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Molybdenum–vanadium supported on mesoporous alumina catalysts for the oxidative dehydrogenation of ethane

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Abstract

Vanadium and/or molybdenum oxides supported on mesoporous alumina have been prepared by a ''wet'' impregnation method, characterized (by using several physico-chemical techniques TPR, DR-UV–vis, Raman spectroscopies) and tested in the oxidative dehydrogenation (ODH) of ethane. For comparison Mo–V-mixed oxides supported on γ-Al_2O_3 have also been studied. The characterization results indicate that the main vanadium species in both Mo-free and Mo-containing V-based samples present low aggregation and coordination, whereas molybdenum is present as monomeric or polymeric tetrahedral molybdenum species. Interestingly, no apparent interaction between molybdenum and vanadia takes place. The catalytic results show that V-containing catalysts are ca. four times more active than pure Mo-catalyst, whereas Mo–V-containing catalysts resulted to be the most selective ones in the ODH of ethane to ethylene, indicating that a synergetic effect between Mo and V takes place. In all cases, catalysts supported on mesoporous alumina were more active and selective in the ODH of ethane than the corresponding catalysts supported on γ-Al_2O_3.

Keywords: Ethane oxidation; Supported Mo–V–O catalysts; Mesoporous alumina as support; Catalyst characterization (diffuse reflectance, FT-Raman, XRD, TPR)

1. Introduction

The lower price of light alkanes in comparison to the corresponding olefins makes the dehydrogenation of lower alkanes an attractive industrial process. However, simple dehydrogenation to yield the olefin plus hydrogen present thermodynamic limitations and deactivation due to the formation of coke. In contrast, oxidative dehydrogenation, ODH, feeding oxygen as well as the alkane, overcomes these problems since coke is not formed (but carbon oxides) and yields to olefin of ~100% can be theoretically obtained even at room temperature.

Al_2O_3-supported vanadia catalysts have been shown as one of the most active catalytic systems in the ODH of lower alkanes, especially ethane [1–4], while molybdenum supported on alumina materials have been reported to be relatively active for the ODH reactions [5–7]. In both cases the most selective catalysts present vanadium or molybdenum species with low aggregation and/or coordination (such as isolated tetrahedral vanadium species).

On the other hand, the ODH of short chain alkanes on V-containing catalysts has been demonstrated to depend on the nature of the support. Thus, basic supports seem to be preferable if *n*-butane or propane is the alkane fed, whereas acid supports are more appropriate in the obtaining of ethylene from ethane [8,9]. Thus, the relatively high acid character of alumina makes more interesting its use in ODH of ethane rather than in propane or *n*-butane.

In all cases, γ-Al_2O_3 (that presents a surface area of around 100–200 m^2/g) was mainly used [1–7]. However, a better metal dispersion can be achieved by using a high surface area alumina, as it has recently been reported by our group [10]. A mesoporous alumina was used as support for vanadium oxide in the ODH of ethane, obtaining high productivity to ethylene as a consequence of a remarkable dispersion of vanadium on the surface of the support.

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Table 1
Physico-chemical and catalytic properties of V and/or Mo oxides supported on mesoporous alumina or γ-Al_2O_3

Catalyst	Type of alumina	S_{BET} (m^2/g)	Mo-loading (wt.%)	V-loading (wt.%)	Mo/(Mo + V) ratio	Θ[c]	Conv. (%)[d]	Selectivity (%)			Productivity to ethylene[e]
								C_2H_4	CO	CO_2	
MA	Mesoporous	573	0	0	–	0	5.0	8.0	35.8	56.2	0.03
M0V5	Mesoporous	344	0	5.0	0	0.15	25.5	59.8	21.6	18.6	0.91
M0V10	Mesoporous	256	0	9.8	0	0.32	36.6	57.6	28.6	13.9	1.25
M0V14	Mesoporous	Nd	0	13.4	0	0.46	45.2	41.3	39.4	19.3	1.11
M4V9	Mesoporous	248	4.1	8.6	0.32	0.38	37.5	61.1	28.0	10.9	1.37
M6V8	Mesoporous	239	6.1	7.5	0.45	0.41	35.7	64.6	27.6	7.8	1.38
M10V5	Mesoporous	235	9.6	5.3	0.64	0.43	33.8	70.7	19.8	7.5	1.43
M12V4	Mesoporous	213	12.3	3.7	0.77	0.45	24.0	76.8	16.2	7.0	1.11
M18V0	Mesoporous	216	18.7	0	1.0	0.50	21.2	56.4	30.3	13.2	0.72
MVA-1[a]	γ-Al_2O_3	124	10.2	5.4	0.65	1.30	24.1	50.4	40.4	9.2	0.73
MVA-2[b]	γ-Al_2O_3	188	3.4	1.9	0.65	0.40	15.1	72.5	22.8	4.6	0.66

[a] Same metal content that M10V5 sample but prepared with γ-Al_2O_3 ($S_{BET} = 187\ m^2/g$) as support.

[b] Same Mo/(Mo + V) ratio and similar support surface coverage that M10V5 sample but prepared with γ-Al_2O_3.

[c] Coverage of the support by the metals assuming the monolayer to be 7.5 at-V/nm^2 or 4.8 at-Mo/nm^2 [32,33].

[d] Ethane conversion at 580 °C and a contact time of 10 $g_{cat}\ h\ mol^{-1}_{C_2H_6}$; [e] Productivity to ethylene in $g_{C_2H_4}\ h^{-1}\ g^{-1}_{cat}$ (reaction temperature = 580 °C).

Recently, Mo–V-mixed oxides supported on γ-Al_2O_3 have been studied in the ODH of propane [11,12]. Iglesia and co-workers [11] reported an enhanced reaction rate and a higher propylene formation when vanadium oxide was supported on Al_2O_3 containing a nominal polymolybdate layer. This better performance of Mo-containing catalyst was ascribed to the formation of V–O–Mo bonds between the dispersed vanadia and the polymolybdate monolayer. Bañares and Khatib [12] proposed that the catalytic performance of these catalysts strongly depend on the level of the support coverage. Thus, no interaction between V and Mo was observed on catalysts below Mo + V monolayer coverages, while V- and Mo-species seems to react on alumina into mixed Mo–V–(Al)–O above Mo + V monolayer coverages.

The present work shows comparatively the catalytic performance for the oxidative dehydrogenation of ethane of Mo- and/or V-supported on mesoporous alumina and γ-Al_2O_3 below the monolayer coverage. In addition, the characterization results have help to understand the nature of V- and/or Mo-species in these catalysts.

2. Experimental

Mesoporous alumina has been synthesised in propanolic media using estearic acid as surfactant and aluminium trisecbutoxide (ASB) as the inorganic aluminium source [10]. The final surface area of the mesoporous alumina resulted to be about 572 $m^2\ g^{-1}$. Vanadium and/or molybdenum oxides supported on mesoporous alumina were prepared by the wet impregnation method, using ethanolic solutions of vanadyl acetyl acetonate and/or ammonium heptamolybdate. The samples were dried overnight at 120 °C and calcined in static air at 600 °C for 6 h. The vanadium supported on mesoporous alumina catalyst used as a reference was that with a vanadium content of 10 wt.%, M0V10 catalyst, which resulted to be the optimal for the OXDH of ethane [10]. For Mo and mixed Mo–V-catalysts, a part of vanadium was replaced by molybdenum in different ratios, but keeping the same number of total metal atoms (∼1.9 × 10^{-3} mol metal g^{-1} of catalyst). For a comparative purpose, two molybdenum/vanadium catalysts supported on a conventional alumina (γ-alumina, $S_{BET} = 187\ m^2\ g^{-1}$) were also prepared and tested. These catalysts presented the same Mo/(Mo + V) ratios but different metal oxide loading. The characteristics of catalysts are shown in Table 1.

Catalyst characterization has been carried out by different physico-chemical techniques [10]: N_2 and Ar adsorption isotherms, X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy (DR-UV–vis), temperature-programmed reduction (TPR), and infrared spectra of adsorbed–desorbed pyridine (IR-Py).

The catalytic tests for the oxidation of ethane were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor [10]. The catalyst weight was varied from 50 to 250 mg and the total flow of ethane/oxygen/helium with a molar ratio of 4/8/88 was maintained in 100 ml min^{-1}. The reaction temperature was increased up to 600 °C that is the temperature at which the catalysts had been previously calcined. Analysis of the reaction products was carried out on-line using gas chromatography [9].

3. Results and discussion

The characteristics of catalysts are presented in Table 1. A drop of the surface area after the impregnation of the metals higher than 50% was observed when mesoporous alumina was used as support. It can also be observed that the substitution of vanadium by molybdenum leads to a slight drop in the surface area and to an increase of the support coverage.

X-ray diffraction patterns of the catalysts supported on mesoporous materials (not shown here) confirmed the presence of mesoporous alumina after the calcinations step. Neither V_2O_5 nor MoO_3 crystallites were identified in the XRD patterns, in agreement to previous results obtained on mesoporous alumina-supported vanadia catalysts.

Fig. 1 shows Raman spectra of Mo- and/or V-containing catalysts supported on mesoporous alumina after dehydration at 475 °C. The Raman spectra of **M18V0** sample shows a main

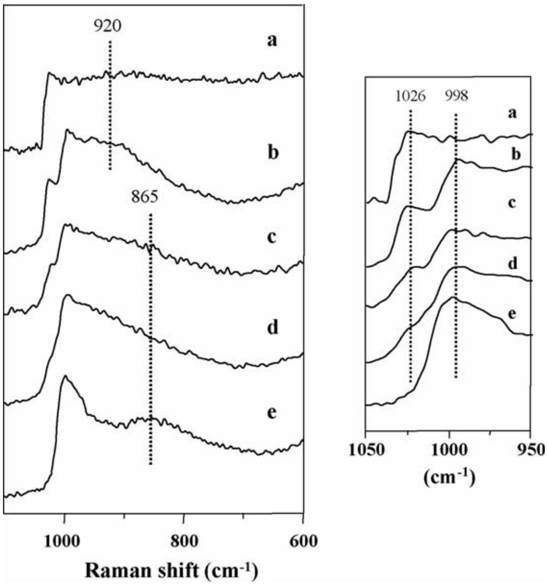

Fig. 1. Raman spectra of catalysts dehydrated in dry air at 475 °C: (a) **M0V10**; (b) **M4V9**; (c) **M10V5**; (d) **M12V4**; (e) **M18V0**.

band at 998 cm^{-1} that is characteristic of the Mo=O stretching mode of surface monooxo molybdenum oxide species [13]. A second broad and low intensity band centred at 865 cm^{-1} could also be observed. This second band has been related to the presence of Mo–O–Mo bonds (stretching mode) in polymeric molybdenum oxide species on the surface of the support [14]. On the other hand, the dehydrated spectra of Mo-free **M0V10** sample shows a sharp band at 1026 cm^{-1} typical of isolated monovanadate species (V=O stretching mode) and a wide and poor-defined band around 920 cm^{-1} related to terminal V=O stretching vibration of polyvanadate groups [15].

The spectra of dehydrated Mo–V-containing catalysts exhibits two Raman bands at 997 and 1022 cm^{-1}, similar to those observed in **M18V0** and **M0V10** catalysts, respectively. Therefore, a modification of the nature of molybdenum or vanadium species in mixed Mo–V-catalyst cannot be expected. In fact the absence of a band at around 775 cm^{-1}, that has been related to the presence of V–O–Mo vibrations for polymolybdovanadate species [11,16], permit us to suggest that Mo–O–V bridges in our catalysts are not formed. This is in agreement to those reported on γ-Al_2O_3 below the Mo + V coverages [12].

It must be noted that the characteristic bands of MoO_3 crystallites (825 and 990 cm^{-1}) or V_2O_5 crystallites (700 and 996 cm^{-1}) have not been detected in the catalyst tested, what means a high dispersion of the metals on the mesoporous alumina.

In order to study the catalyst reducibility, TPR profiles of **M18V0**, **M0V10** and **M10V5** catalysts have been compared (not shown here). Mo-free sample (M0V10) shows a single reduction peak centred at 477 °C that, in agreement with the Raman spectra, would correspond to the reduction of low coordination polymeric V^{5+} species whilst both Mo- and mixed Mo–V-catalysts show several reduction bands. The V-free sample (M18V0) presents three reduction peaks at 421, 536 and 727 °C. The first two bands have been related to the reduction of Mo(VI) species to Mo(IV), to low aggregation and coordination Mo-species (tetrahedral isolated) and to higher coordination (octahedral), respectively [17–19]. However, the wide peak at 727 °C, likely indicates the reduction of MoO_2 to metallic molybdenum [17–19].

Mixed Mo–V-catalyst shows a TPR profile that looks like a superposition of both Mo and V-catalysts TPR profiles but shifted to higher reduction temperatures. Therefore, it is apparent that no interaction between Mo and V takes place in mixed MoV-catalyst. The presence of both molybdenum and vanadium in the same catalyst would seem to decrease the reducibility of both metals. However, it cannot be ruled out that the first reduction peak at 471 °C corresponds to the reduction of V-species, since it appears at the same temperature that in the case of V-catalyst.

DR-UV–vis spectra of the catalysts were carried out (not shown here). A band at 300 ± 10 nm is observed in all catalysts indicating the presence of similar (low aggregated/coordinated) vanadium and molybdenum species regardless the chemical composition of the catalyst [20–22].

The IR spectra upon degassing pyridine at 150 °C of some of the most representative catalysts are shown in Fig. 2. Six bands centred at 1450, 1492, 1540, 1580, 1622 and 1638 cm^{-1} can be appreciated in these spectra. Those at 1450, 1492 and 1622 cm^{-1} are associated to pyridine coordinated with Lewis acid sites [23]. Bands at 1540 and 1638 cm^{-1} have been related to the presence of Brönsted acid sites whereas that at 1580 cm^{-1} is likely due to the physisorption of the pyridine on the sample [23].

In Mo-free catalysts, the amount of Lewis acid site decreases when increasing the V-loading. Moreover, the incorporation of molybdenum seems to favour also a decrease in the number of Lewis acid sites. In fact, when comparing the IR spectra of

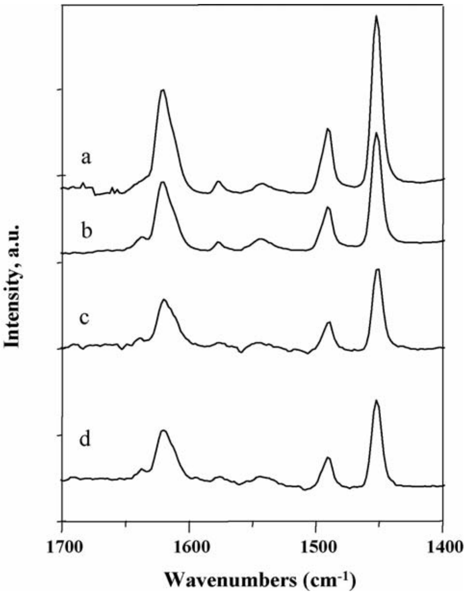

Fig. 2. FT-IR spectra of pyridine adsorbed on supported catalysts after evacuation at 150 °C. Catalysts: (a) **M0V5**; (b) **M0V10**; (c) **M10V5**; (d) **M18V0**.

M10V5 sample with that of a Mo-free sample with similar V content (i.e. **M0V5** catalyst), it can be seen that the sample with Mo presents a lower amount of Lewis acid sites. This different acidity should be related to the presence of molybdenum that apparently covers the alumina surface and therefore decreases the number of acid sites. So, the partial substitution of vanadium by molybdenum also means a decrease in the amount of the Lewis acid sites: **M0V5** $>$ **M0V10** $\gg$ **M10V5** $>$ **M18V0**.

Brönsted sites have not been observed on our catalysts. In this way, we must inform that the presence of Brönsted acid sites on vanadia supported on alumina was only observed on samples with V-contents higher than 17%.

Table 1 also shows comparatively the catalytic behaviour of V- and/or Mo-containing catalysts for the oxidative dehydrogenation of ethane at 580 °C. Ethylene, CO and CO_2 were the main reaction products observed. Neither partial oxygenated products nor methane were detected in these reaction conditions. It can be seen that the catalytic performance strongly depends on the catalyst composition.

Fig. 3 plots the variation of both the catalytic activity for ethane conversion at isothermal conditions (580 °C) and the selectivity to ethylene at isoconversion (ethane conversion of 30%) conditions for Mo- and/or V-containing catalysts. Mo-free vanadium catalyst resulted to be about four times more active than pure molybdenum catalyst. However, the partial substitution of V by Mo did not lead to a significantly drop in the catalytic activity but it kept nearly stable, up to a Mo/(Mo + V) wt. ratio of 0.77. It must be noted that Mo–V-based catalysts present higher catalytic activity than that corresponding to the linear relation between pure vanadium and pure molybdenum catalysts.

On the other hand, the results of Fig. 3 indicate that the selectivity to ethylene on pure V-catalyst is higher than over pure Mo-catalyst. However, a remarkable increase of the selectivity to ethylene is observed in mixed Mo–V-catalysts. In fact, all mixed catalysts are more selective than the pure V or Mo ones. It is important to highlight that the improved catalytic behaviour of mixed Mo–V-catalysts are compared to a V-catalyst whose loading had been previously optimised (**M0V10** sample) [10]. In particular, **M10V5** catalyst presented the optimal composition achieving a high selectivity to ethylene of 76% at an ethane conversion of 30%.

To check the promoter effect of molybdenum, a Mo-free catalyst (**M0V5** sample) with a vanadium content similar to that in the most selective Mo–V-catalyst (**M10V5** sample) was also tested. However, a substantial lower selectivity to ethylene was obtained when Mo was not present (Table 1).

The influence of the nature of the alumina on catalytic behaviour of these catalysts is comparatively presented in Fig. 4. Although the catalysts supported on γ-alumina present either the same metal loading (**MVA**-1 sample) or the same support surface coverage (**MVA**-2 sample) than that of **M10V5** sample, the catalytic behaviour is quite different. According to the catalytic results, both the use of a high surface area mesoporous alumina and the addition of molybdenum to a V-catalyst lead to an enhancement of the yield to ethylene.

One likely advantage of using high surface area alumina instead a conventional alumina is the possibility of a better dispersion of the active sites on the surface of the support. In fact, a better dispersion of vanadium using mesoporous supports has been observed in vanadium oxide supported on siliceous materials as MCM-41 [24,25], SBA-15 [26] or on mesoporous alumina [10]. As it has been widely reported dispersed vanadium species, especially isolated VO_4 units, are the most selective species for short chain alkane oxidative dehydrogenation reactions [8,27], and their presence should be favoured by the use of a mesoporous alumina. In fact, mixed MoV-catalysts presented here show vanadium and molybdenum species with a low degree of aggregation and coordination, as observed by Raman and DR-UV–vis.

On the other hand, the high surface area of the mesoporous alumina means a higher number of acid sites in the catalyst. The presence of acid sites has been described as negative for ODH of alkanes with longer C chains, but in the case of ethane the acidity of the support favours the selectivity to the olefin [8].

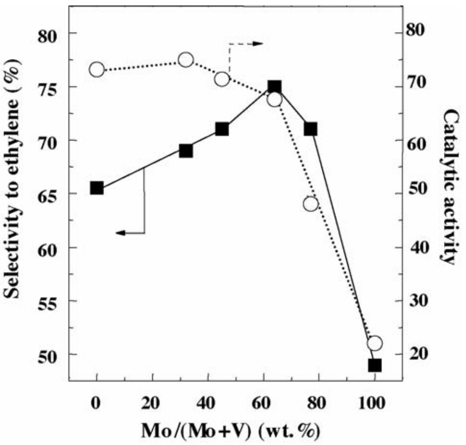

Fig. 3. Variation of the catalytic activity at 580 °C (in $mol_{C_2H_6}\ h^{-1}\ kg_{cat}^{-1}$) (○) and the selectivity to ethylene (at an ethane conversion of 30% and reaction temperature of 580 °C) (■) with the Mo/(Mo + V) ratio of catalyst.

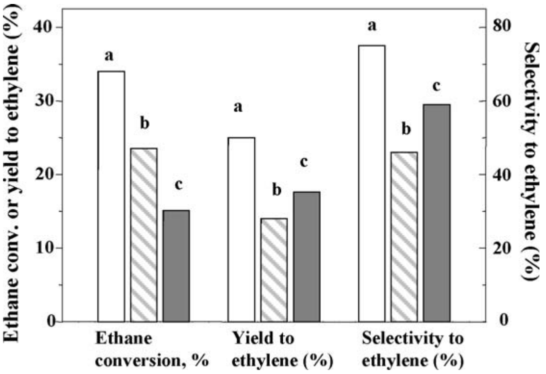

Fig. 4. Influence of the nature of the support on the catalytic performance (selectivity to ethylene, yield to ethylene and ethane conversion) of Mo–V-containing catalysts during the oxidative dehydrogenation of ethane. Symbols: **M10V5** (a); **MVA-1** (b); and **MVA-2** (c). Note: the selectivities and yields of ethylene have been obtained at 580 °C and an ethane conversion of 30%, while the ethane conversion was obtained at 580 °C and a contact time, *W*/*F*, of $10\ g_{cat}\ h\ mol_{C_2}^{-1}$.

Therefore, the acidic character of mesoporous alumina would not negatively influence the catalytic behaviour of catalysts with this support. However, mesoporous alumina alone has been shown to be active and selective to CO_x formation during ethane oxidation (see Table 1). Then, the part of the support of the catalysts that is not covered by metals will activate unselectively the alkane to yield carbon oxides. If the mesoporous alumina is covered by molybdenum oxide species the formation of carbon oxides would be prevented, as molybdenum species are remarkably more selective to ethylene than the support itself. As appreciated by IR-Py, two catalysts with the same vanadium content, as **M0V5** and **M10V5** catalysts, present different amount of acid sites on the support surface. These acid sites are likely to be the unselective acid sites of the support [8]. Molybdenum species in **M10V5** hinders a part of the interaction between ethane/ethylene with the support, preventing the consecutive oxidation with the formation of carbon oxides, and therefore increasing the selectivity to ethylene.

At the present work the catalytic activity keeps stable when molybdenum loading increases up to Mo/(Mo + V) wt. ratio reaches 0.64. Higher Mo-loadings led to a drop in the catalytic activity. The mechanism of the synergetic effect between Mo and V is not clear. It is well known that for oxydehydrogenation reactions vanadium catalysts are more active than molybdenum catalysts [28]. Therefore, a drop in the catalytic activity would be expected when V is replaced by Mo. In fact, a decrease in the catalytic activity has been reported when Mo was added to VMg-catalysts for the oxidative dehydrogenation of *n*-butane [29]. This drop was associated to the decrease of the vanadium reducibility when molybdenum content increased.

Iglesia and co-workers [11] have observed that the rate for ODH of propane is supported vanadium oxides catalysts was higher when using MoO_x-coated Al_2O_3 as support than for pure Al_2O_3. The higher activity was related to the formation of V–O–Mo bonds between the dispersed vanadia and the molybdena layer. In the same way, Ruth et al. [30] studied the reducibility of polymolybdovanadates species and found that they were more reducible than both vanadium oxide and molybdenum oxide species. Unfortunately, no molybdovanadate species are apparently present in our catalysts, as XRD and Raman results suggest.

TPR results indicate that the reducibility of mixed MoV-catalysts decreases in comparison with pure catalysts. Therefore, we cannot completely discard a change in the nature of Mo or V species as i.e. the formation of mixed Mo–V–O species. In addition, from the temperature-programmed reduction results obtained we cannot correlate the high catalytic activity of mixed Mo–V-catalysts with the reducibility of our catalysts.

As proposed before, the higher selectivity to ethylene obtained when Mo is added to the V-catalyst would be mainly due to two factors: (i) presence of highly selective vanadium/molybdenum species, as isolated VO_4 units and (ii) the coverage of non-selective sites of the support by molybdenum oxide species.

A synergetic effect between Mo and V is not so surprising since the best catalysts reported up to date for this reaction, MoVTeNb-based catalysts [31], present in their composition both elements as main components, forming mixed Mo–V–O crystalline phases. However, the characterization results of our MoV/mesoporous alumina catalysts suggest the absence of mixed Mo–V–O oxides. Bañares and Khatib [12] observed the formation of mixed Mo–V–O phases in γ-Al_2O_3-supported VMoO catalysts for metal loadings above the monolayer coverage whereas mixed Mo–V–O phases were not apparently formed below the monolayer. Thus at low metal contents, Mo and V share the alumina support contributing to the catalytic reaction with their own catalytic properties. In agreement with the former authors, the support coverage of the catalysts of the present work is far from that of the theoretical monolayer (Table 1), and therefore no (or low) interaction would be expected.

In conclusion, promising catalytic results have been obtained for the dehydrogenation of ethane in presence of oxygen. In this way, the use of mesoporous alumina instead conventional alumina led to an increase of both the catalytic activity and the selectivity to ethylene. Moreover, a systematic improvement in the ethylene formation has been observed with Mo–V-mixtures in comparison with pure V- or Mo-mesoporous alumina catalysts. The improved selectivity to ethylene obtained in MoV-catalysts would be mainly due to two factors: (i) presence of highly selective vanadium species, as isolated VO_4 units, and (ii) the coverage of non-selective sites of the support by molybdenum oxide species. The role of molybdovanadate species in the enhanced catalytic performance cannot be conclusively ruled out although these mixed species have not been detected by the characterization techniques studied.

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