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Synthesis and characterization of nanostructured $Co_{1-x}Ni_xMoO_4$ catalysts active in the ODH of propane

Jaume Vila[1]*, Fernando Sapiña[1], Eduardo Martínez[1], Vicente Cortés[2], Jerzy Podobinski[2]

1. Institut de Ciència dels Materials, Universitat de València

2. Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas (CSIC), Madrid

Resum

La reacció de deshidrogenació oxidativa de propà (ODH) és altament prometedora quant a l'obtenció de propé, comparada amb els mètodes industrials empleats en l'actualitat, però presenta una sèrie d'inconvenients difícilment superables. En el present treball s'aborda la síntesi, caracterització, i estudi del comportament en la ODH de propà de molibdats mixts de Co i Ni, obtinguts per calcinació a baixes temperatures de precursors liofilitzats.

Paraules clau: deshidrogenació oxidative · propà · propè · molibdats mixts de cobalt i níquel · liofilització

Abstract

The oxidative dehydrogenation (ODH) of propane is a highly promising reaction for the obtaining of propene, compared to the industrial methods currently used. However, it presents a series of disadvantages that are difficult to overcome. In this work we study the synthesis, characterization and catalytic behavior of mixed Ni/Co molybdates in the ODH of propane. The molybdates are obtained by calcination of freeze-dried precursors at low temperatures.

Keywords: oxidative dehydrogenation · propane · propene · mixed cobalt-nickel molybdates · freeze-drying

1. Introduction

Light olefins, and especially ethene and propene, constitute basic raw materials for the industry based on polymers and other petrochemical products.

At present, demand for these olefins and their derivatives is steadily increasing and rapidly approaching production capacity [1,2,3]. Until the 1990s, light olefins were obtained by cracking natural gas or nafta in refineries. The products thus obtained must be separated and purified before treatment, and the supply and demand of the different products rarely balance. This situation reveals the necessity to cover the increasing demand for olefins by means of direct production, using selective processes.

At present, there are several industrial processes for synthesizing light olefins by dehydrogenation (DH) of paraffins. The most common products are propene, butene, butadiene, isobutene and isoprene [1]. The main advantage of these commercial processes is that H_2 is a by-product. The main disadvantages are:

A. Thermodynamic limitations to the conversion of paraffin. These reactions are very endothermic, and require the input of a great amount of heat, thus making the process inefficient from both the energetic and economic points of view.
B. Parallel reactions, such as thermal cracking, due to the high temperatures required (550 – 650 ºC) that diminish selectivity.
C. Coke formation in the catalyst, which decreases its activity. The catalyst requires frequent regeneration to remove the coke.

Different means of overcoming these problems include:

A. The development of more selective, stable, environmentally friendly and low-cost catalysts, in order to improve the DH technologies.
B. Coupling DH with hydrogen oxidation in order to provide (within the catalytic bed) the heat necessary to move the balance towards the formation of the target products. In addition, oxygen can contribute to the regeneration of the catalysts through coke combustion.
C. The development of oxidative DH (ODH) processes, which overcome the thermodynamic limitations, operate at lower temperatures in exothermic reactions and avoid the necessity to frequently regenerate the catalyst [1].
D. Performing the DH and the ODH processes with membranes, to obtain greater conversions and selectivities at lower temperatures, and avoid the separation of products.

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*Author for correspondence: Jaume Vila. Institut de Ciència dels Materials de la Universitat de València. P.O. Box 22085, E-46071 València, Spain. Tel. +34 963543266. Fax: +34 963543633. E-mail: Jaume.Vila@uv.es

In the present work we study the ODH of propane to obtain propene. For an alkane with a general formula C_nH_{2n+2}, the reaction is:

$$C_nH_{2n+2} + \frac{1}{2}O_2 \rightarrow C_nH_{2n} + H_2O$$

This reaction can take place using catalysts that are not active in DH, in which case, the desorption of hydrogen to the gas phase does not take place.

Although ODH is more promising than simple DH, allowing the total conversion of the hydrocarbon at lower temperatures, it has an important limitation: the formation—due to the presence of oxygen in the reaction environment—of secondary products that are not necessarily economically beneficial. Because the reactivity of the alkene is greater than the reactivity of the original alkane, the ODH of alkanes normally produces a large amount of carbon oxides, which entails a decrease in the selectivity to alkenes. The products of partial oxidation of the alkane to aldehydes or acids may also be obtained. Therefore, the main objective in this area is to develop catalysts able to activate only the C-H bonds of the alkane molecules in a flow of oxygen at the required temperature, and also able to reduce the residence time of the resulting alkene in the catalytic bed, thus preventing its total combustion [1,2].

The product distribution observed in the ODH of light alkanes does not only depend on the catalyst, it also depends on the nature of the alkane. Thus, the selectivity of the ODH tends to increase with the number of carbon atoms in the alkane molecule [1,4]. This is related to the ability of oxidation of linear alkanes, which increases in the same way, due to the decrease in the weakest C – H bond energy [1]. The limiting step of the reaction is thus the breakage of the weakest C-H bond. This can be heterolitic, with abstraction of a hydride and formation of a carbocation, or homolitic, with the formation of a desorbed alkyl radical. The former mechanism is believed to act in the ODH of propane and butane on acid catalysts [1,2], whereas homolitic breakage of C-H bonds is more probable for catalysts with redox properties [4]. A third type of activation could occur: the abstraction of one proton from the alkane to form a carbanionic intermediate that is later transformed into a radical that could finally be dehydrogenated [1]. This last heterolitic activation would require the presence of strong basic sites on the surface of the catalyst.

2. Catalytic systems for the ODH of light alkanes

Many catalytic systems have been proposed as activators of alkanes, but none of them is able to completely preserve the olefin from oxidation. According to Cavani and Triffirò [1], the best catalysts must:

- be heterogeneous systems able to activate propane at relatively elevated temperatures.
- decompose the desorbed radical homogenously to propene. In fact, low temperatures favor the later oxidation of propene on the surface of the catalyst, because the energy of activation for gaseous DH is greater than that of heterogeneous combustion.

A general characteristic of many catalytic systems is that the selectivity to propene decreases with the increase in the conversion of propane [1]. This is probably due to the fact that propene has labile allyl hydrogen atoms, which act as centers for later oxidation. The catalytic systems proposed for the ODH of propane include from superbasic oxides, such as Li/MgO, to very acid zeolites. Most of the catalysts described in the literature are based on vanadium oxides [2,3,4,7,8,9]. The most successful to date are the V/Nb/O, V-silicate, V/Mg/O and Co-Ni/Mo/O [1] systems.

2.1. Co/Ni molybdates: characteristics

The ABO_4 molybdates, where A = Mn, Fe, Co, Ni or Zn and B = Mo, can present three different monoclinic structures. At high pressures (higher than 60 kbar), they adopt the relatively dense $NiWO_4$-type (*wolframite*) structure, with both cation types occupying a portion of octahedral holes in a hexagonal *pseudo* closest-packing of oxygen atoms [2]. The other two more open structures, which are the relevant ones in this work, are usually referred to as α-$MnMoO_4$ type [2] and α-$CoMoO_4$ type [2] structures. Both of them can be described on the basis of a defective cubic closest-packing of oxygen atoms, with one vacant per each nine anionic positions. They differ in the coordination environment of molybdenum atoms. These show a distorted tetrahedral coordination in the α-$MnMoO_4$ type structure, while they are octahedrally coordinated in the relatively denser α-$CoMoO_4$ type structure. On the other hand, the partner cations (like Mn or Co) have approximately octahedral coordination in both structural types.

Our discussion centers on the cobalt and nickel molybdates. We will denominate α *phase* both α-$CoMoO_4$ (card JCPDS 25-1434) and α-$NiMoO_4$ (JCPDS card 33-0948) which present the same α-$CoMoO_4$-type structure. We will call β *phase* both β-$CoMoO_4$ (JCPDS card 21-0868) and β-$NiMoO_4$ (JCPDS card 45-0142) which display the α-$MnMoO_4$-type structure.

The low-temperature stable structure for cobalt molybdate is the β phase. The β phase undergoes a polymorphic transformation, $\beta \rightarrow \alpha$, at temperatures above 500ºC. This α phase can be partially stabilized at room temperature by tempering, which results in a mixture of the two phases. The relative abundance of the two phases depends on the experimental conditions (preparation route, thermal treatment, etc.).

The $\beta \rightarrow \alpha$ transformation can also be induced by applying slight pressure to the sample. An instantaneous change in color is observed: from purple (characteristic of the β phase) to dark green (characteristic of the α phase). The transformation can be confirmed by means of X-ray diffraction. In spite of the pronounced change in color, mixtures of the phases are observed in the green product. The relative ease with which the process can be carried out seems to indicate that the difference in energy between the positions that the molybdenum atoms occupies in the different structures - tetrahedral partially distorted in the β phase as opposed to octahedral in the α phase- is very small. Some authors [2] suggest that the $\beta \rightarrow \alpha$

transition is an intermediate step towards more dense structures, with the $NiWO_4$-type structure as the hypothetical end phase. In studies conducted at high temperatures, decomposition of the cobalt molybdate is observed at around 760ºC, with MoO_3 segregation and sublimation.

In the nickel molybdate, the stable phase at low temperature is the α phase, in contrast to Co. An $\alpha \rightarrow \beta$ polymorphic transformation is observed with the increase in temperature, and the β phase cannot subsequently be stabilized at room temperature. The temperatures of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions differ according to the literature. According to Rodriguez et al. [2,3], the $\alpha \rightarrow \beta$ transition takes place between 500 and 670 ºC, following a kinetic of first order, and is highly dependent on the heating rate. The $\beta \rightarrow \alpha$ transition does not follow the same kinetic, and is fundamentally affected by the final temperature of the process. This latter transformation, according to Mazzocchia et al. [2], takes place at around 180ºC and, thus, according to these authors, we can only obtain the α phase at room temperature.

However, it has been observed that, in the presence of a small excess of NiO, the β phase can be stabilized at room temperature [2]. It seems that the $\beta \rightarrow \alpha$ transformation upon cooling is impeded by the presence of the excess NiO. In spite of, this result has not been achieved by our research group [2]. Furthermore, catalytic properties of products obtained by this route are not those exhibited by stoichiometric ones [2].

2.2. The Co-Ni-Mo system in the ODH of light alkanes

When comparing the activity of different transition metal molybdates in the ODH of propane, the greatest conversions are obtained with $NiMoO_4$ and $Co_{0.5}Ni_{0.5}MoO_4$, whereas the best selectivity towards propene is obtained when working with cobalt molybdate [2], at the cost of limited conversion.

Recent work that studies the activity of molybdates in the ODH of propane [2,3,4] has centered on cobalt and/or nickel molybdates. The former has been found to work exclusively in the β phase (which is stable at room temperature) independently of the treatment history of the sample. The α phase has not caused as much interest because, at the reaction temperatures (always higher than 350°C) the $\alpha \rightarrow \beta$ transition takes place. This is why efforts to stabilize the α phase at room temperature are useless. In the case of the pure nickel molybdate, however, most studies take place using the α phase, because at the working temperatures it is not possible to stabilize the β phase. Nevertheless, researchers who have obtained the β phase - supporting it on SiO_2 or working with an excess of nickel [2,25,28] - point out that its activity is of the order of three times higher than that of the α phase. This may be due to the tetrahedral nature of molybdenum in the β phase [2] (in the α phase it is octahedral). This claim requires certain caution because the conditions in which the process is carried out (especially the feeding of the reactor, which will determine the oxidizing or reducing character of the working atmosphere) can strongly influence the results. What these studies make clear is that the catalytic activity of the α and β phases of $NiMoO_4$ are significantly different.

Measurements of the electrical conductivity of the molybdates after they have been used in the ODH of propane reveal the presence of anionic vacancies. This suggests that propene forms through the reaction of the propane with surface O^{2-} anions [30]. The difference in the selectivity to propene can be attributed to the reactivity of the O^{2-} anions present in the two phases, which varies according to the coordination of the molybdenum at the catalytic active site. Both phases are n-type semiconductors, that is, the conductivity is proportional to the concentration of charge transporters. However, if there is an excess of Ni or Mo in the structure, the conductivity is p-type, due to electronic defects [2].

In V-based catalysts it is assumed that oxygen bridges, V-O-V or V-O-M, are responsible for the selective ODH [14], whereas the electrophilic vanadyl oxygen (V=O), is considered to be responsible for the formation of oxygenated products. Owen and Kung [15], on the one hand, and Michalakos et al. [8], on the other, have postulated that selectivity to alkenes is determined by the ease of elimination of the lattice oxygen, probably an M-O-V oxygen bridge. In the same way, the addition of Co and/or Ni to MoO_3 causes an increase in the selectivity to propene in the ODH of propane, decreasing the total activity, for which MoO_3 (Mo=O bond) [31] is responsible.

Catalytic tests performed with the Co and Ni molybdates using temperatures between 450 and 550°C lead to values of conversion and selectivity of around 15% and 73% respectively. These results vary in the literature consulted, due to the different natures of the materials studied, determined mainly by the preparative route used in each case [2,3,24,26,27,30]. Grasselli et al. [26] observed that, for materials from the $Co_{1-x}Ni_XMoO_4$ series prepared by coprecipitation, activity in propane ODH diminishes with the increase in cobalt content, although the selectivity to propene improves.

Numerous redox studies have been carried out on these phases [2,28] and show that $NiMoO_4$ can be reduced at lower temperatures than $CoMoO_4$. In addition, Ni/Co molybdates react more readily with H_2 and are more easily reduced than pure Mo oxides. The order is: $MoO_2 < MoO_3 < CoMoO_4 < NiMoO_4$ [35]. This confirms the greater activity of $NiMoO_4$, since it has been demonstrated that the catalytic activity of these systems is mainly determined by the reducibility of the surface of the catalyst: an easily reducible oxide is very active, but less selective [2]. However, this means that $NiMoO_4$ needs a greater excess of oxygen to maintain its catalytic activity stable, and so the productivity of $CoMoO_4$ may be greater than that of $NiMoO_4$ for a constant residence time [2].

Finally, it must be stressed that the basic character of the surface of the catalyst is important in facilitating desorption, and that the basicity of the surface of the catalyst influences its activity in the ODH of propane [33]. Weak acid sites favor ODH at high reaction temperatures -desorption of the propene obtained- whereas strong acid sites cause a decrease in the propene selectivity -propene is strongly adsorbed and can be oxidized to carbon oxides. However, superficial oxygen also determines the activity and selectivity to propene in this reaction. If the surface of the catalyst is slightly reduced (a decrease in superficial oxygen) the selectivity to propene is improved until it reaches a constant value.

3. Experimental

3.1. Characterization techniques

We used X-ray diffraction (XRD) to identify the crystalline phases present in our samples. XRD patterns were obtained using an automatic Siemens D-5000 diffractometer and using graphite-monochromated Cu Ka radiation. The morphology of the products was observed using a scanning electron microscope (Hitachi S-4100) operating at an accelerating voltage of 30 kV. All the preparations were covered with a thin film of gold for better image definition. Physisorption measurements were performed with a Micromeritics ASAP 2000 instrument. The BET surface areas of the products obtained at 673 K (t_{hold} 5 h) were determined by nitrogen adsorption at 77 K assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule. Prior to adsorption measurements, the samples were outgassed in a vacuum at 423 K for 18 h.

3.2. Nomenclature and compositions studied

We prepared materials with different compositions, $Co_{1-x}Ni_xMoO_4$, following a synthetic method previously developed [24]. The values of x were, 0.25, 0.5, 0.75 and 1. For the sake of simplicity, the samples of composition x calcined at temperature T (ºC) are named (x, T). Thus, sample x = 0.25 ($Co_{0.75}Ni_{0.25}MoO_4$) calcined at 500ºC is sample (0.25, 500).

3.3. Synthesis

The materials used as reagents were $Co(NO_3)_2\cdot 6H_2O$ (Panreac, 98.0%), $Ni(NO_3)_2\cdot 6H_2O$ (Fluka, 98%), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Panreac, 99.0%).The initial Co-, Ni-, or Mo-containing solutions were prepared by dissolving their respective salts in distilled water. Then they were combined to obtain (Co, Ni)-Mo source solutions having a total cationic concentration of 0.25 M, a total volume of 220 mL, and nominal molar compositions $Co_{1-x}Ni_xMo$ (x = 0.00, 0.25, 0.50, 0.75, 1.00). The masses of the different reagents were adjusted to obtain 6 g of the final products. A small amount of nitric acid was added to the solution after mixture (until pH was approximately 1.15) to ensure long-term stability of the solutions [2]. Droplets of these solutions were flash frozen by projection onto liquid nitrogen and then freeze-dried at a pressure of 1-10 Pa and at a temperature of 228 K in a Telstar Cryodos freeze-dryer. In this way, dried solid precursors were obtained as amorphous (XRD) loose powders.

$Co_{1-x}Ni_xMoO_4$ samples were synthesized by thermal decomposition of the amorphous precursor solids. A sample of the selected precursor (about 0.5 g) was placed in an alumina boat and introduced into the furnace. Several runs were performed under different experimental conditions to determine the appropriate conditions for the preparation of the samples. The precursor powder was heated at 5 K·min^{-1} to a final temperature T_f (T_f = 673 and 773 K) that was held for a period of time t_{hold} = 5 h under flowing oxygen. Then the solid was cooled, leaving the sample inside the furnace (slow cooling, approximately 2 K min^{-1}). All products were stored in a desiccator over $CaCl_2$.

3.4. Catalyst testing

The catalytic activity of the $Co_{1-x}Ni_xMoO_4$ system in the ODH of propane was studied using a fixed bed microreactor of 10 mm diameter, in the 400-475ºC temperature interval. Helium was chosen as the inert gas for the reaction mixture since its use avoids the presence of the chromatographic peak of nitrogen, which could overlap with the oxygen peak. The reactor was fed with a slightly reducing gas mixture to avoid superoxidation of the product formed:

Propane : Oxygen : Helium = 2 : 4.6 : 93.4

The volumes were regulated using three independent mass flow controllers, so that W/F (see “parameters used in the measurement of activity”), the residence time, expressed as *mass of catalyst · hour/mol of hydrocarbon*, was constant and equal to 70 g·h/mol of propane in all the experiments. The exhaust gases from the reactor were analyzed directly in a Varian 3400 CX gas chromatograph, provided with two columns; one containing a 5-Å molecular sieve, which separates the O_2 and the CO, and the other containing Porapak Q, which separates carbon dioxide (CO_2), propene (C_3H_6) and propane (C_3H_8), in that order. The detector was a thermal conductivity detector (TCD) that analyzes the electrical signal caused by the difference in thermal conductivity between the carrying gas (reference) and products. In all reaction conditions, the mass and carbon balances were within 100 ± 5%.

In propane ODH, the homogenous reaction can contribute at temperatures above 450 ºC, which may distort the results. It is therefore necessary to reduce its potential influence as far as possible. Thus, the empty volume of the reactor was filled with silicon carbide particles, to prevent the gases reacting with each other in the absence of the catalyst. By means of a test in the absence of the catalyst, it was verified that the contribution of the homogenous reaction is negligible in the conditions used in this study. The catalyst was diluted with silicon carbide in proportion 2:1 (SiC: catalyst) to avoid overheating of the catalytic bed. The catalyst particle size was between 0.25 and 0.42 mm, to avoid internal diffusion, and the total flow rate of gases in the reactor was 140 mL/min, to avoid external diffusion.

3.5. Parameters used in the measurement of activity

Total conversion (X_T): defined as the percentage of the molar flow of transformed propane compared to that of the fed propane. It is equivalent to the sum of the yields of all the reaction products:

$$X_T = \frac{(transformed \;\; propane \;\; mols)/h}{(fed \;\; propane \;\; mols)/h} \cdot 100 = \sum_i Y_i$$

Yield of product i (Y_i). The reaction studied is not equimolar and thus, the yield is defined as the quotient of the molar flow of the product and the fed propane, for the ratio of their corresponding carbon atoms:

$$Y_i = \frac{(produced \;\; i\, mols/h) \cdot number \;\; of \;\; carbons \;\; of \;\; i}{(fed \;\; propane \;\; mols/h) \cdot 3} \cdot 100$$

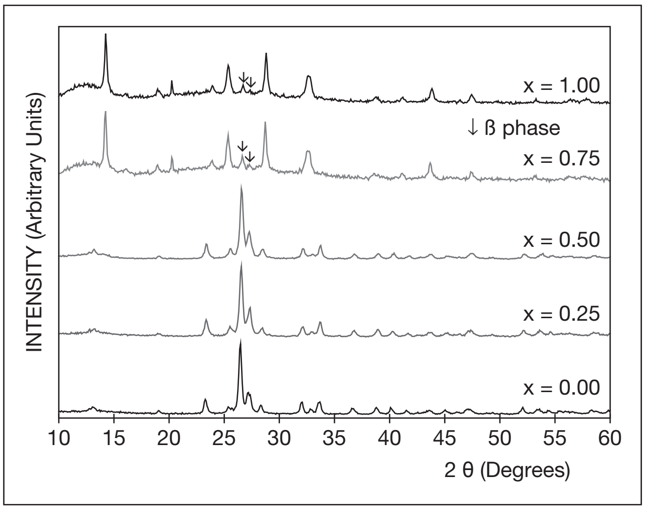

Figure 1. XR patterns of samples calcined at 400ºC.

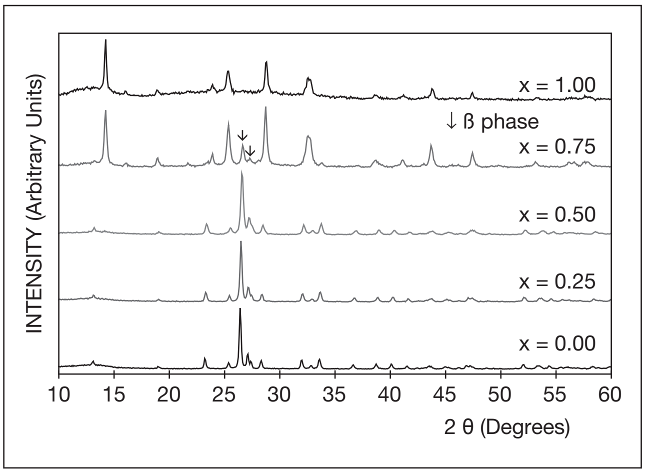

Figure 2. XR patterns of samples calcined at 500ºC.

Selectivity to product i (S_i): defined as the proportion of the molar flow of a product i compared to the total product flow (equivalent to the total flow of transformed propane). The selectivity also takes account of the number of carbon atoms:

$$S_i = \frac{(produced\ \ i\,mols\,/h)\cdot number\ \ of\ carbons\ \ of\ i}{(transformed\ \ \ propane\ \ mols\,/h)\cdot 3}\cdot 100$$

Residence time (W/F): defined as the quotient of the mass catalyst and the molar flow of propane in the feed:

$$\frac{W}{F} = \frac{catalyst\ \ mass}{fed\ propane\ \ mols\,/h} \qquad \left[\frac{g\cdot h}{mol\ of\ C_3H_8}\right]$$

3.6. Result of the catalytic tests

The catalytic tests were carried out on samples of composition $Co_{1-x}Ni_xMoO_4$, where x = 0, 0.25, 0.5, 0.75 and 1, prepared at 400 and 500ºC. Thus, the influence of the temperature of preparation and of the stoichiometry of the catalysts was evaluated.

The following table shows the catalysts used in each test, their BET areas and the residence times of propane in the reactor in the corresponding experiment. The BET area of the samples increases with the content of Ni and diminishes with the temperature of calcination. It is, furthermore, greater than the BET area of materials obtained by other routes, such as coprecipitation [24].

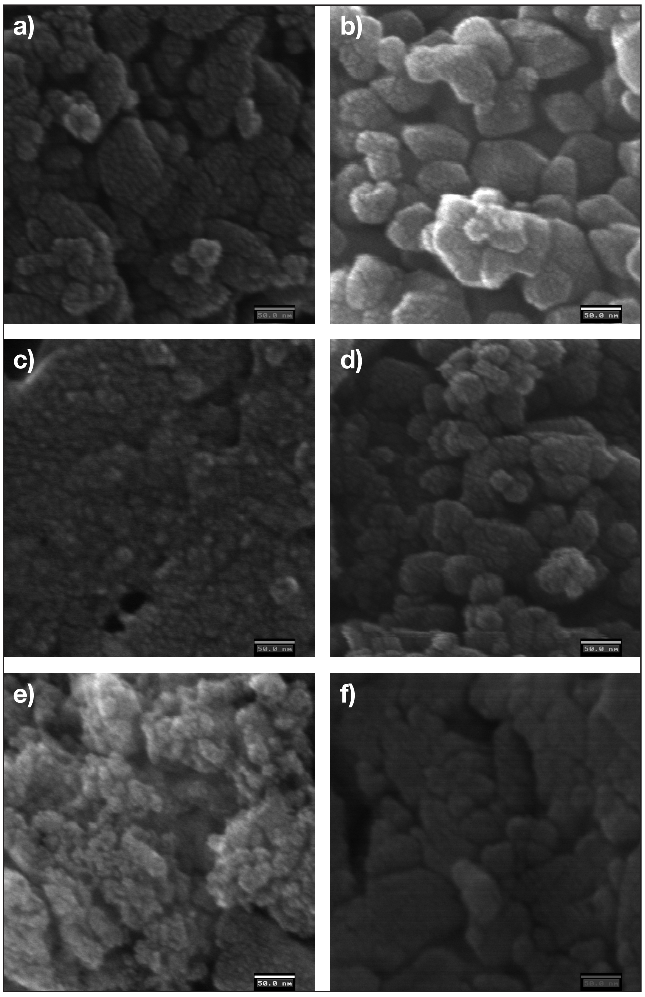

Figure 3. Microstructure of some samples obtained. a, c, e: x = 0, 0.5 and 1, calcined at 400ºC; b, d, f: x = 0, 0.5 and 1, calcined at 500ºC. Scale bars correspond to 50 nm.

XRD patterns show that, up to x = 0.5, the β phase is the only one present. However, if x ≥ 0.75, a mixture of phases is observed, with the α phase dominating, except for (1, 500), in which only the α phase is detected. (Figures 1 and 2).

The SEM images, Figure 3, show how, independently of the composition of the samples, the microstructure of the materials is constituted by aggregates of variable sizes of nanoparticles with typical dimensions around 10 nm. [24].

3.7. Catalytic activity

The catalytic activity of the two series of samples is showed in figures 4 and 5. The values of propane conversion obtained with the catalysts calcined at 400ºC (Figure 4) indicate that, in general, conversion increases with Ni content, but there isn't any sharp trend. In the catalysts calcined to 500ºC (Figure 5), conversion increases progressively with the Ni content.The sample (0.5, 500) underwent deactivation and therefore is not mentioned in the results. Causes are under study.

In Figure 6 we can observe that the selectivity to propene of samples (0, 400) and (0.25, 400) are lower than the selectivity

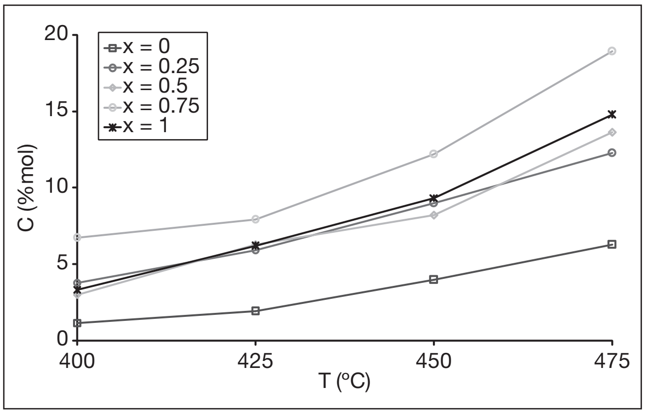

Figure 4. Total conversion, catalysts calcined at 400ºC.

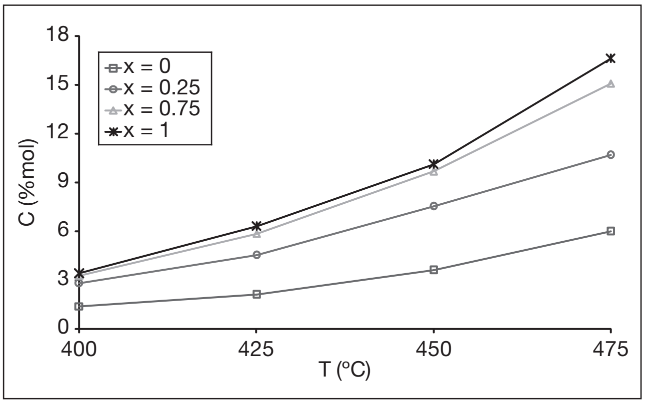

Figure 5. Total conversion, catalysts calcined at 500ºC.

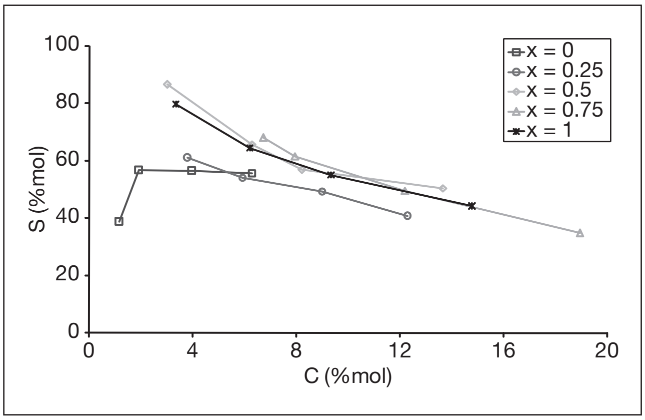

Figure 6. Selectivity to propene, catalysts calcined at 400ºC.

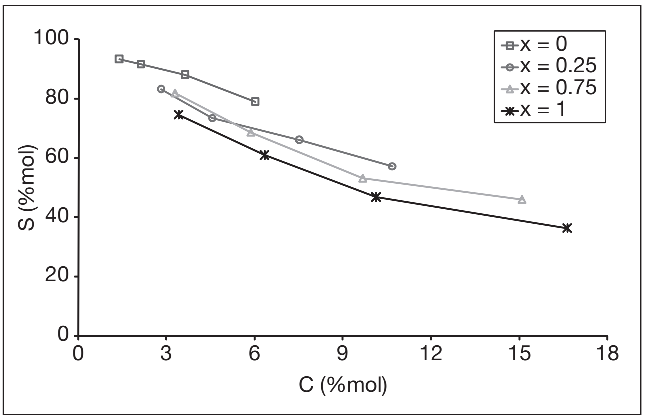

Figure 7. Selectivity to propene, catalysts calcined at 500ºC.

of samples with high Ni contents (x ≥ 0.5). The selectivity to propene increases with the temperature of calcination of the catalysts, and decreases with increasing Ni content (Figure 7).

These results seem to indicate that the Co catalysts are more sensitive to the calcination temperature than the Ni catalysts. The difference in behavior could be attributed to the lower reducibility of the Mo (VI) in the Co-rich samples, which contain more superficial oxygen than the Ni-rich samples when both are calcined at 400ºC. The catalytic activities are in agreement with the results reported in the literature: propane conversion increases and propene selectivity decreases with increasing Ni content. This may be due to the superposition of two factors: the greater reducibility of the Mo (VI) conferred by Ni, and the greater acidity of Ni compared to Co.

Table 1. Catalysts used in ODH of propane.

Catalyst	*BET area (m2/g)*	*W/F (g·h/mol)*
(0, 400)	16.91	70.5
(0.25, 400)	20.30	70.5
(0.5, 400)	30.11	70.5
(0.75, 400)	40.11	70.5
(1, 400)	45.18	70.9
(0, 500)	12.12	70.4
(0.25, 500)	12.75	70.4
(0.5, 500)	17.23	70.4
(0.75, 500)	32.15	70.4
(1, 500)	30.95	70.5

4. Conclusions

The use of amorphous precursors of high reactivity and chemical homogeneity, prepared by freeze-drying, allowed us to obtain nanostructured materials at low temperatures and in a single step. These materials are solid solutions throughout the interval of composition studied, in which the Co and Ni ions are homogenously distributed. The materials obtained by freeze-drying present BET areas greater than materials with the same composition obtained by other routes.

The catalytic activity of Co-rich samples differs when they are calcined at 400ºC or at 500ºC, whereas the activity of Ni-rich samples does not vary substantially with the calcination temperature. The samples with x=0 or 0.25 have to be calcined at higher temperature (500ºC) to acquire optimal catalytic properties.

The conversion of propane in the samples obtained increases with the Ni content, whereas the selectivity to propene decreases, in agreement with the literature. This is attributed to the greater reducibility that Ni confers to Mo (VI), as well as to its greater acidity, which makes the desorption of propene difficult, and favors its oxidation.

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About de authors

***Jaume Vila** (1979) got the degree in Chemistry at the* Universitat de València *in 2002. He is working since 2004 in the Laboratory of Nanomaterials in the Institute of Materials Science of the* Universitat de València*, where, with the Institute of Catalysis and Petroleum Chemistry of the* Universidad Autónoma de Madrid*, he is carrying out his PhD studies.*

***Fernando Sapiña** (1964), PhD in Chemistry, Professor of the Department of Inorganic Chemistry and researcher of the Institute of Materials Science of the* Universitat de València*. His investigation is oriented to the design of routes of synthesis of materials with controlled composition, microstructure and properties, and their characterizaion. He is author of the books* "¿Un futuro sostenible?" *and* "El reto energetic"*, published by* Publicacions de la Universitat de València *and, in València, by* Edicions Bromera*.*

***Eduardo Martínez** teachs inorganic and materials chemistry at the* Universitat de València *since 1976. Nowadays leads the Laboratory of Nanomaterials in the Materials Science Institute of the* Universitat de València*, and his research activity is focused on the synthesis and characterization of inorganic nanostructured materials, inorganic and hybrid polymers with technological applications.*

***Vicente Cortés** (1954), PhD. in Chemistry and Research Scientist of the CSIC in the Institute of Catalisys and Petroleumchemistry, is nowadays Member of the "International Scientific Council" (international advisory scientific committee) of the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Cracovia (Poland), and Secretary of the International Committee of the World Congresses on Oxidation Catalysis. Dedicated to the research and development of catalysts and reactions for oxidation, he is author of more than 80 works (including a review with 340 appointments) in international journals and more than 50 communications to conferences, editor of a book and three special volumes of Catalysis Today.*

***Jerzy Podobinsky**, PhD in Chemistry, is member of the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences. Nowadays is beneficiary of a Marie Curie research fellowship`in the Institute of Catalysis and Petroleumchemistry of Madrid.*