

Zinc-modified, alumina-supported vanadium oxides as catalysts for propane oxidative dehydrogenation

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Abstract

Zinc-modified, γ -Al₂O₃ supported vanadium oxides were prepared by dry impregnation and co-precipitation methods. The solids were characterized by X-ray diffraction, UV–VIS, ⁵¹V NMR and X-ray photoelectron spectroscopy and compared as catalysts in propane oxidative dehydrogenation (ODH). It was shown that only true co-precipitation methods lead to interaction of amorphous zinc vanadates with the surface of alumina. Selectivity spectra in propane ODH were used as a fingerprint to characterize superficial vanadates. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supported vanadium oxides have been recently studied as catalysts for propane oxidative dehydrogenation (ODH). The kinetic aspects of the reaction have been correlated to the structure of the active site [1,2]. It is known that the activity and selectivity of these catalysts depend on the nature of the support and on vanadium dispersion and may be influenced by the pretreatment conditions the catalysts were submitted to [3,4]. Basic oxide supports such as MgO, Bi₂O₃, La₂O₃ and Sm₂O₃ originated catalysts which were more selective towards alkenes than acidic oxide supports [5–7]. It seems however that γ -Al₂O₃ supported vanadium oxides do give the best performance in the reaction

[8–12]. Tetrahedrally coordinated, monomeric and oligomeric vanadate (V⁵⁺) species which are dispersed on these supports were found to be active and selective in producing alkene through alkane ODH. Basically the same observations were done in the case of bulk ternary catalysts; selective compounds were mixed oxides formed from vanadia and a basic oxide in which vanadium had tetrahedral coordination and low condensation degree. One should thus ask whether supported ternary complexes combining vanadia and basic oxides may be dispersed on the surface of alumina and what their catalytic properties could be.

With this view, the present work reports a study of zinc-modified, γ -Al₂O₃ supported vanadium oxides. The solids were characterized by X-ray diffraction, UV–VIS, ⁵¹V NMR and X-ray photoelectron spectroscopy and compared as catalysts in propane ODH.

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2. Experimental

2.1. Preparation of the catalysts

$\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ was prepared by the adsorption equilibrium method [8,13,14]. Typically, 6.00 g of $\gamma\text{-Al}_2\text{O}_3$ (Engelhard, 180 m²/g), previously calcined at 500 °C for 1 h, were introduced in 200 ml of a 0.05 M NH_4VO_3 aqueous solution adjusted at pH = 2.5 with nitric acid. The suspension was kept under stirring for 1 h, filtered under vacuum and dried at 50 °C for 24 h before calcination at 300 °C for 1 h.

Three zinc-modified, $\gamma\text{-Al}_2\text{O}_3$ supported catalysts were obtained by dry impregnation of zinc nitrate solutions on the previously prepared $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$, using V/Zn ratios of 6/1, 1/1 and 1/2, respectively. For comparison, a pure alumina-supported, zinc oxide catalyst was prepared in the same way using the same zinc content as in the second sample (V/Zn = 1/1). The solids were dried at 50 °C for 24 h and calcined at 500 °C for 1 h.

Two more catalysts were prepared by co-precipitation methods [15]. In the first case, zinc nitrate was added dropwise to a suspension of the support in aqueous ammonium *meta*-vanadate, using the ratio V/Zn = 2/1. The solid was filtered off, dried at 50 °C for 24 h and calcined at 500 °C for 1 h. Another sample with V/Zn = 1 was obtained by evaporating the solution instead of filtering.

The seven samples were denominated VO/Al, ZnO/Al, VZnO/Al(I,6/1), VZnO/Al(I,1/1), VZnO/Al(I,1/2), VZnO/Al(F,2/1) and VZnO/Al(E,1/1), respectively, indicating whether the zinc-containing solids were prepared by impregnation (I), filtration (F) or evaporation (E), and summarizing the theoretical V/Zn ratio.

2.2. Physicochemical characterization

Vanadium and zinc mass contents were determined by atomic absorption spectroscopy using a Varian CARY|1E| equipment.

X-ray diffraction was performed with a Siemens type F diffractometer with Philips PW 1830/25 generator equipped with a Siemens FK 60-10 cobalt tube, a graphite monochromator and a NaI Siemens detector. α -Alumina was used as a reference.

BET surface areas were measured in a Micromeritics ASAP 2000 apparatus.

XPS analyses were performed on a Perkin Elmer 1257 instrument, using Mg K α radiation. The C 1s peak at 284.8 eV was taken as a reference for correction of binding energies due to sample charging. The sensibility factors used for calculations of surface composition were those provided with the apparatus.

UV–VIS diffuse reflectance spectra in the range of 200–800 nm were recorded in a Varian CARY|5| spectrophotometer using a Harrick diffuse reflectance cell with Praying Mantis geometry.

MAS ⁵¹V NMR spectra were recorded using a Bruker DRX 300 (7.05 T) spectrometer operating at 78.95 MHz. The spectra were obtained at spinning rates of 8 and 15 kHz using the Bloch decay sequence, in order to obtain the isotropic values of chemical shifts, with pulse width of 1 μ s ($\pi/8$), and delay time of 1 s. Chemical shifts are related to neat VOCl_3 by use of an external 0.16 M sodium *meta*-vanadate aqueous solution ($\delta = -573.17$ ppm) as a secondary reference [16].

Catalytic measurements for propane oxidation were performed at 350 °C and at atmospheric pressure, with 100–200 mg of catalyst using a microreactor and a gas mixture of 1% propane/air (vol.%) flowing in the range of 30–35 ml/min.

3. Results and discussion

Table 1 shows the Zn and V mass contents of the catalysts, obtained by chemical analysis, and their BET surface area. Zn and V mass contents are in rough agreement with theoretical values. It is worth noting, however, that the V/Zn ratio in VZnO/Al(F,2/1) is much higher than the corresponding values in zinc *meta*-, *pyro*- and *ortho*-vanadate compounds (ZnV_2O_6 , $\text{Zn}_2\text{V}_2\text{O}_7$ and $\text{Zn}_3\text{V}_2\text{O}_8$, respectively); this should indicate the presence of free vanadium oxides at the surface of the support. In all materials, the BET surface areas are seen to decrease with increasing the total oxide content, suggesting pore filling of the support by deposited species. However, the loss is more significant for precipitated materials than for impregnated ones, which could indicate a worst dispersion of Zn and V in precipitated solids, with the presence

Table 1
BET surface area and chemical composition of the catalysts

Catalyst	BET area (m ² /g)	V (mass%)	Zn (mass%)	V/Zn (atomic ratio)
VZnO/Al(E,1/1)	135.88	9.2	7.7	1.53
VZnO/Al(F,2/1)	147.23	5.0	2.1	3.07
VO/Al	174.72	4.2	–	–
VZnO/Al(I,6/1)	173.24	4.4	0.68	8.30
VZnO/Al(I,1/1)	157.06	4.6	6.30	0.94
VZnO/Al(I,1/2)	143.11	4.6	10.40	0.57
γ -Al ₂ O ₃	191.96	–	–	–

of bulk phases deposited on the external surface of the support.

Fig. 1 displays the X-ray diffraction patterns of VZnO/Al(I,1/2) and ZnO/Al compared with that of the support. Two peaks at $d = 1.54$ and $d = 2.84$ Å indicate the presence of crystalline zinc oxide in VZnO/Al(I,1/2). Crystallite dimensions of 20 Å were determined by using the Debye–Scherrer formula. Only the first peak, at $d = 1.54$ Å, is observed in ZnO/Al, probably due to the lower zinc content in this sample. Fig. 2 shows the X-ray diffraction patterns of precipitated catalysts, VZnO/Al(E,1/1) and VZnO/Al(F,2/1). The former displays the characteristic pattern of zinc *meta*-vanadate (brannerite phase), in agreement with the Zn/V ratio [17]. The pattern

of the latter sample does not evidence the presence of crystalline phases belonging to the ternary system V–Zn–O.

The MAS ⁵¹V NMR spectra of the six catalysts are reported in Figs. 3 and 4. Table 2 lists the isotropic chemical shifts measured from these spectra. According to the literature [18–20], the two signals obtained for VO/Al and impregnated solids correspond to V⁵⁺ sites with tetrahedral coordination and low condensation degree (signal close to –480 ppm) or high condensation degree (signal close to –570 ppm). The chemical shifts obtained for precipitated solids indicate a mixture of zinc vanadate compounds [16–22]. VZnO/Al(E,1/1) presents the characteristic signals of zinc *pyro*-vanadate ($\delta = -620$ ppm)

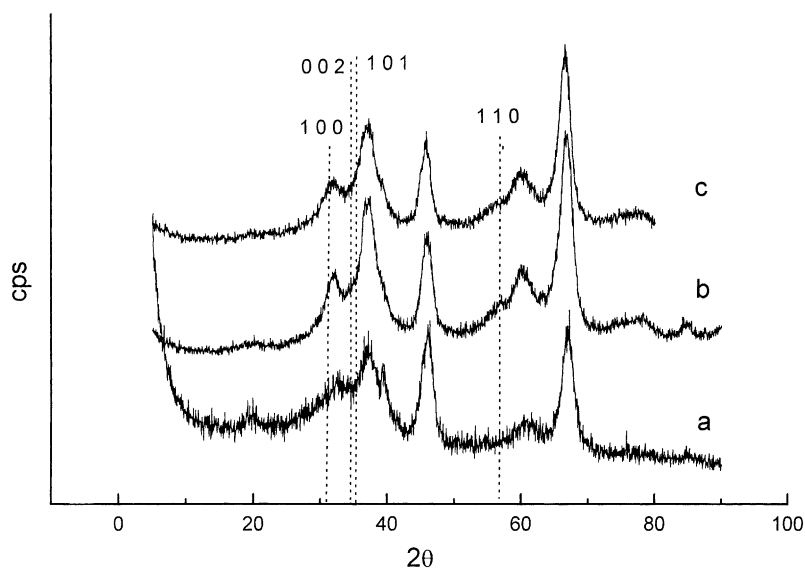


Fig. 1. XRD patterns of (a) γ -Al₂O₃, (b) ZnO/Al and (c) VZnO/Al(I,1/2) with ZnO peaks indicated by vertical lines and *hkl* planes.

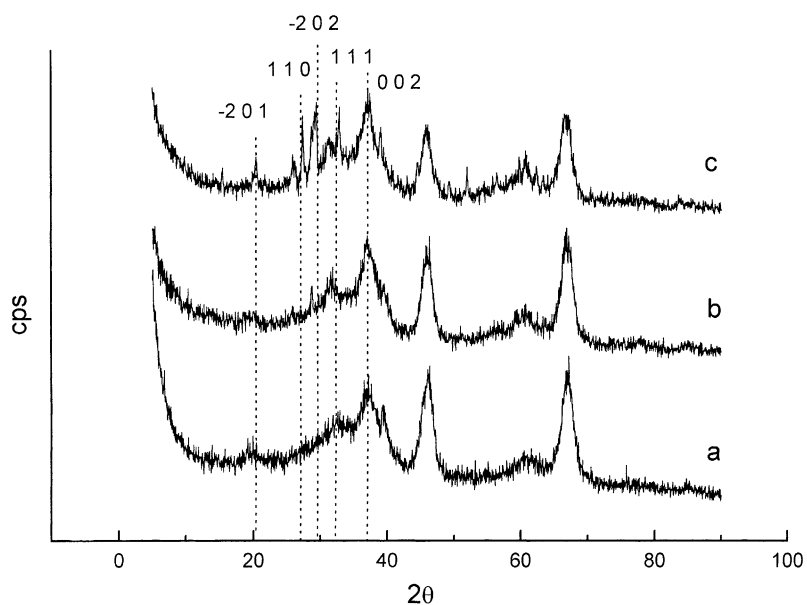


Fig. 2. XRD patterns of precipitated catalysts, (a) γ -Al₂O₃, (b) VZnO/Al(F,2/1) and (c) VZnO/Al(E,1/1).

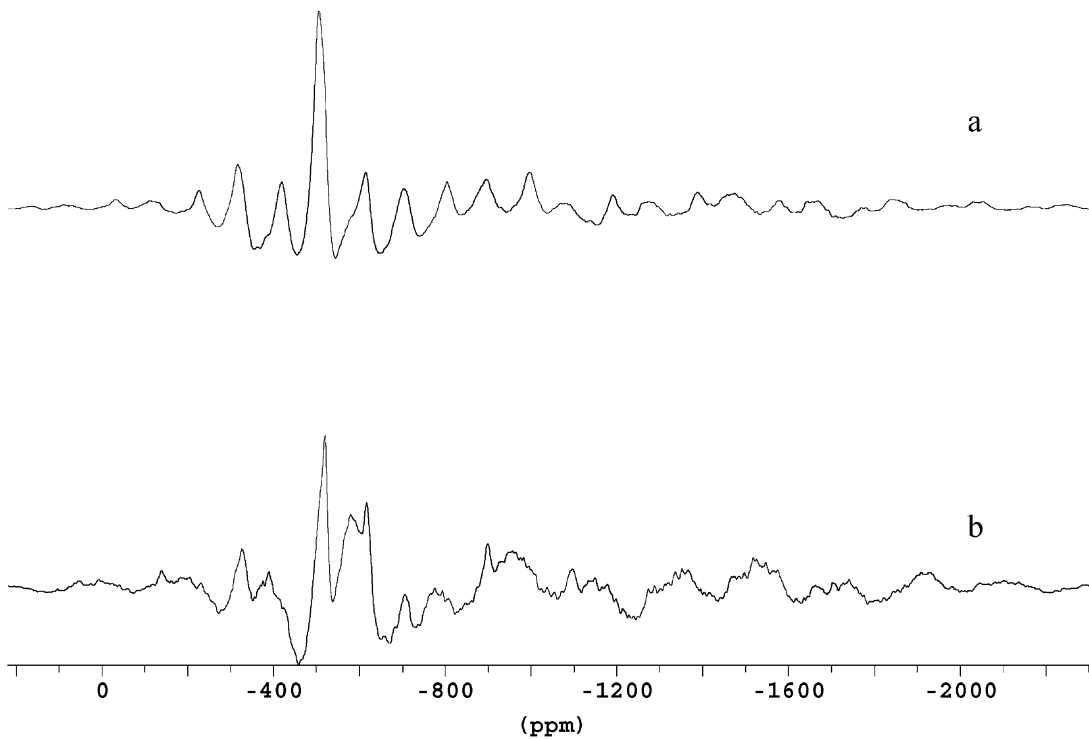


Fig. 3. ⁵¹V NMR spectra (MAS) of precipitated catalysts, (a) VZnO/Al(E,1/1) and (b) VZnO/Al(F,2/1).

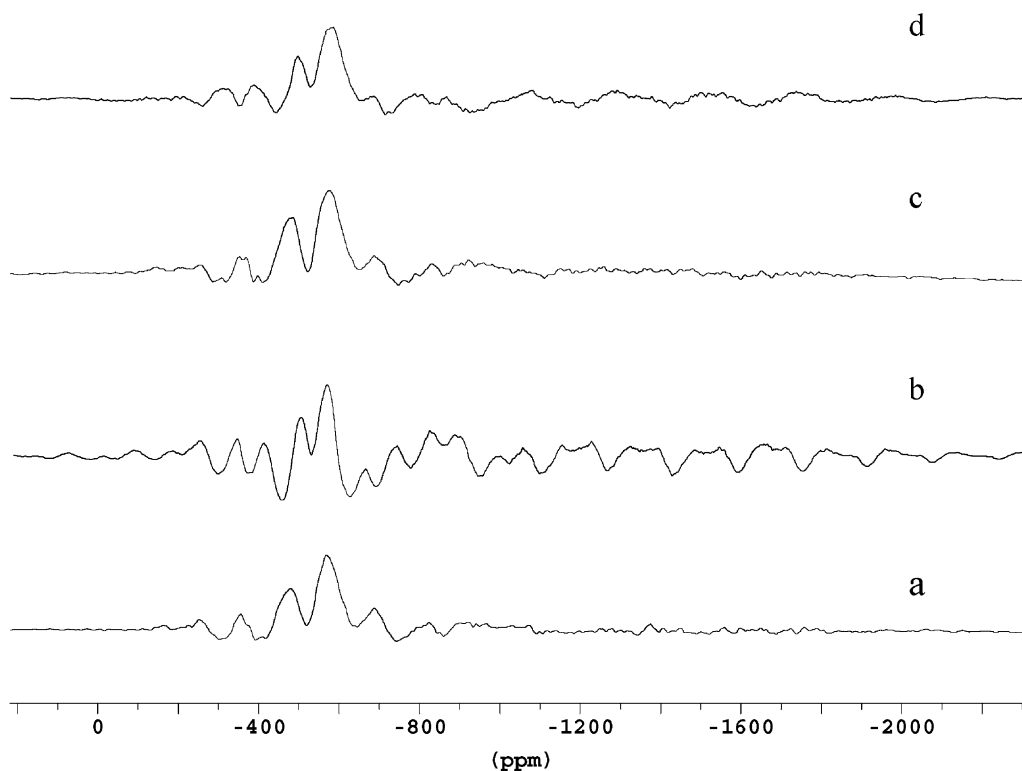


Fig. 4. ^{51}V NMR spectra (MAS) of impregnated catalysts, (a) VO/Al, (b) VZnO/Al(I,6/1), (c) VZnO/Al(I,1/1) and (d) VZnO/Al(I,1/2).

and zinc *meta*-vanadate ($\delta = -505$ ppm). The higher intensity of the latter signal suggests this species predominates in the sample, in agreement with XRD observations. VZnO/Al(F,2/1) presents the signals of zinc *pyro*-vanadate and zinc *ortho*-vanadate ($\delta = -522$ ppm), the latter compound being preponderant. No signal associated with supported vanadium oxides could be observed in precipitated samples.

The XPS data are collected in Table 3. According to the literature, the binding energy values of V

$2p_{3/2}$ around 518 eV are currently admitted for V^{5+} [2,4,23]. This way, the results in Table 3 indicate the presence of V^{5+} in precipitated solids. In contrast, a shift of about 0.8 eV to lower energy in impregnated catalysts suggests the presence of some V^{4+} , currently admitted to give a signal around 517 eV [2,4,23]. However, this hypothesis was not confirmed by UV–VIS analyses reported in the next paragraph. The superficial V/Zn ratio for VZnO/Al(E,1/1) is compatible with the presence of a mixture of zinc *meta*-vanadate (V/Zn = 2) and zinc *pyro*-vanadate (V/Zn = 1), as shown by DRX and NMR results. The value obtained for VZnO/Al(F,2/1) is close to the composition of zinc *ortho*-vanadate (V/Zn = 0.67), in agreement with NMR results. The superficial V/Zn ratios of the three impregnated catalysts are significantly lower than bulk ratios given in Table 1, which suggests zinc segregation at the external surface of the support, probably in oxide form, as seen by XRD.

Table 2
 ^{51}V NMR isotropic chemical shifts of the catalysts

Catalyst	δ (ppm)
VZnO/Al(E,1/1)	-620/-505
VZnO/Al(F,2/1)	-623/-522
VZnO/Al(I,1/2)	-582/-504
VZnO/Al(I,1/1)	-577/-487
VZnO/Al(I,6/1)	-586/-507
VO/Al	-569/-480

Table 3
XPS data of the catalysts

Catalyst	Binding energy (eV)			V/Zn (atomic ratio)
	O 1s	V 2p _{3/2}	Zn 2p _{3/2}	
VZnO/Al(E,1/1)	530.63	517.87	1021.64	1.45
VZnO/Al(F,2/1)	531.46	517.62	1022.40	0.61
VZnO/Al(I,6/1)	530.91	516.84	1021.23	3.05
VZnO/Al(I,1/1)	531.17	516.94	1022.20	0.50
VZnO/Al(I,1/2)	530.94	516.66	1021.40	0.23

The UV–VIS spectra of the six catalysts are shown in Figs. 5 and 6. Ill-defined bands in the range of 20,000–50,000 cm^{-1} are attributed to ligand to metal charge transfer transitions (LMCT) in highly distorted V^{5+} complexes [24]. The absorption edge energy values of impregnated catalysts were calculated following the method described in [25,26], and listed in Table 4. The results show that increasing Zn content led to decreasing maximum absorption intensity as well as absorption edge energy values. The latter effect, although weak, suggests that zinc addition to the catalyst promotes an increase of the condensation degree of vanadium oxide [23,24]. The spectrum of VZnO/Al(F,2/1) is very similar to that of impregnated catalysts; this observation reinforces the hypothesis of some adsorption

of vanadium on the support during the synthesis of the solid, occurring in parallel with precipitation of amorphous zinc vanadate as seen by NMR. In comparison with this sample, the spectrum of the catalysts prepared by evaporation displays a lower intensity, which was unexpected, due to its higher vanadium content; this effect might be attributed to the presence of crystalline compounds, as detected by XRD.

The rate values in propane ODH and selectivity data measured at 10% conversion for the different catalysts are reported in Table 5. The results show that stepwise addition of Zn to VO/Al by impregnation did not modify significantly the activity of the catalyst but led to progressively increasing selectivity to CO_2 and decreasing selectivity to CO and propene.

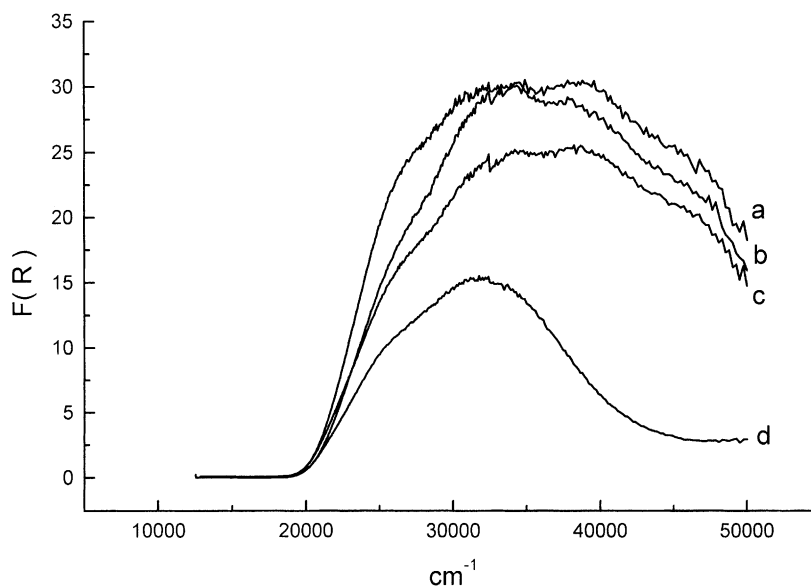


Fig. 5. UV–VIS spectra of impregnated catalysts, (a) VO/Al, (b) VZnO/Al(I,6/1), (c) VZnO/Al(I,1/1) and (d) VZnO/Al(I,1/2).

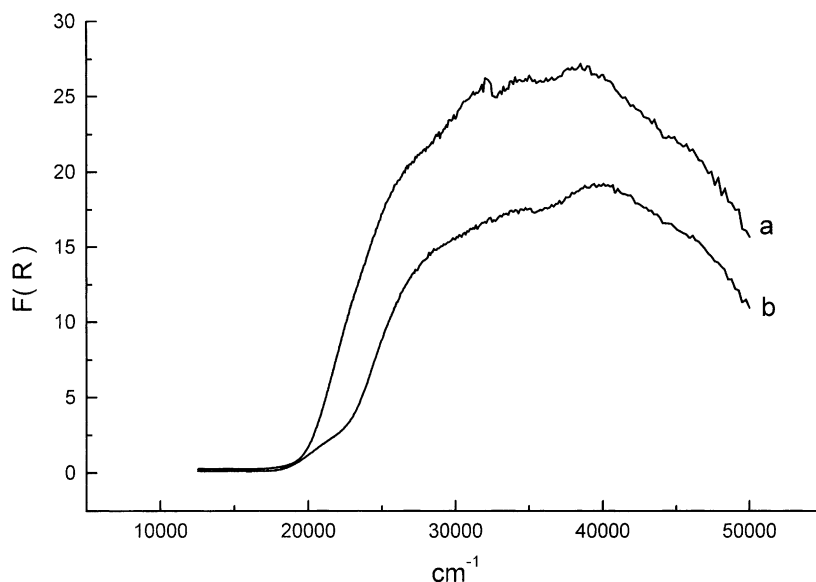


Fig. 6. UV–VIS spectra of precipitated catalysts, (a) VZnO/Al(E,1/1) and (b) VZnO/Al(F,2/1).

Table 4
 $F(R)$ and edge energy values for impregnated catalysts

Catalysts	$F(R)$	E_g (eV)
VO/Al	30.47	2.57
VZnO/Al(I,6/1)	30.68	2.33
VZnO/Al(I,1/1)	23.94	2.31
VZnO/Al(I,1/2)	14.64	2.30

Characterization results of impregnated samples suggested the agglomeration of zinc in oxides particles without formation of mixed oxides and, only a small increase of the condensation degree of vanadium. The results for rate values are in good agreement

with these observations, since alumina-supported zinc oxide itself showed very low activity in the reaction. Continuous selectivity variations along the series might be attributed to the regular variation of the degree of condensation of vanadium, unless it is due to decomposition of propene to CO₂ on zinc oxide. Fig. 7 displays the variation of selectivity to propane as a function of conversion for the catalysts. It is clear, from this graph and from data of Table 5, that VZnO/Al(F,2/1) presents selectivity values slightly higher than those of impregnated materials. A much higher selectivity towards CO₂ is observed for VZnO/Al(E,1/1). The well differentiated behavior of the latter catalyst is confirmed by the analysis of

Table 5
Reaction rates (R) and selectivity at 350 °C for propane ODH^a

Catalysts	R (mol/g s)	C (%)	S_1 (%)	S_2 (%)	S_3 (%)
VZnO/Al(E,1/1)	1.85×10^{-7}	10.8	51.8	19.6	28.6
VZnO/Al(F,2/1)	1.33×10^{-7}	8.8	27.8	27.7	40.6
VZnO/Al(I,1/2)	1.16×10^{-7}	10.2	34.2	31.5	27.5
VZnO/Al(I,1/1)	1.57×10^{-7}	9.3	33.5	32.8	32.0
VZnO/Al(I,6/1)	1.40×10^{-7}	8.7	22.1	36.5	40.7
ZnO/Al	0.22×10^{-7}	1.5	60.0	30.3	6.4
VO/Al	1.57×10^{-7}	9.3	20.0	36.7	42.9

^a C : conversion; S_1 : selectivity to CO₂; S_2 : selectivity to CO; S_3 : selectivity to C₃H₆.

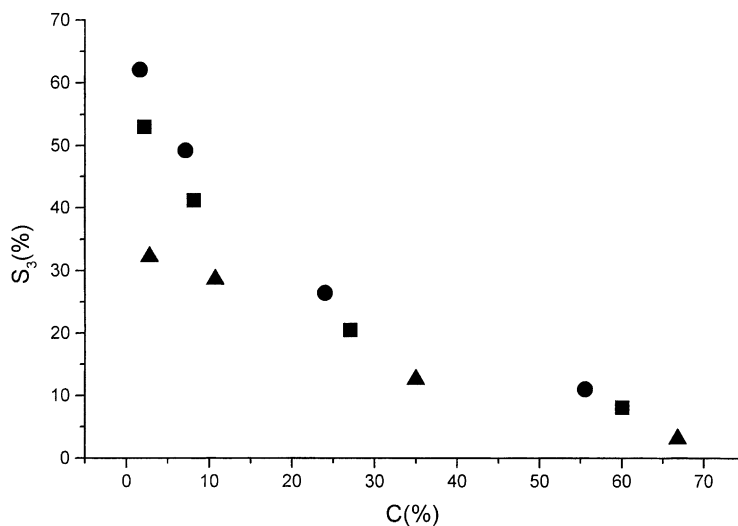


Fig. 7. Selectivity values as a function of conversion in propane ODH, (●) VO/Al, (■) VZnO/Al(F,2/1), (▲) VZnO/Al (E,1/1).

activation energy values listed in Table 6. The catalytic properties of this solid were attributed to crystalline zinc *meta*-vanadate. It is known, in comparison, that magnesium *meta*-vanadate is not very selective for alkane ODH [4,23]. On the other hand, VO/Al, impregnated solids and VZnO/Al(F,2/1) present similar activation energies and close selectivity values at equal conversion. Taking into account the zinc content of the latter solid, however, it is seen that the corresponding selectivity values given in Table 5 do not fit the values expected in the case of the impregnated series. The selectivity towards CO is unexpectedly low and the selectivity to propene is higher than it ought to be. This confirms different structures of the active sites, in accordance with the NMR analysis showing the presence of amorphous zinc vanadates in VZnO/Al(F,2/1). The enhancement of selectivity for this sample could be due to the presence of less condensed vanadates.

Table 6
Apparent activation energy values

Catalysts	E_a (kcal/mol)
VZnO/Al(E,1/1)	41.0
VZnO/Al(F,2/1)	33.5
VO/Al	34.1

4. Conclusions

Zinc was used as a probe cation in a comparison of preparation methods aiming at dispersing ternary oxides over the surface of an alumina support. We have shown that dry impregnation of zinc nitrate solutions on alumina-supported vanadium oxides generates mainly zinc oxide particles deposited on the external surface of the material. Co-precipitation methods followed by evaporation led to the undesired formation of bulk crystalline vanadates. On the other hand, true co-precipitation methods led to a better interaction of amorphous zinc vanadates with the surface of alumina, with a small enhancement of selectivity to propene. The method opens a unexplored investigation field for preparation of alumina-supported basic vanadates.

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