Mo-V-M-O (M = Ni, Cu, Zn, Sb, Ta) MIXED METAL OXIDES PREPARED BY SOLID-SOLID REACTIONS FOR OXIDATIVE DEHYDROGENATION OF ISOBUTANE

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Oxidative dehydrogenation of isobutane to isobutene was investigated over MoVO and MoVMO (M = Ni, Cu, Zn, Sb, Ta) mixed metal oxide catalysts prepared by solid-solid reactions. All catalysts were characterized by XRD and BET techniques. The addition of Ni, Zn, Cu, Sb and Ta improved the activity of Mo-V-O catalyst and decreased the isobutene selectivity, but the overall yield was in all cases improved. The optimal performance towards isobutene yield was found for Mo-V-Sb-O and Mo-V-Ta-O systems.

INTRODUCTION

The substitution of alkenes by alkanes as feedstock in selective oxidation processes has been drawing increasing interest from the chemical industry in recent years as an attractive way to reduce environmental impact and costs. Alkanes are more economical and readily available raw materials than alkenes. The demand of light olefins and of products made from them, is increasing steadily and the present capacity might become insufficient to meet this demand. This is specially the case for isobutene, which is the most versatile chemical intermediate among all C_4 olefins. The selective oxidation of small organic molecules is performed over oxide catalysts comprising the elements V and Mo as essential ingredients.[1-10]

It is commonly accepted that highly specific local electronic structures of the active metal sites are essential for the catalytic performance.[11] Oxidation catalysts can be quite complex, often with multiple phases and with different active sites to fulfill multiple function. Multiple functions the selective oxidation catalysts need to perform may include activation of the organic molecule, hydrogen abstraction, oxygen activation, oxygen insertion and regeneration of the active sites.[12]

During selective oxidation and oxidative dehydrogenation (ODH) of hydrocarbons, non-selective mechanisms can also exist, in which oxygen, from the lattice or activated from the gas phase, can be inserted into the hydrocarbon, and several reaction steps advance ultimately to form carbon oxides. For selective catalysts, an optimal balance should exist between the oxygen activity, acid-base characteristics and lattice diffusivity. It is therefore essential for an oxidation catalyst to possess a certain degree of structural and/or phase complexity. Oxygen mobility represents the characteristic determined to be essential for selective oxidation. Molybdenum oxide-based catalysts are active and selective in many reactions belonging to very different types such as reactions with the participation of hydrogen or oxygen, which may be considered as redox processes. Parameters which determine the catalytic behaviour of molybdenum oxides are the valence state of molybdenum ions, their local environment and the type of crystal plane on which they are exposed. It may thus be anticipated that MoO_3 surface must contain catalytically active sites which are active in different types of elementary steps.[13]

On the other hand, the vanadia-based systems are active and selective in various types of hydrocarbon oxidation reactions comprising: a) oxidative dehydrogenation of alkanes and olefins (on V-Mg-O compounds, alkaline earth, metal vanadates and on systems containing $[VO_x]_n$ groups dispersed on basic oxide supports),[14-17] and b) reactions with formation of oxygenated

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products. In the latter reactions they are particularly active in formation of acidic organic products such as anhydrides, acids or their derivates-esters.

The main objective of this work was to exanimate the performance of some Mo-V-M-O (M = Ni, Cu, Zn, Sb, Ta) mixed oxides for ODH of isobutane to isobutene in the temperature range 350-550°C.

RESULTS AND DISCUSSION

a) Catalysts characterization

The crystal structures of Mo-V-O and Mo-V-M-O (M = Ni, Cu, Zn, Sb, Ta) samples were examined by X-ray diffraction (Fig. 1), and the observed phases are listed in Table 1. Diffraction peaks assigned to orthorhombic phase of MoO_3 (JCPDS 035-0609) was detected in all samples. Mo-V-O sample contain a diffraction peak assigned to monoclinic phase of vanadium molybdenum oxide ($V_{3.6}Mo_{2.4}O_{16}$) (JCPDS 084-1952).

In the catalytically active Mo-V-Ni-O system, three crystalline phases have been identified: orthorhombic MoO_3 (JCPDS 035-0609), monoclinic nickel molybdenum oxide $NiMoO_4$ (JCPDS 033-0948) and monoclinic vanadium molybdenum oxide V_2MoO_8 (JCPDS 074-1510). The structure model of $NiMoO_4$ is described as a α-phase and V_2MoO_8 is described as a β-phase.
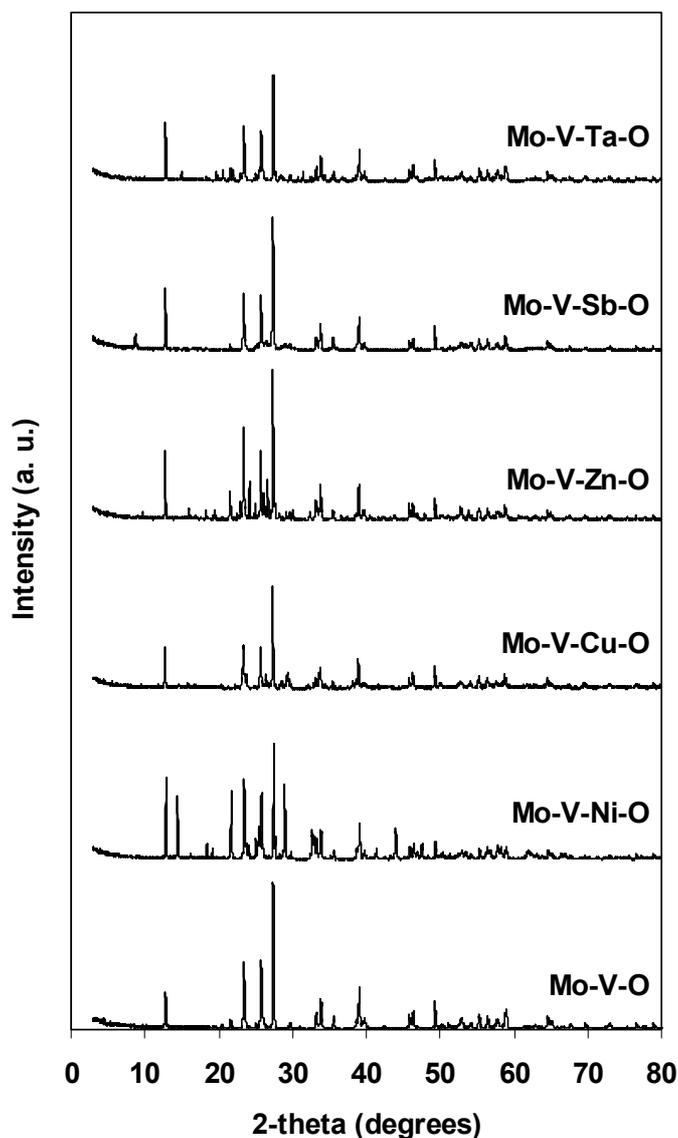

Fig. 1 – XRD patterns of the prepared catalysts.

Table 1

Main crystalline phases determined by XRD and specific surface areas of V-Mo-M-O catalysts

Catalysts	Surface area (m^2/g)	Phases detected by XRD
Mo-V-O	2.3	MoO_3 (S), $V_{3.6}Mo_{2.4}O_{16}$ (W)
Mo-V-Ni-O	2.3	MoO_3 (S), $NiMoO_4$ (S), V_2MoO_8 (W)
Mo-V-Cu-O	1.0	MoO_3 (W), $Cu_{1.3}V_9O_{22}$ (W)
Mo-V-Zn-O	0.9	MoO_3 (S), $ZnMoO_4$ (W), V_2MoO_8 (W)
Mo-V-Sb-O	2.5	MoO_3 (S), Sb_2O_5 (W), V_6O_{13}(W)
Mo-V-Ta-O	1.7	MoO_3 (S), $V_{3.6}Mo_{2.4}O_{16}$ (W), $TaVO_5$ (W)

S – Strong intensity; W – Weak intensity.

In the Mo-V-Cu-O system two crystalline phases have been identified: orthorhombic MoO_3 (JCPDS 035-0609) and monoclinic copper vanadium oxide $Cu_{1.3}V_9O_{22}$ (JCPDS 046-0362).

In the catalytically active Mo-V-Sb-O and Mo-V-Ta-O systems three crystalline phases have been identified: orthorhombic MoO_3 (JCPDS 035-0609) for both systems, monoclinic antimony oxide Sb_2O_5 (JCPDS 033-0110) and monoclinic vanadium oxide V_6O_{13} (JCPDS 043-1050) for the first system, and monoclinic vanadium molybdenum oxide $V_{3.6}Mo_{2.4}O_{16}$ (JCPDS 084-1952) and orthorhombic tantalum vanadium oxide $TaVO_5$ (JCPDS 042-0433) for the second one.

In the Mo-V-Zn-O system three crystalline phases have also been identified: orthorhombic MoO_3 (JCPDS 035-0609), triclinic zinc molybdenum oxide $ZnMoO_4$ (JCPDS 035-0765) and monoclinic vanadium molybdenum oxide V_2MoO_8 (JCPDS 020-1377).

BET surface areas of the samples are shown in Table 1. It is observed that surface areas for all the catalysts are low, under 3 m^2/g, normal values for oxides prepared by solid-solid reaction.

b) Catalytic properties

The catalytic properties of the prepared catalysts are compared in Table 2, for the same reaction conditions: T = 450°C, VHSV = 2000 h^{-1} and isobutane/oxygen molar ratio = 1.

The Mo-V-O sample has poor efficiency, in terms of yield, for the target reaction. All the ternary Mo-V-M-O systems demonstrates substantially higher activity and the incorporation of Zn and Sb to the binary Mo-V-O system causes a substantial improvement of the isobutene yield, which is more than doubled with respect to the binary Mo-V-O system (3.4 % versus 1.6 %). On the other hand, the addition of the third component into Mo-V-O catalyst led to important decreases in isobutene selectivity, to the benefit of cracking products and carbon oxides (except Zn).

Figure 2 shows the catalytic performance of Mo-V-O and Mo-V-M-O systems in the oxidative dehydrogenation of isobutane as a function of the reaction temperature. As expected, the conversion of isobutane increased with increasing reaction temperature for all catalysts. On the Mo-V-O catalyst the conversion of isobutane was lower than that on Mo-V-M-O catalytic systems, in all the temperature range studied. The order of activity was Mo-V-Sb-O > Mo-V-Ta-O > Mo-V-Ni-O > Mo-V-Cu-O > Mo-V-Zn-O > Mo-V-O, except at 550°C when Mo-V-Ni-O system passed in the second position.

The higher activity of Mo-V-Sb-O, Mo-V-Ta-O and Mo-V-Ni-O systems could be explained by the presence of Sb_2O_5, $TaVO_5$ and $NiMoO_4$ phase, respectively, which are active for the activation of isobutane.

The selectivity to isobutene decreased with increasing temperature over Mo-V-O and Mo-V-Zn-O and for the others catalysts the selectivity increased with increasing temperature up to 500°C, then decreased. The increase of the selectivity with increasing temperature was also observed by Pless et al.[18] in the oxidative dehydrogenation of propane at temperatures higher than 400°C and was related to the complete depletion of O_2 from the reactant stream: when depletion of O_2 in the reactant stream occurs and as the temperature increases, a more efficient utilization of oxygen is realized leading to an increase in selectivity. In our case, the oxygen is far from a complete depletion which means that other factors must also be considered for explaining this phenomenon. At higher temperature the selectivities in isobutene decreased to the benefit of those in cracking products which were formed by endothermic parallel reactions and CO_x formed by overoxidation of intermediate products.

Table 2

Oxidative conversion of isobutane on Mo-V-O and Mo-V-M-O (M= Ni, Cu, Zn, Sb, Ta) systems.
Reaction conditions: T = 450°C, VHSV = 2000 h^{-1}, molar ratio isobutane/oxygen = 1

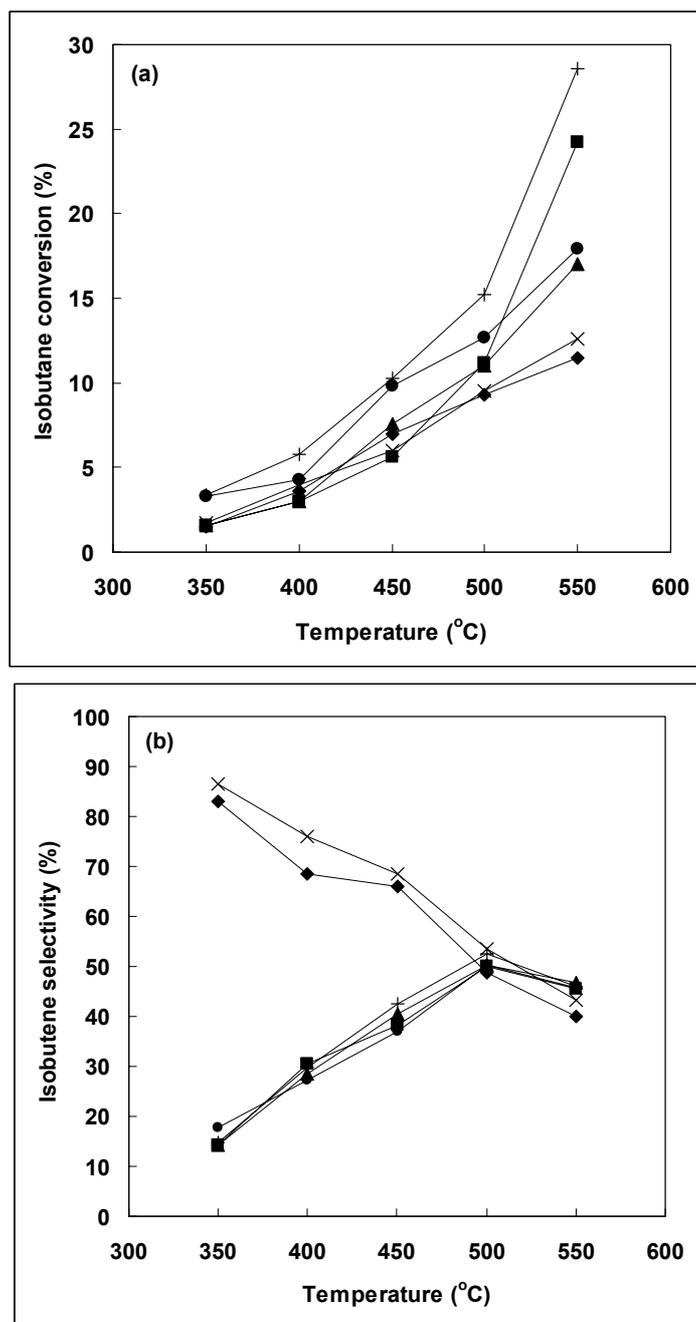| Catalyst	Isobutane conversion (%)	Selectivity (%)			Isobutene yield (%)
		i-C$_4$H$_8$	Cracking products	CO$_x$	
Mo-V-O	2.0	68.2	-	31.8	1.4
Mo-V-Ni-O	5.6	46.0	7.3	46.7	2.6
Mo-V-Cu-O	4.7	47.3	8.6	44.1	2.2
Mo-V-Zn-O	4.9	69.5	2.3	28.2	3.4
Mo-V-Sb-O	6.7	50.2	4.3	45.4	3.4
Mo-V-Ta-O	6.7	39.2	2.8	58.0	2.6

Fig. 2 – Variation of the isobutane conversion (a) and isobutene selectivity (b) with the reaction temperature over Mo-V-O and Mo-V-M-O (M = Ni, Cu, Zn, Sb, Ta) catalysts (VHSV = 1500 h^{-1}, i-C$_4$H$_{10}$:O$_2$ molar ratio = 1). ♦ – Mo-V-O, ■ – Mo-V-Ni-O, ▲ – Mo-V-Cu-O, x – Mo-V-Zn-O, + – Mo-V-Sb-O, ● – Mo-V-Ta-O.

A summary of the gas phase data from the isobutane ODH experiments, with the isobutene selectivity at isoconversion, is presented in Table 3. The main products obtained during the catalytic testing were isobutene, CO and CO_2. Ocasionally minor amounts of cracking products and liquid oxygenated products (methacrolein, acetic acid, acetone and unknowns) were detected. Significant differences in the conversions and selectivities exist between the catalysts.

Table 3

Catalytic performances of Mo-V-O and Mo-V-M-O (M= Ni, Cu, Zn, Sb, Ta) systems at isoconversion (5 % and 10 %) and for the reaction at 550°C.

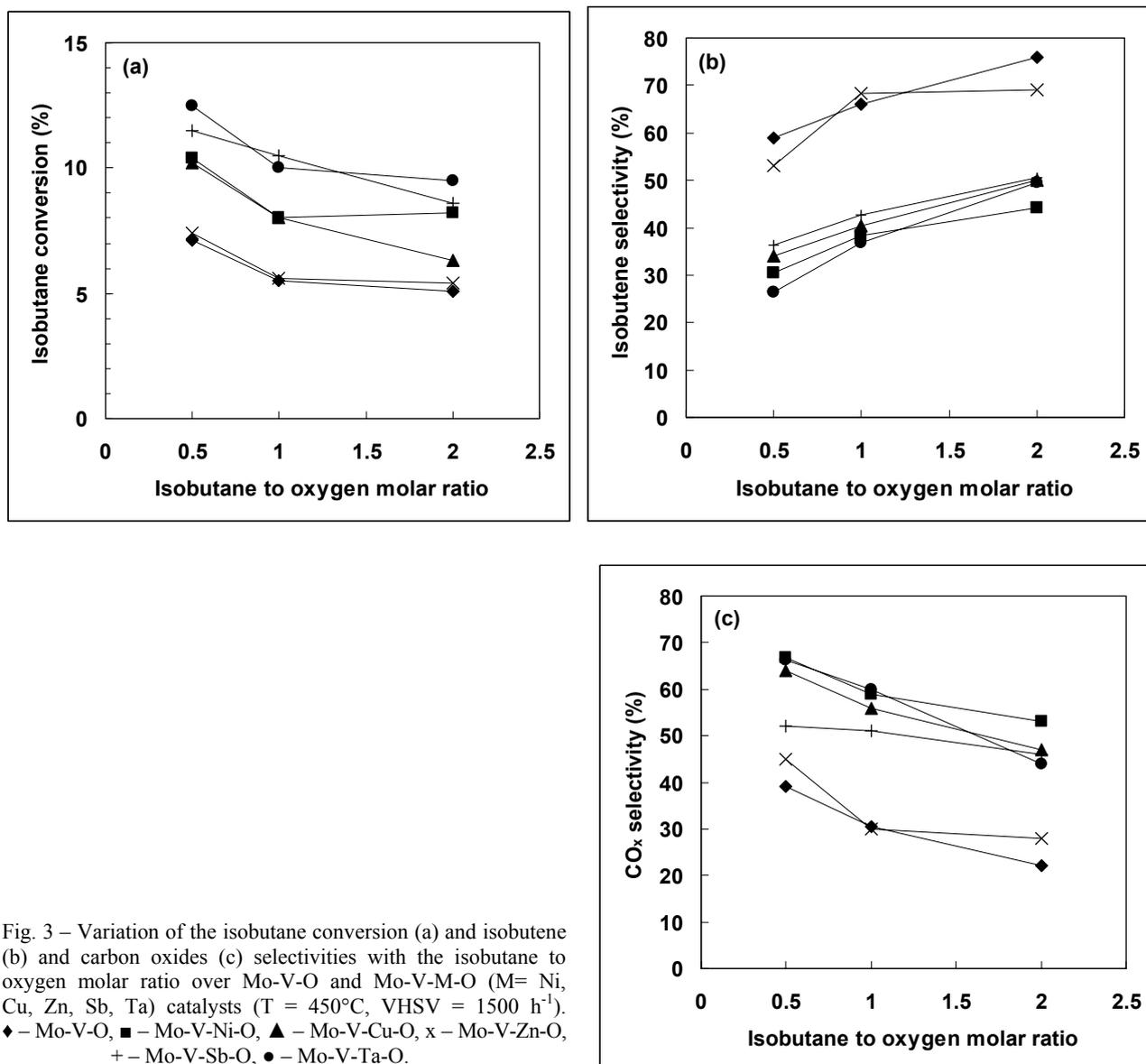| Catalysts	Mass tested (g)	5 % conversion		10 % conversion		Reaction temperature 550°C	
		Selectivity (%)	Temp. (°C)	Selectivity (%)	Temp. (°C)	Conversion (%)	Selectivity (%)
Mo-V-O	1.7	48.0	500	46.0	535	11.5	40.0
Mo-V-Ni-O	2.0	37.0	435	40.0	485	24.2	45.4
Mo-V-Cu-O	2.9	38.0	435	42.0	480	26.6	46.8
Mo-V-Zn-O	2.8	52.0	470	48.0	520	12.6	43.3
Mo-V-Sb-O	2.2	29.4	390	45.0	445	28.6	46.1
Mo-V-Ta-O	2.2	25.0	420	36.2	455	17.9	45.7

Fig. 3 – Variation of the isobutane conversion (a) and isobutene (b) and carbon oxides (c) selectivities with the isobutane to oxygen molar ratio over Mo-V-O and Mo-V-M-O (M= Ni, Cu, Zn, Sb, Ta) catalysts (T = 450°C, VHSV = 1500 h^{-1}). ♦ – Mo-V-O, ■ – Mo-V-Ni-O, ▲ – Mo-V-Cu-O, x – Mo-V-Zn-O, + – Mo-V-Sb-O, ● – Mo-V-Ta-O.

A significant improvement in the conversion of Mo-V-O catalyst was observed at addition of third component into the structure, for the reaction at the same temperature (550°C), the most active being Mo-V-Sb-O and Mo-V-Cu-O catalysts. On the other hand, the Mo-V-O catalyst reached 10 % of conversion at 535°C while the other catalysts reached the same conversion at lower temperatures (the lowest temperature, 445°C, corresponds to Mo-V-Sb-O catalyst).

Comparing the isobutene selectivities at isoconversion for all the catalysts prepared in this research it can be seen that, for both conversions chose (5 % and 10 %), the Mo-V-Zn-O catalyst has the highest selectivity. At 10 % conversion the selectivity is lower than at 5 % for Mo-V-O and Mo-V-Zn-O catalysts, while for the other catalysts is higher. At identical conversion, the catalysts which contain the molibdate phases were more selective than those containing vanadate phases.

The role played by the oxygen partial pressure on the activity and selectivity is shown in Figure 3. There are no significant differences between the catalysts behavior with respect to the isobutane to oxygen molar ratio. The isobutane conversion decreased, for all the catalysts, when the oxygen partial pressure in the feed was decreased (Fig. 3.a). At the same time, a low oxygen partial pressure allows improving the selectivity to isobutene (Fig. 3.b) probably due to the decrease in the degradation of the dehydrogenation product

formed. This is supported by the fact that CO_x selectivity decreased by decreasing the oxygen partial pressure in the feed (Fig. 3.c). These results are explained by the decrease of the available oxygen related to the increase in the isobutane to oxygen molar ratio. When the amount of oxygen was higher (for low isobutane to oxygen molar ratios), the excess oxygen could oxidize the hydrocarbon species adsorbed on the catalyst surface to overoxidation products, such as CO and CO_2 and, consequently, the selectivity for isobutene was lower.

EXPERIMENTAL

a) Catalysts preparation and characterization

Six catalysts, Mo-V-O and Mo-V-M-O (M= Ni, Cu, Zn, Sb, Ta), have been obtained by solid-solid reactions. Mo-V-O catalyst was prepared using $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and NH_4VO_3 as starting materials. The two components were mixed and water was added in order to obtain a paste. Mo-V-M-O catalysts were prepared under the same conditions using $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, NH_4VO_3 and $Ni(NO_3)_2\cdot6H_2O$, $Zn(CH_3COO)_2\cdot2H_2O$, Sb_2O_3, $Cu(CH_3COO)_2\cdot H_2O$ or Ta_2O_5 as starting materials.

The same method of thermal treatment was used, for all catalysts, knowing that the calcination temperature influence the phase composition of catalysts.[19-21] The resulting mixture was dried at 120°C for 15 h, followed by grinding into a fine powder, calcination at 200°C for 2 h, 400°C for 2 h and finally at 600°C for 4 h in air. The chemical compositions of the catalysts and the symbols used are shown in Table 4.

Table 4

The calculated catalyst compositions and the symbols used.

Catalyst	Calculated catalyst composition
Mo-V-O	10 % V_2O_5 – 90 % MoO_3
Mo-V-Ni-O	10 % V_2O_5 – 80 % MoO_3 – 10 % NiO
Mo-V-Cu-O	10 % V_2O_5 – 80 % MoO_3 – 10 % CuO
Mo-V-Zn-O	10 % V_2O_5 – 80 % MoO_3 – 10 % ZnO
Mo-V-Sb-O	10 % V_2O_5 – 80 % MoO_3 – 10 % Sb_2O_3
Mo-V-Ta-O	10 % V_2O_5 – 80 % MoO_3 – 10 % Ta_2O_5

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D5005 diffractometer and CuK_α radiation. They were recorded with 0,02° (2θ) steps over 3-80⁰ angular range with 1s counting time per step.

The specific surface areas were measured by the BET method using nitrogen adsorbtion.

b) Catalytic activity tests

The oxidative dehydrogenation of isobutane was carried out in a fixed bed quartz tube down-flow reactor (i. d. 15 mm) operated at atmospheric pressure. Quartz chips were placed above and below the catalyst bed to reduce the reactor void volume and to avoid the homogeneous reactions in free space. The temperature of the catalyst bed was monitored by a thermocouple in a coaxial thermowell in its center. The gas

mixture consisting of isobutane and air was fed into the reactor at a volume hourly space velocity (VHSV) in the range of 1000-2500 h^{-1}. The reaction temperature was varied between 350 and 550°C, the isobutane/O_2 molar ratio, between 0.5 and 1, and the catalyst bed volume was always kept to 2 cm^3.

In all studies, the reactor effluent passed through a condenser to remove water and liquid oxygenated products. Gas-phase reactants and products were analyzed with a Thermo Finnigan gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector. Chromatograph separation was accomplished with an alumina column and a CTRI column. The condensate was analyzed with a Thermo Finnigan chromatograph using a DB-5 column and a flame ionization detector. Isobutene, CO and CO_2 were the major products formed under our reaction conditions.

Minor amounts of the liquid oxygenated products, acetic acid, methacrolein and unknowns were detected. Conversion of isobutane and olefin selectivity is expressed as mol % on a carbon atom basis.

CONCLUSION

All the multiphase Mo-V-M-O catalytic systems tested were effective for the oxidative dehydrogenation of isobutane. The addition of Ni, Zn, Cu, Sb and Ta improved the activity of Mo-V-O catalyst but decreased the isobutene selectivity. However, the overall yield was in all cases improved. Mo-V-Sb-O and Mo-V-Ta-O catalysts showed the best catalytic properties in all the range of conditions used. In all cases, the conversion of isobutane was increased by increasing the reaction temperature and the oxygen partial pressure in the feed, but the isobutene selectivity decreased to the benefit of the cracking products and carbon oxides.

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