

## OXIDATIVE DEHYDROGENATION OF ISOBUTANE OVER V-Mo-(Ni)-O CATALYSTS

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V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and three V-Mo-O based catalysts, which were prepared either by solid state reaction or by slurry method, were tested in the oxidative dehydrogenation reaction of isobutane. The catalytic activities in the oxidative dehydrogenation of isobutane to isobutene were compared in order to elucidate the roles of constituent elements and crystal structure during the isobutane oxidative dehydrogenation. It was observed that the rate of isobutane oxidation was almost the same over all catalysts except V<sub>2</sub>O<sub>5</sub> for which it was higher. The Ni-containing catalyst showed a lower selectivity to isobutene than Mo-V-O catalyst prepared by the same method, but a higher activity. Since isobutene was formed as a main product at low conversion levels, over each catalyst (except V<sub>2</sub>O<sub>5</sub>), it can be concluded that Ni located in the Mo-V-O structure promoted effectively the conversion of intermediate isobutene to carbon oxides.

### INTRODUCTION

The oxidation of light alkanes is usually a difficult reaction because of the low reactivity of the reactant and normally requires more severe reaction conditions than in the case of olefin oxidation. The subsequent oxidation of the partially oxidized products takes place unavoidably, resulting in low selectivity of the desirable products.<sup>1</sup>

Light olefins can be produced by dehydrogenation, at high temperatures, of the corresponding alkanes. However, the catalytic dehydrogenation still suffers from a number of limitations including high energy input and catalyst deactivation. The light alkanes oxidative dehydrogenation (ODH) represents an alternative for the production of these chemicals, highly selective catalysts being developed.<sup>2-9</sup>

The main problems, which have to be overcome in those difficult selective oxidation reactions, are the activation of the highly stable C-H methyl bonds and the higher reactivity of the products (alkenes or oxygenates) for further oxidations to undesired products or to CO<sub>x</sub>.

A lot of selective oxidation reactions take place in the heterogeneous catalysis and almost all of them proceed with high or significant selectivity over a small number of high-valence metal oxide

catalysts. Among them V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub> oxides are the most efficient and frequently used, being known as classic selective oxidation catalysts.<sup>10-15</sup>

The aim of this work has been to study the catalytic activity of V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, V-Mo-O and V-Mo-Ni-O mixed oxide catalysts in the oxidative dehydrogenation of isobutane. Thus, the influence of different factors such as the composition of the catalysts and the preparation conditions, temperature and space velocity feed on the catalytic activity of our systems were investigated.

### RESULTS AND DISCUSSION

#### 1. Catalysts characterization

Five types of catalysts (C1-C5) were prepared and studied in the oxidative dehydrogenation of isobutane. The XRD patterns of the prepared catalysts are shown in Figure 1, and the observed phases are listed in Table 1.

The examination of the powder diffraction patterns for catalysts C3, C4 and C5 reveals that multi-phase materials are formed. Thus, in the 10 % V<sub>2</sub>O<sub>5</sub> – 90 % MoO<sub>3</sub> (SM) (C3) catalyst three phases were observed, MoO<sub>3</sub>, V<sub>2</sub>MoO<sub>8</sub> and VO<sub>2</sub>, but the predominant one was MoO<sub>3</sub>. In the 10 %

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$V_2O_5 - 90\%$   $MoO_3$  catalyst (C4), only two phases were observed,  $MoO_3$  and  $V_{3.6}Mo_{2.4}O_{16}$  while in the  $10\%$   $V_2O_5 - 10\%$   $NiO - 80\%$   $MoO_3$  (C5) three phases were observed  $MoO_3$ ,  $V_2MoO_8$  and  $NiMoO_4$ . It can be observed from XRD patterns of all these catalysts that the  $V_2O_5$  phase is not present. The structural model of  $V_2MoO_8$  is described as a  $\beta$ -phase. The structure of  $V_2MoO_8$ , monoclinic with space group C2, can be described as a shear structure of octahedra forming  $ReO_3$ -type slabs which are infinite in the  $b$  and  $c$  direction, but only extending over three layers of

octahedra.<sup>16</sup> Such slabs are joined together by octahedra with common edges. We can therefore state that the preparation route leads to differences between phases, the catalyst prepared by solid-solid reaction presents a  $V_{3.6}Mo_{2.4}O_{16}$  phase. In the fifth catalyst (C5) the structural model of  $NiMoO_4$  is described as an  $\alpha$ -phase. The incorporation of Ni in this catalyst affects drastically the compositional phases, which are different from that of the Mo-V-O catalysts. All catalysts contain a pure and well-crystalline ortho- $MoO_3$  phase.

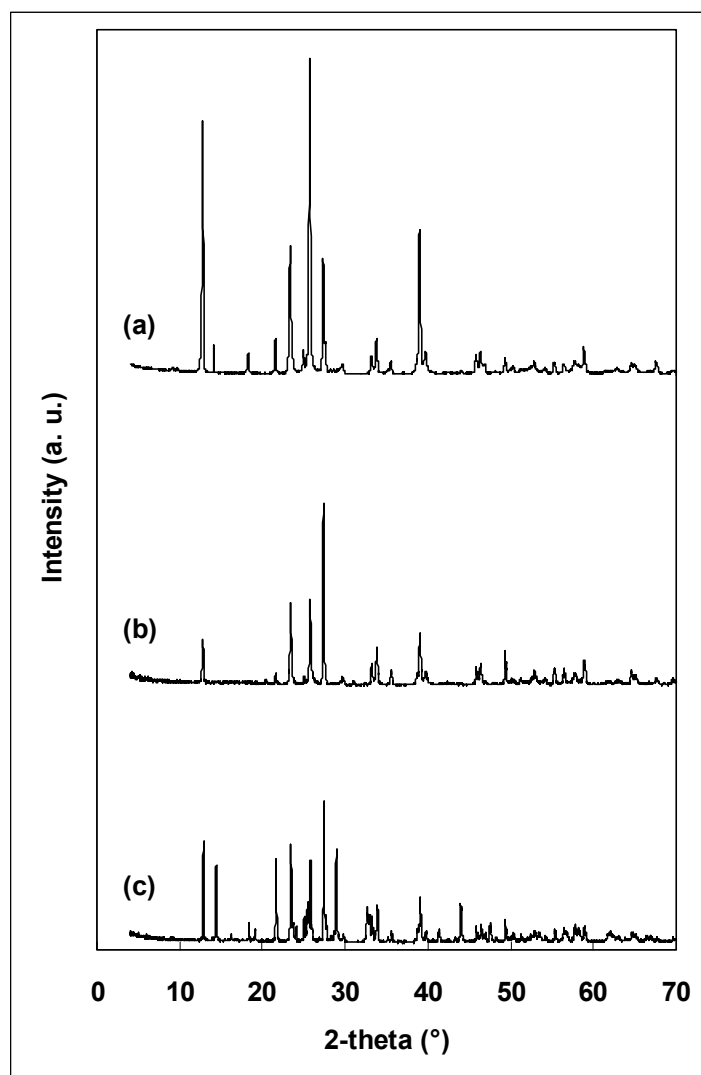


Fig. 1 – X-ray diffraction patterns of V-Mo-O (SM) (a), V-Mo-O (b) and V-Mo-Ni-O (c) catalysts.

Table 1

Main crystalline phases determined by XRD in V-Mo mixed oxide catalysts

Catalyst	Crystalline phase observed		
V-Mo-O (SM)	$MoO_3$	$V_2MoO_8$	$VO_2$
V-Mo-O	$MoO_3$	$V_{3.6}Mo_{2.4}O_{16}$	-
V-Mo-Ni-O	$MoO_3$	$V_2MoO_8$	$NiMoO_4$

The porosity of the calcined materials was characterized by nitrogen adsorption-desorption isotherms. The specific surface areas, calculated with the BET method, were between 2-5 m<sup>2</sup>/g, and the average pore diameters were between 11-15 nm for all five catalysts.

## 2. Catalytic properties

The catalytic properties of the five catalysts were evaluated in the ODH of isobutane. Under the experimental conditions adopted, the main reaction products were isobutene, carbon monoxide and carbon dioxide. The by-products methane, ethane, propane and propene were observed only in small amounts while the oxygenates (acid acetic, methacrolein and acetone) were detected in a fairly low amount.

The obtained conversions and the product distributions are listed in Table 2. We can observe that C1 catalyst is the most active in the ODH of isobutane but its selectivity for isobutene is low. In this case CO<sub>x</sub> were observed in higher quantities. From the two catalysts, C3 and C4, prepared by different methods, the C4 catalyst, obtained by solid-solid reaction, is less active than C3 catalyst, obtained from solution. The selectivity for isobutene is almost the same for both catalysts. C3 and C4 catalysts have activities comparable with the other catalysts but higher selectivities.

Table 2 also presents the transformation rates of isobutane for all catalysts. As it can be seen, the rates of transformation of isobutane are almost the same for C2, C4 and C5 catalysts, and decrease with increasing the volume hourly space velocity (VHSV). The highest transformation rate was observed for the reaction over pure V<sub>2</sub>O<sub>5</sub> (C1 catalyst).

Table 2

Catalytic performance of the catalysts in the oxidative dehydrogenation of isobutane (molar ratio i-C<sub>4</sub>H<sub>10</sub>:O<sub>2</sub> = 1:1)

Catalyst	VHSV (h <sup>-1</sup> )	Temp. (°C)	i-C <sub>4</sub> H <sub>10</sub> conversion (%)	Selectivity (%)				Reaction rate (mmol/g h)
				i-C <sub>4</sub> H <sub>8</sub>	Oxig.	Cracking products	CO <sub>x</sub>	
C1	2000	400	8.9	40	0.6	2.3	57.1	1.5
	2000	450	12.5	47.7	3.3	3.8	45.2	2.1
	2500	400	4.3	42.5		3.1	54.4	0.8
	2500	450	11.4	50.2	1.5	3.4	44.9	2.3
C2	2000	400	2.0	66.8			33.2	0.2
	2000	450	3.1	60.0		5.2	34.8	0.4
	2500	400	1.2	69.7			30.3	0.2
	2500	450	2.6	66.5			33.5	0.4
C3	2000	400	2.6	78.7			21.3	0.4
	2000	450	4.6	66.9		9.0	24.1	0.8
	2500	400	1.4	85.3			14.7	0.3
	2500	450	3.2	75.4			24.6	0.6
C4	2000	400	1.1	75.5			22.5	0.2
	2000	450	2.0	68.2			31.8	0.4
	2500	450	1.0	82.4			17.6	0.2
	2500	450	1.2	72.1		2.7	25.2	0.3
C5	2000	400	2.1	36.0		6.3	57.7	0.2
	2000	450	5.6	45.9		7.3	46.8	0.6
	2500	400	1.9	37.8		4.1	58.1	0.1
	2500	450	4.7	45.2		6.8	48.0	0.5

Figure 2 shows the conversions of isobutane for all catalysts as a function of the reaction temperature. The conversion of isobutane increased with increasing reaction temperature for all catalysts. Pure V<sub>2</sub>O<sub>5</sub> catalyst was the most active from all five catalysts for all the temperature range considered, the highest activity being observed at 450-550°C.

For the same reaction, MoO<sub>3</sub> catalyst is usually active at higher temperatures than V<sub>2</sub>O<sub>5</sub> catalyst. Grzybowska<sup>17</sup> explained that these differences may arise from: (i) lower reducibility of MoO<sub>3</sub> compared

with V<sub>2</sub>O<sub>5</sub>, (Taman temperatures: 690°C for V<sub>2</sub>O<sub>5</sub> and 261°C for MoO<sub>3</sub>) the lattice oxygen mobility of the latter oxide being higher, (ii) differences in redox potentials of the V<sup>+5</sup>/V<sup>+4</sup> and Mo<sup>+6</sup>/Mo<sup>+5</sup> couples which controls the oxidation state of vanadium or molybdenum in a hydrocarbon/oxygen mixture. The presence of vanadium ions in different oxidation states, which is a characteristic of vanadia catalysts, facilitates the electron transfer between the substrates of oxidation reactions and the catalyst. On the other hand, on the molybdena-based catalysts, usually fully oxidized in reaction conditions, only traces of mo-

lybdenum ions with valencies lower than 6 are observed.

The incorporation of nickel to the binary Mo-V-O system causes a slight improvement to the isobutane conversion, compared to Mo-V-O catalyst prepared by the same method. The isobutane conversion is comparably whith that obtained by the binary Mo-V-O system prepared by slurry method.

The effect of reaction temperature on isobutene and CO<sub>x</sub> selectivities is shown in Figure 3. Isobutene selectivity decreased with increasing temperature for all catalysts, excepting C1 and C5 catalysts, where the selectivity to isobutene increased with increasing temperature. The same behaviour was observed by Le Bars *et al.*<sup>18</sup> in the oxidative dehydrogenation of ethane over V<sub>2</sub>O<sub>5</sub> and they suggest that better selectivity seems to be a characteristic of the reduced surface. However, it can hardly be maintained under the reaction conditions because of the oxygen diffusion from the bulk. At the steady state, the surface of V<sub>2</sub>O<sub>5</sub> is close to be fully oxidized. To enhance the isobutene selectivity, an optimum regeneration of the surface acidic properties and a rapid removal of the isobutene from the reaction zone are claimed to be essential.

The selectivity to isobutene is higher over C2, C3 and C4 catalysts, which contain mainly MoO<sub>3</sub> and V<sub>2</sub>MoO<sub>8</sub> or V<sub>3.6</sub>Mo<sub>2.4</sub>O<sub>16</sub> phases and do not contain V<sub>2</sub>O<sub>5</sub> phase. For these catalysts the selectivity to isobutene is higher at low temperatures, but when the temperature increases the selectivity to cracking products increases at the expense of isobutene. By comparing C3 and C4 catalysts, which have the same chemical

composition but are prepared by different methods, we think that V<sub>2</sub>MoO<sub>8</sub> phase is more selective then V<sub>3.6</sub>Mo<sub>2.4</sub>O<sub>16</sub> phase. The presence of V<sup>+4</sup> species on C3 catalyst increase the activity of this catalyst.

Very reducible oxides (such as V<sub>2</sub>O<sub>5</sub>) may become ineffective in ODH reactions because their surfaces start to lose oxygen when the reduction steps become more facile than reoxidation. In such systems, O<sub>2</sub> chemisorption rates become rate-determining and the rates actually decrease with increasing reducibility of the metal cations. Similarly, intermediate basicity of lattice oxygens leads to maximum rate. As basicity increases, activation steps of C-H bonds become faster, but the subsequent recombination of OH groups to form water slows down and the surface becomes predominantly covered with OH groups. This, would decrease the rate of desorption of the desired alkenes and increase the probability that they will be instead oxidized to undesired CO<sub>x</sub> products.<sup>19</sup>

CO<sub>x</sub> selectivities increase with increasing temperature on these catalysts while for C1 the CO<sub>x</sub> selectivity decreases with increasing temperature. The higher selectivity to isobutene over MoO<sub>3</sub> compared to V<sub>2</sub>O<sub>5</sub> could be explained by the fact that on the MoO<sub>x</sub> oxide surface, the limited and structurally determined number of metallic cations M<sup>n+</sup> and oxygen anions O<sup>2-</sup> are concerned to get selectively the desired product and not CO<sub>2</sub> (the formation of which requires more oxygen atoms).<sup>20</sup> The presence of nickel affects selectivity to isobutene, the catalytic results obtained show that over α-NiMoO<sub>4</sub> catalysts the isobutene formed is extremely reactive.<sup>21</sup>

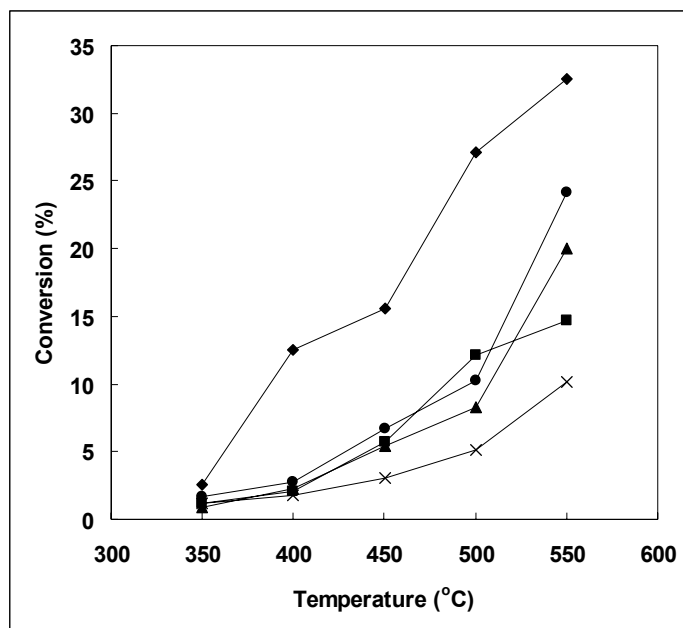


Fig. 2 – Variation of the isobutane conversion with the reaction temperature (VHSV 1500h<sup>-1</sup>, molar ratio i-C<sub>4</sub>H<sub>10</sub>: O<sub>2</sub>= 1:1); ♦ – C1, ■ – C2, ▲ – C3, x – C4, ● – C5.

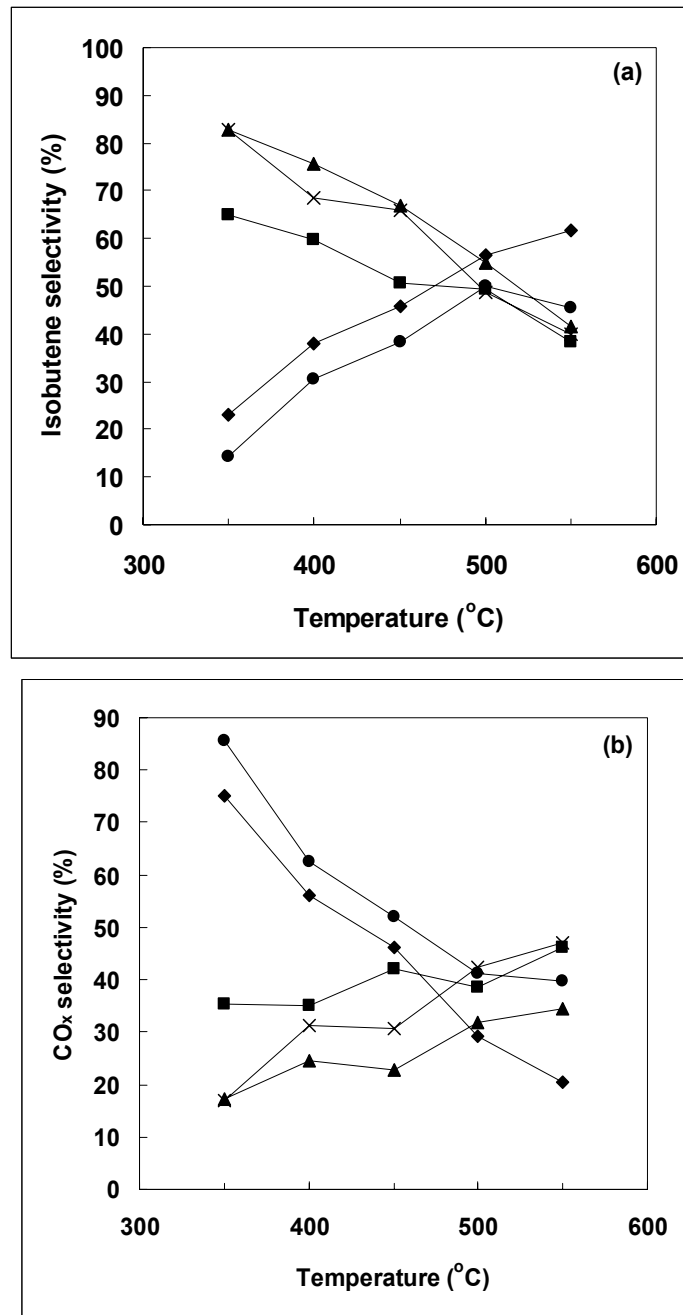


Fig. 3 – Selectivity to: a) isobutene, b) CO<sub>x</sub>, as function of temperature (VHSV 1500 h<sup>-1</sup>, molar ratio i-C<sub>4</sub>H<sub>10</sub>: O<sub>2</sub>= 1:1); ♦ – C1, ■ – C2, ▲ – C3, x – C4, ● – C5.

Table 3 shows a comparison of isobutene selectivities at isoconversion for all five catalysts prepared in this research. It can be seen that for both conversions chose (5 % and 10 %) the C3 catalyst has the highest selectivity. At 10 % conversion the selectivity is a little lower than at 5 % (except C1 catalyst). For the C5 system it can be seen that the introduction of Ni produced a decrease in the selectivity for the same conversion.

The variation of isobutane conversion and products selectivities as a function of i-C<sub>4</sub>H<sub>10</sub>:O<sub>2</sub>

molar ratio at 400°C are shown in Figure 4. For all catalysts the higher activity was obtained at a molar ratio equal to 0.5, when O<sub>2</sub> is in excess, but the selectivity to isobutene is lower at this molar ratio. The highest selectivities to isobutene were obtained for all catalysts at a i-C<sub>4</sub>H<sub>10</sub>:O<sub>2</sub> molar ratio equal to 2. For all catalysts, the CO<sub>x</sub> selectivity decreased with the increasing this molar ratio.

Table 3

Isobutene selectivity at isoconversion in the oxidative dehydrogenation of isobutane over all five catalysts  
(molar ratio  $i\text{-C}_4\text{H}_{10}:\text{O}_2 = 1:1$ ,  $\text{VHSV} = 1500 \text{ h}^{-1}$ )

Catalyst	5 % Conversion		10 % Conversion	
	$i\text{-C}_4\text{H}_8$ Selectivity (%)	Temperature ( $^{\circ}\text{C}$ )	$i\text{-C}_4\text{H}_8$ Selectivity (%)	Temperature ( $^{\circ}\text{C}$ )
C1	28	370	38	390
C2	53	430	48	475
C3	69	440	53	510
C4	48	500	40	540
C5	37	435	46	480

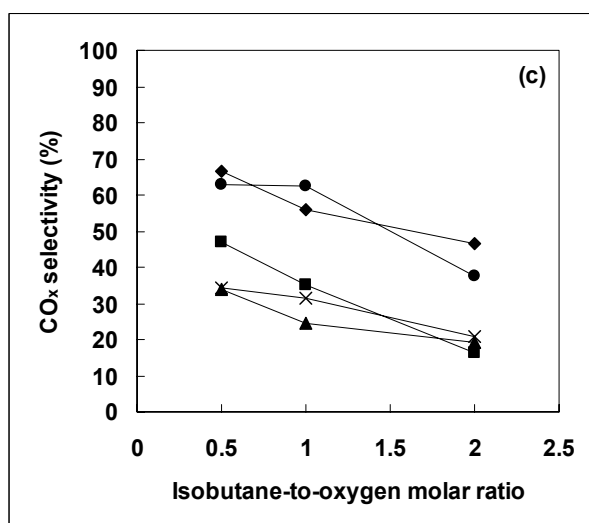
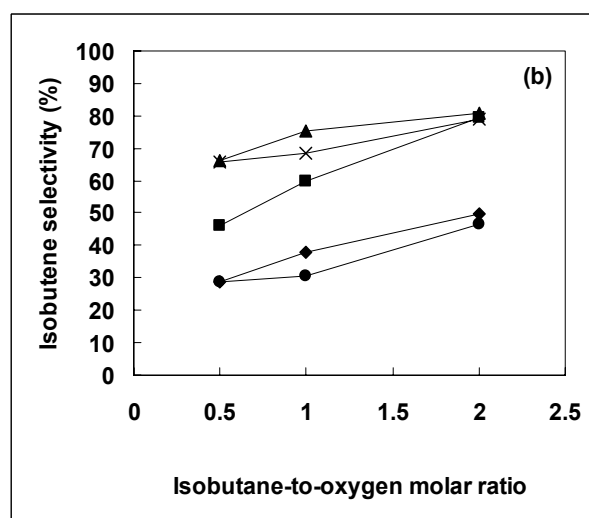
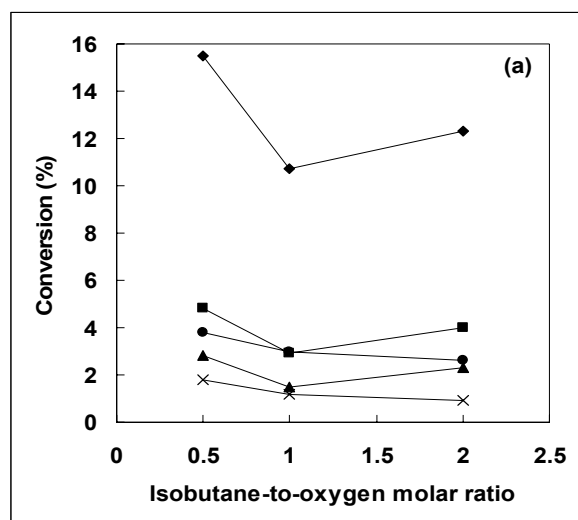


Fig. 4 – Conversion of isobutane (a) and selectivity to isobutene (b) and  $\text{CO}_x$  (c) as a function of molar ratio  $i\text{-C}_4\text{H}_{10}:\text{O}_2$  at  $400^{\circ}\text{C}$  and  $\text{VHSV} = 1500 \text{ h}^{-1}$ ;  $\blacklozenge$  – C1,  $\blacksquare$  – C2,  $\blacktriangle$  – C3,  $\times$  – C4,  $\bullet$  – C5.

## EXPERIMENTAL

### 1. Catalysts preparation and characterization

$\text{V}_2\text{O}_5$  (C1) and  $\text{MoO}_3$  (C2) catalysts were prepared by thermal decomposition of  $\text{NH}_4\text{VO}_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  precursors, respectively. Thus, they were calcinated at  $200^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$  and  $600^{\circ}\text{C}$  for 2 h, 2 h and 4 h, respectively.

10 %  $\text{V}_2\text{O}_5$  – 90 %  $\text{MoO}_3$  systems (C3 and C4) were prepared starting from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (99.8%) and  $\text{NH}_4\text{VO}_3$  precursors using two methods. In the first method, the slurry method (SM), the precursors were dissolved

separately in distilled water, and then the  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  solution was added to the  $\text{NH}_4\text{VO}_3$  solution. The obtained mixture was heated at  $90^{\circ}\text{C}$  to evaporate water. The resulted powder was dried in air at  $120^{\circ}\text{C}$  for 15 h and then calcined at  $200^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$  and  $600^{\circ}\text{C}$  for 2 h, 2 h and 4 h, respectively, to obtain the final C3 catalyst. The second method consist in a solid state reaction between the precursors carried out at  $200^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$  and  $600^{\circ}\text{C}$  for 2 h, 2 h and 4 h, respectively, to obtain the final C4 catalyst.

10 %  $\text{V}_2\text{O}_5$  – 10 % NiO – 80 %  $\text{MoO}_3$  system (C5) was obtained by solid state reaction between  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (99.8%),  $\text{NH}_4\text{VO}_3$  and  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  precursors. The

resulted mixture was dried at 120°C for 15 h and then calcined at 200°C, 400°C and 600°C for 2 h, 2 h and 4 h, respectively, in order to obtain the final catalyst.

We used for all catalysts the same calcination procedure because it is known that the calcination temperature influence

the compositional phase of catalysts.<sup>22-24</sup> The symbols used for the catalysts prepared are listed in Table 4.

Table 4

The calculated catalyst compositions and symbols used

Catalyst	Calculated catalyst composition
V <sub>2</sub> O <sub>5</sub> (C1)	100 %
MoO <sub>3</sub> (C2)	100 %
V-Mo-O (SM)* (C3)	10 % V <sub>2</sub> O <sub>5</sub> – 90 % MoO <sub>3</sub>
V-Mo-O (C4)	10 % V <sub>2</sub> O <sub>5</sub> – 90 % MoO <sub>3</sub>
V-Mo-Ni-O (C5)	10 % V <sub>2</sub> O <sub>5</sub> – 10 % NiO – 80 % MoO <sub>3</sub>

SM – slurry method

Catalysts were analyzed by X-ray diffraction using a PW 3710 diffractometer with CuK<sub>α</sub> radiation for Bragg's angles (2θ) from 4 to 80°.

Surface areas of the catalysts were measured from the adsorption isotherms of N<sub>2</sub> at – 196°C using the BET method with an ASAP 2000 sorptometer.

## 2. Catalytic reactions

The selective oxidation of isobutane was carried out in a fixed bed quartz tube down-flow reactor operated at atmospheric pressure. The calcinated catalyst was placed in the middle of the reactor on a layer of quartz wool. Normally, 2 cm<sup>3</sup> (1,7-2,5 g) of catalyst was used. The axial temperature profile was measured using a thermocouple placed in a thermowell centered in the catalyst bed. The reactor temperature was controlled using a thermocouple attached to the exterior of the reactor. Quartz chips were used to fill the dead volumes, before and after the catalyst bed, to minimize potential gas-phase pyrolysis reactions at higher reaction temperatures. The reaction mixture, consisting in isobutane and air, was passed through the catalyst bed at a volume hourly space velocity (VHSV) of 1000-2500 h<sup>-1</sup>. The influence of the isobutane-to-oxygen ratio on the oxidative dehydrogenation of isobutane was studied by varying this ratio in the range 0.5-2. Flow rates were controlled by fine needle valves and were measured by capillary flow meters. The catalyst was activated in air at 550°C for 2 h before reaction. In all studies, the reactor effluent was passed through a condenser to remove water and liquid oxygenated products. The reactants and products in the gas-phase were analyzed with a Thermo Finnigan gas chromatograph, equipped with a flame ionization detector and a thermal conductivity detector. Chromatographic separation was accomplished with an alumina column and a CTR I column. The condensate was analyzed with a Thermo Finnigan chromatograph using a DB-5 column and a flame ionization detector. Isobutene, CO, CO<sub>2</sub> were the major products formed under our reaction conditions. Minor amounts of the liquid oxygenated products, acetic acid, methacrolein and unknowns were also detected. The carbon balance based on the main reaction products listed above was within the range 95-105 % for all of the reactions.

## CONCLUSIONS

Five catalysts (V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, V-Mo-O (SM), V-Mo-O and V-Mo-Ni-O) were examined for the

oxidative dehydrogenation of isobutane. We found that there is a strong relationship between the catalyst phase composition and the isobutane oxidation activity. No correlation was observed between the activities and the specific surface areas of these catalysts, because the surface areas are low for all catalysts. These suggest that the chemical properties of the catalysts govern the activity and the selectivity in the oxidative dehydrogenation of isobutane.

The most active catalyst is C1, but it has the disadvantage that is less selective for isobutene. For the same reaction, C2 catalyst is usually more active at higher temperatures than C1 catalyst. The other catalysts (except C5) are less active but more selective to isobutene. The presence of vanadium ions in different oxidation states, which is a characteristic of vanadia catalysts, facilitates the electron transfer between the substrates of oxidation reactions and the catalyst improving the catalytic activity. On the other hand, the molybdena-based catalysts, which are usually fully oxidized in working conditions, are less active but more selective.

The incorporation of nickel to the binary Mo-V-O system causes a slight improvement in the isobutane conversion compared to Mo-V-O catalyst, prepared by the same method, but the isobutene selectivity decreases.

The discussion on the type of catalytic sites which can be present on the surface of molybdenum-vanadium-based catalysts and their role in particular steps of the oxidation reactions is still incomplete.

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