table 2

Influence of the order of aggregation of the active phase  $V_{1.4}Mo_x/Al_2O_3$ 

Temperature (°C)	$V_{1.4}Mo_4$		$Mo_4V_{1.4}$		$V_{1.4}Mo_8$		$Mo_8V_{1.4}$	
	% Conversion	% Selectivity	% Conversion	% Selectivity	% Conversion	% Selectivity	% Conversion	% Selectivity
470	8.7	75.7	9.6	73.8	13.7	65.1	12.2	69.0
500	14.6	67.1	15.7	65.3	20.4	54.5	21.4	55.4
550	28.5	53.0	29.9	51.9	29.2	47.6	30.4	48.9

Table 3

Influence of the order of aggregation of the active phase  $V_{2.8}Mo_x/Al_2O_3$ 

Temperature (°C)	$V_{2.8}Mo_4$		$Mo_4V_{2.8}$		$V_{2.8}Mo_8$		$Mo_8V_{2.8}$	
	% Conversion	% Selectivity	% Conversion	% Selectivity	% Conversion	% Selectivity	% Conversion	% Selectivity
470	17.1	53.8	21.7	54.4	18.5	47.7	25.2	39.0
500	26.9	46.3	27.9	46.2	26.2	41.6	26.6	41.0
550	29.3	47.7	29.6	48.4	29.4	43.8	28.3	43.5

There is a slight influence of the catalytic behavior due to the changes in the order of aggregation of the active phases, for  $V_{1.4}Mo_x/Al_2O_3$ . However, there is a tendency to increase the conversion when Mo is incorporated in the first instance as can be observed in Table 2.

An increase in the concentration of Mo for  $V_{1.4}Mo_x/Al_2O_3$  leads to a conversion increase; while olefins selectivity reaches a maximum for  $V_{1.4}Mo_4/Al_2O_3$ . Fig. 6 shows these results for all the studied temperatures.

For  $V_{2.8}Mo_x/Al_2O_3$ , the solids are more active when Mo is incorporated in the first instance, which confirms the tendency observed for  $V_{1.4}Mo_x/Al_2O_3$ . Table 3 shows these results.

At a temperature higher than 470 °C, a maximum hydrocarbon conversion is reached. This level has a direct correspondence with the total  $O_2$  consumption, and the results obtained show a kinetic effect which is due to the limitation of this reactive.

Experimental measures could show overlapping between this effect and those effects related with the structure of the solids.

By comparing the results obtained for  $V_xMo_y/Al_2O_3$ , it can be observed that as the concentration of vanadium becomes greater, conversion also increases with an olefins selectivity loss.

Aggregation of the second phase leads to a decrease in the specific surface area, and a better definition of Raman spectra.

As previously discussed, spectra for  $V_{1.4}Mo_4/Al_2O_3$  and  $Mo_4V_{1.4}/Al_2O_3$  are significantly similar, with a maximum intensity which could be associated with both species  $M=O$  and  $M-O-M$ . The profile observed in the respective spectrum, together with the increase of the second oxide load, produce a greater resolution of these bands.

According to the results obtained from the characterization of the solids and the catalytic activity, we can conclude that the order of aggregation of the phases does not modify the nature or the acidity of the dispersed species on the surface of the alumina for  $V_{1.4}Mo_x/Al_2O_3$ – $Mo_xV_{1.4}/Al_2O_3$  catalysts.

For  $V_{1.4}Mo_x/Al_2O_3$  series, conversion increases when the concentration of molybdenum oxide phase becomes greater; while selectivity reaches a maximum for  $V_{1.4}Mo_4/Al_2O_3$ .

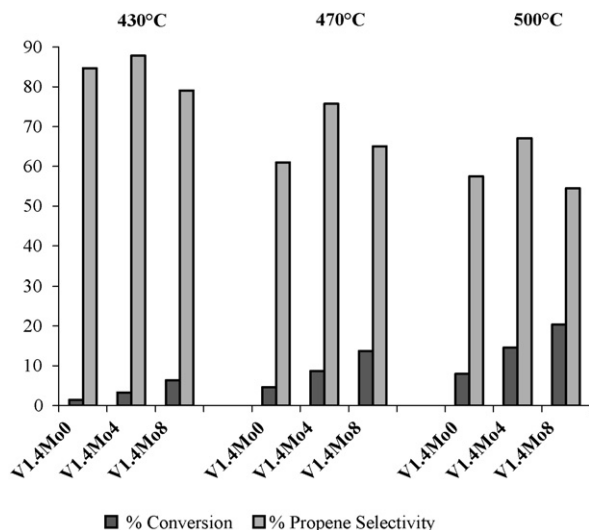
Studies of pyridine adsorption show that incorporation of molybdenum produces acid sites of a Brönsted type, which can be more easily detected when there is greater concentration of molybdenum oxide.

Production of this type of acid centers involves modification in the coordination environment of the surface species, thus it affects catalytic behavior.

In the studied catalysts, the greatest olefins selectivity is obtained with those solids containing both types of acid centers on the surface, with moderate acid strength.

The more concentration of molybdenum there is, the more the strength of Brönsted acid sites increases, which is favorable to achieve greater olefin–surface interaction, and therefore, a complete degradation of combustion products.

For solids,  $V_{2.8}Mo_x/Al_2O_3$ – $Mo_xV_{2.8}/Al_2O_3$ , a decrease in the specific surface area can be observed, as well as greater propane conversion when Mo is incorporated in the first instance. The band at  $770\text{ cm}^{-1}$  for  $Mo_4V_{2.8}/Al_2O_3$  could be due to the presence of polymolybdovanadate species, which are responsible for the greatest catalytic activity observed in these catalysts.

Fig. 6. % Propene selectivity and % conversion for  $V_{1.4}Mo_x/Al_2O_3$ .

#### 4. Conclusions

For low concentration of vanadium, the order of aggregation of the active phases does not affect catalytic behavior, which means that the nature of the surface species is not substantially modified by this difference in the method of preparation.

For a greater concentration of vanadium, the order of incorporation of the active phases leads to alteration of catalytic properties, thus greater conversion can be observed when molybdenum is incorporated in the first instance. Species Mo–V–O which is formed may be the responsible for this behavior.

Incorporation of molybdenum modifies the superficial amorphous phases with an involvement of activity and selectivity of the catalyst. It can be observed that the catalytic properties of this type of materials are influenced by the nature and strength of the acid sites on the surface.

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