

On the nature of highly dispersed vanadium oxide catalysts: effect of the support on the structure of VO_x species

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Abstract

The nature of VO_x specie supported on TiO₂, γ-Al₂O₃ and SiO₂ is analyzed. The plausibility of different VO_x specie (mono, di, pyrovanadates) is evaluated by means of a theoretical study of the extended Hückel (EH) type. Theoretical results are compared with published characterization data and discussion is performed taking account both results. The interaction of VO_x with the support and the structure of supported surface vanadia are influenced by the composition of the oxide carrier. On SiO₂, only the monovanadate species are formed. On γ-Al₂O₃, dimers seem to be the more plausible supported form of VO_x. On TiO₂, monomers and dimers are present; however, the latter species being the most abundant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: VO_x catalysts; Catalysts characterization; Supported vanadia; Extended Hückel; Partial oxidation catalysts

1. Introduction

Supported vanadium oxides (VO_x) are extensively used as catalysts in a large number of oxidation processes [1–3]. Depending on the oxide carrier, VO_x exhibit different catalytic pattern; for example, in the partial oxidation of methane, VO_x/SiO₂ exhibits the best performance in catalyzing the formation of partial oxidation products [4,5], while alternative systems such as VO_x/TiO₂ or VO_x/γ-Al₂O₃ are not selective catalysts [6,7]. Titania presents a peculiar efficiency to support VO_x for the oxidation of *o*-xylene to phthalic anhydride [2,8], meanwhile SiO₂ and Al₂O₃ show poor selectivity [9].

The difference in the catalytic behavior has been attributed to modifications of the nature of VO_x due

to V-oxide support interactions [10–12]. However, the structure–catalytic behavior relationship is a subject of discussion, mainly due to the difficulties associated with the characterization of VO_x catalysts.

The present study has been carried out in order to investigate the role of the composition of the oxide carrier on the structure of vanadia catalysts. In order to do so, a theoretical study of the extended Hückel (EH) type was performed to gauge the plausibility of different surface V-structures supported on γ-Al₂O₃, SiO₂ and TiO₂ (anatase). In a previous study we have discussed the nature of VO_x supported on γ-Al₂O₃ by a combination of a theoretical study and experimental characterization. Some of those results will be included and compared here [13].

Theoretical treatment of catalysts should be considered as an adjunct to experimental surface studies. While comparing this, the present theoretical results have been corroborated with available experimental

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Table 1
Number of oxygen, cation and hydrogen atoms of SiO₂, TiO₂ and γ -Al₂O₃ clusters

Cluster	Number of O atoms	Number of cation	Number of H atoms
SiO ₂ (1 0 0)	18	9	36
SiO ₂ (1 1 1)	14	22	32
TiO ₂ (0 0 1)	35	21	35
γ -Al ₂ O ₃ (1 0 0)	53	12	46
γ -Al ₂ O ₃ (1 1 0)C	24	8	19
γ -Al ₂ O ₃ (1 1 0)D	28	7	42

data taken from published chemical and spectroscopic characterization results.

1.1. Modeling the oxide support

For the three supports, the present model represents the surface as a two-layer oxide cluster. When modeling a crystal by a portion of the infinite solid, the so-called dangling bonds appears; this disadvantage was overcome by completing the internal cation coordination with hydrogen atoms. The surfaces were considered to be as neutral and fully hydrated. The number of cations, oxygen and hydrogen atoms for each modeled cluster are reported in Table 1.

1.1.1. SiO₂

The structure of silica is similar to that of β -cristobalite. The (1 0 0) and the (1 1 1) faces were considered to be as the most abundant exposed planes in amorphous silica. Faces (1 0 0) present geminal OH groups, while isolated silanol groups are on the (1 1 1) face. The latter plane is presented at the 85% of the surface.

1.1.2. TiO₂

Titania, in its anatase form, presents a tetragonal structure [14]. Titanium oxide exposes preferably the (0 0 1) plane [15].

1.1.3. γ -Al₂O₃


We have considered three planes: (1 0 0), (1 1 0)C and (1 1 0)D, which have been already modeled in the previous study [13].

1.2. Modeling of VO_x species on oxide supported surface

A large variety of supported VO_x species have been postulated in the literature [2,16–19]. It is gen-

erally accepted that at low loading vanadia forms mono or oligomeric vanadate species; with increasing concentration polymeric two-dimensional species appear. Finally, for concentration, above the monolayer capacity of a given support, crystalline V₂O₅ is formed. The present study only accounts for catalysts with low vanadia loading. Thus, we have not considered the two-dimensional surface monolayer or crystalline V₂O₅. We have modeled the following specie: a monoxo vanadate (**V**), VO₄³⁻ [10,16,20] a divanate (**VV**), V₂O₇⁴⁻ [13,18,21] and the corresponding hydrated forms, a oxohydroxy vanadium complex (**Vh**), VOH₄²⁻ [13,16,22] and a pyrovanate (**VVh**), V₂O₇H₂²⁻ [13].



The plausibility of the complex  was also evaluated, however positive energy values were obtained; thus this species was disregarded.

These supported V-complexes were modeled by fitting VO_x to local regions of the supported surface. Hydrogen atoms were removed from hydroxyl groups and the fragment VO_x was attached to oxygen atoms. The place of the anchoring site is at/or near the center of the cluster surface in order to minimize border effects.

1.3. Theoretical method

The semi-empirical EH method [23] has been extensively applied to study the electronic structure of molecules. In the present study we have employed a modified version of this method, ICONC, developed by Calzaferri [24]. Although this method does not calculate representative absolute energies, it can be used to predict the qualitative trends in model systems. ICONC has been applied to study the CH₃OH adsorption–oxidation process on V₂O₅ [25] and to the analysis of Ziegler-Natta [26] and VO_x/Al₂O₃ catalyst [13].

The EH method, as originally developed, is not suitable to optimize the distance of a determined moiety to the surface of a cluster. Experimental data of bond length and distances must be used in this method and the parameter selection determines the accuracy of the results. However, in the modified version (ICONC) used in this study, repulsive terms are included; thus, besides the determination of relative energies, opti-

Table 2
EH parameters for V, Ti, Si, Al, O and H

Atom	Orbital	Ionization potential (Ev)	Orbital exponents
V	4s	-8.81	1.30
	4p	-5.52	1.30
	3d	-11.10	4.75 (0.4755) ^a 1.70 (0.7052) ^a
O	2s	-31.60	2.163
	2p	-16.78	2.750
Al	3s	-12.30	1.670
	3p	-6.50	1.383
Si	3s	-20.44	1.60
	3p	-12.41	1.60
Ti	4s	-6.30	1.50
	4p	-3.2	1.50
	3d	-5.90	4.55 (0.4206) 1.40 (0.7839) ^a
H	1s	-13.60	1.00

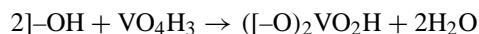
^a Coefficients used in the double expansion of orbitals.

mization of bond length and geometry may be performed with an accuracy of $\pm 10\%$. Hoffman and Juan [27] have used ICONC to carry out the optimization of the bond length of H to a Fe surface.

The experimental parameter (ionization energies taken from spectroscopic data) used in the present calculation are reported in Table 2 for Ti, Al, O, H and V. Since for 4p level no experimental data are available in literature, we have employed parameters taken from ab-initio calculations [28].

The relative stabilization energy (RSE) of a selected supported VO_x species on an oxide carrier is calculated as the difference between the energy corresponding to VO_x anchored to the cluster support and the summatory of the energy of the cluster and a VO_x unit infinitely separated from the surface (Table 3).

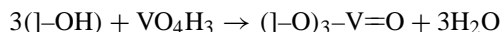
We have also calculated the formation energy as the energy of the reaction between a specific support cluster and a given (modeled) vanadium species. For the **Vh** formation, the involved formation reaction may be represented by the following equation:



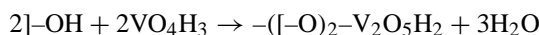
This reaction is also depicted in the following scheme:



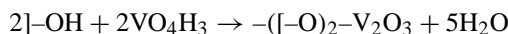
The considered reaction for monovanadate **V** formation is:



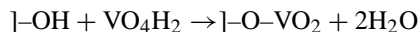
When pyrovanadate **VVh** formation is analyzed, the formation reaction is:



When the divanadate formation is considered, the reaction is



When **VO** formation is involved, the reaction is



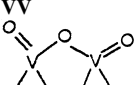
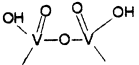



2. Results and discussion

In Table 3 we have reported the RSE and relative formation energy (RFE) of all the modeled VO_x specie supported on silica and titania as calculated with ICONC. Both RSE and RFE determine the plausibility of a given postulated VO_x species. The negative values indicate the favorable situation. Results corresponding to the most plausible species on $\gamma\text{-Al}_2\text{O}_3$, from a previous study [13], are also presented. To allow general comparison between the three oxide carriers, all energy values were referred to the lowest calculated absolute value (-91.08 eV, corresponding to **VVh** on TiO_2). Figs. 1–7 show some of the modeled species supported on titania, alumina and silica clusters. For the sake of simplicity, all the atoms involved in the calculations are not shown in these figures, and only the most relevant features of the structures are depicted.

Regarding SiO_2 , it is interesting to note that none of the postulated V-structure can be attached to the most abundant plane, the (1 1 1) one, since they do not match the structure of this surface. For (1 0 0) plane of silica, calculations have thrown negative RSE and RFE values for **V** and **Vh** (depicted in Figs. 2 and 3) specie, while unfavorable energetic situation arise

Table 3
RSE, RFE and V–O_s bond lengths for the postulated VO_x specie

VO _x species	Support	RSE (eV)	RFE (eV)	V–O _s length (Å)
Vh 	TiO ₂ (001)	–0.78	–0.84	2.01
	Al ₂ O ₃ (110)D	–0.216	–0.035	1.86
	SiO ₂ (100)	–0.14	–0.017	1.61
	SiO ₂ (111)	–	–	–
V 	TiO ₂ (001)	–0.49	–0.588	1.98
	Al ₂ O ₃ (100)	–0.306	–0.027	1.80
	SiO ₂ (100)	–0.208	–	1.40
	SiO ₂ (111)	–	–	–
VV 	TiO ₂ (001)	–0.86	–0.98	2.01
	Al ₂ O ₃ (110)D	–0.47	–0.17	1.86
	SiO ₂ (100)	–0.14	–0.134	3.25
	SiO ₂ (111)	–	–	–
VVh 	TiO ₂ (001)	–0.88	–1.00	2.11
	Al ₂ O ₃ (110)D	–0.21	–0.21	1.82
	SiO ₂ (100)	0.03	–0.10	3.20
	SiO ₂ (111)	–	–	–
VO 	SiO ₂ (111)	–0.146	–0.07	1.3

for both dimeric complexes supported on silica. Thus di- or pyrovanadates could not be formed on silica surface. This result is in agreement with numerous

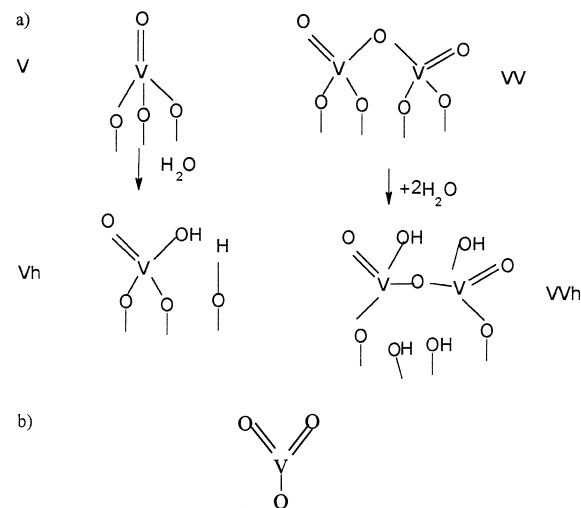


Fig. 1. (a) V, VV specie and their hydrated forms; (b) VO specie.

studies [16,29,30], which indicate that, for low vanadia loading, the V-surface species is an isolated VO_x monomer. On the contrary, the present results are in discrepancy with those from Arena et al. [31], who postulated, from UV–VIS and DRS characterization results that di- or oligomeric structures are present on low loaded VO_x/SiO₂ catalysts. Our results are also in disagreement with the studies carried out by Jonsson et al. [32] and Scharf et al. [33], who proposed the existence of oligomeric VO_x specie on silica surface.

As stated above, the present study is restricted to low loaded catalysts; however, we could speculate that, no surface vanadia monolayer could be formed on SiO₂, since calculations reveal that VO_x units do not polymerize on the surface of silica. The dimer species on SiO₂ (100) are not so stable as the monomeric one (see Table 3).

As commented above, none of the postulated V-structure match the anion array of the most abundant plane of SiO₂, the (111) one. Thus, the reported diminution of the near infrared band corresponding to the isolated Si–OH groups on (111) plane with in-

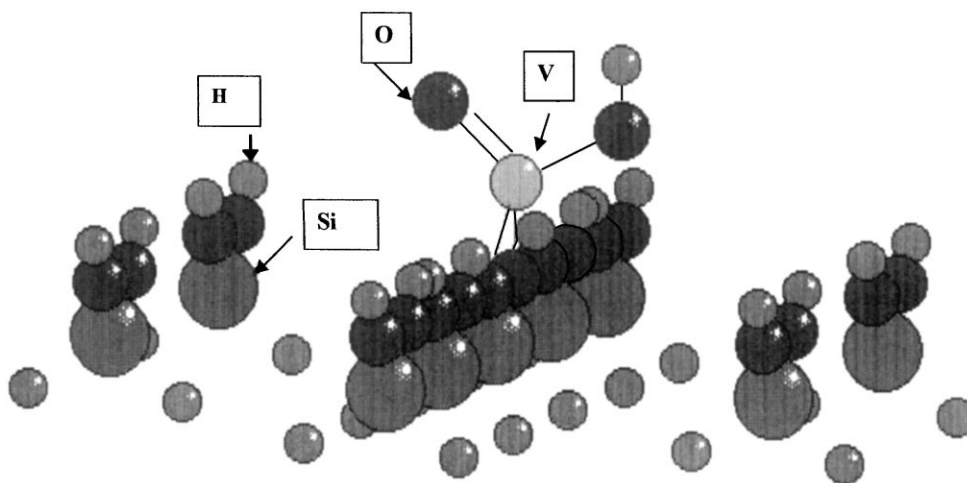


Fig. 2. **Vh** supported on SiO_2 (100).

creasing vanadia loading [34] could not be explained if only **V** or **Vh** species are considered. For this reason we have postulated an additional VO_x species, a dioxovanadate **VO** represented in Table 3 and Fig. 3. Certainly, this structure has not been proposed for V-supported complex, however in the light of the present results it is highly plausible. Furthermore, it could be related with unassigned strong Raman band in the $400\text{--}600\text{ cm}^{-1}$ region [34].

Monomers would be predominant on both planes of silica, monoxo vanadate **V** on the (100) plane, while **VO** would exist on (111) plane.

Regarding TiO_2 and $\gamma\text{-Al}_2\text{O}_3$, RSE and RFE values suggest that dimeric species are more plausible than monomeric ones, since both relative energies are lower for pyro and divanadates than for the monomeric species. However, this trend is more pronounced for $\gamma\text{-Al}_2\text{O}_3$, for which RSE and RFE diminish approximately by half when monomeric structures condense to form dimeric VO_x . This theoretical result would indicate that while on alumina mainly dimer species would be present, for TiO_2 both species could coexist at low vanadia loading. In Fig. 5 the dimeric **VV** supported on (110)C plane of alumina is shown,

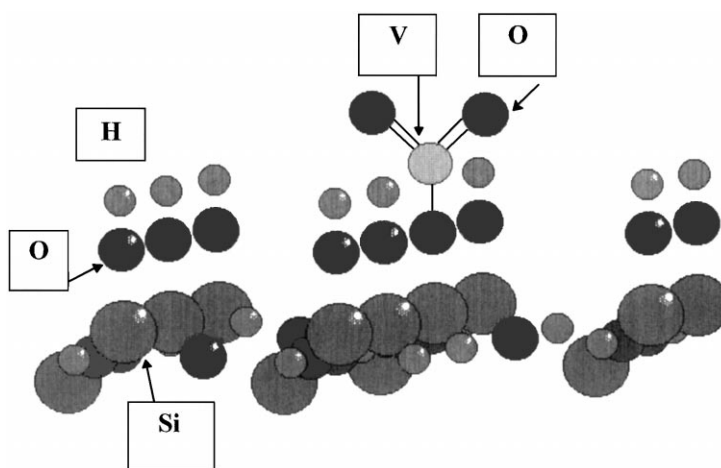


Fig. 3. **VO** supported on (111) plane of SiO_2 .

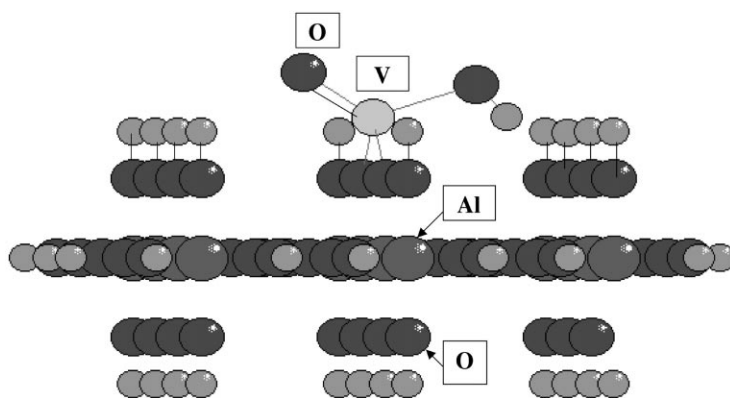


Fig. 4. **Vh** supported on (100) plane of $\gamma\text{-Al}_2\text{O}_3$.

while in Figs. 6 and 7 **Vh** and **VV** supported on titania are represented. Some researchers have suggested the presence of V-dimers on alumina catalysts [21,35]. Unfortunately, we cannot corroborate the result corresponding to titania with experimental facts since, to our knowledge, the relative concentrations of isolated and oligomeric VO_x units have not been quantified.

Summing up, from the evaluation of RSE and RFE, the following scenario could be envisaged; uniquely monomers, **V** and **VO** are present on SiO_2 surface; on TiO_2 **Vh** monomers and **VVh** dimers would coexist,

while on $\gamma\text{-Al}_2\text{O}_3$ **VV** and **VVh** dimers would be the predominant specie.

When comparing the supports of different composition, one can observe that V-surface specie on TiO_2 are the most stable ones since they possess the lowest RSE values (in the $-1.00/-0.49$ eV range). The fact that dispersed vanadia is highly stable on titania is reflected by the long life of VO_x/TiO_2 industrial catalysts [2,8,36]. On the other hand, VO_x on SiO_2 possesses the most unfavorable stabilization energy values (in the $-0.20/-0.14$ eV range). This, in

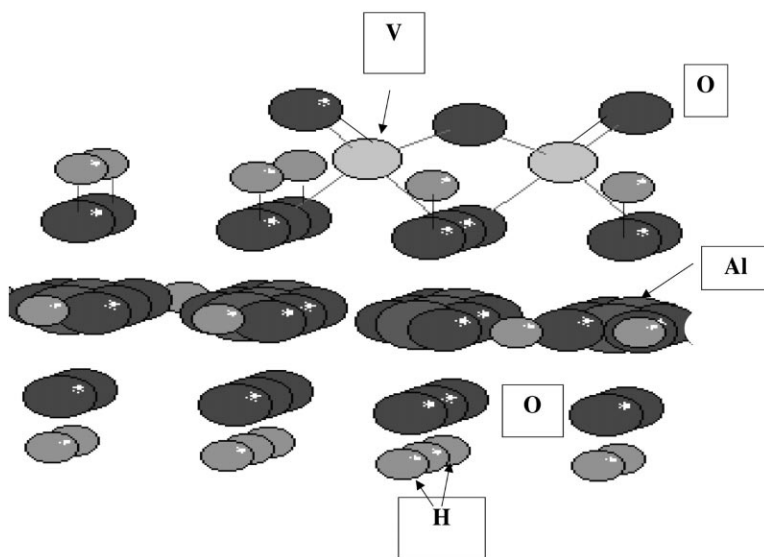


Fig. 5. **VV** supported on (110)C plane of $\gamma\text{-Al}_2\text{O}_3$.

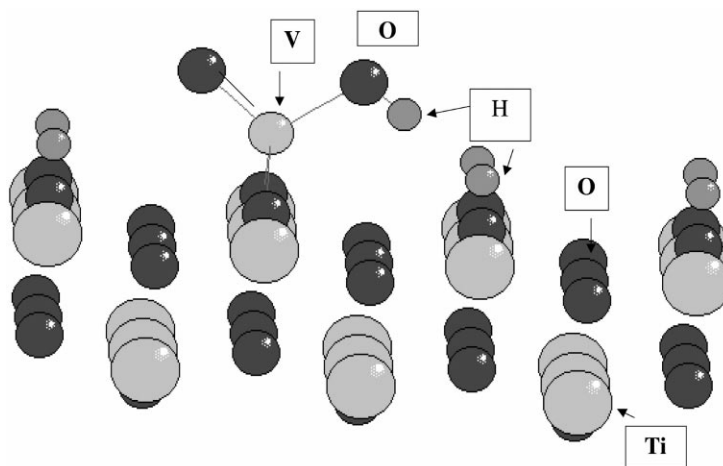


Fig. 6. Vh supported on (001) plane of TiO₂ (anatase form).

agreement with the fact that a sintering of dispersed vanadia, occurs when crystalline vanadium pentoxide is present on silica [19].

The areas corresponding to the most plausible VO_x species were calculated taking into account the structure of the VO_x moieties and the lattice parameters of the support. The minima distances to avoid repulsion were also taken into account. These values are presented in Table 4 (as nm² per VO_x unit). It can be observed that relatively low areas correspond to titania and alumina (0.14 and 0.24 nm², respectively) while the specific surface occupied by a V-surface structure on SiO₂ is rather large (1–0.65 nm²). The areas could be related with the maximum amount of molecularly

dispersed vanadia that can be accommodated without the formation of three-dimensional V₂O₅, on a given support, TiO₂, SiO₂ or γ-Al₂O₃. The calculated maxima loading are reported in Table 4 (as VO_x units per nm² of the carrier). In line with this, one could expect that the specific amount of dispersed vanadia fixed by the support follows the increasing order TiO₂ > γ-Al₂O₃ > SiO₂. The predicted order is in agreement with the results of Went et al. [16] who have established, by means of O₂ chemisorption, that for a given specific vanadium concentration, vanadia is most highly dispersed on TiO₂ than on γ-Al₂O₃, while the capacity of SiO₂ to disperse vanadia is the lowest. In addition, we have calculated the specific concentration of dispersed vanadia from the published data from the specific concentration of dispersed vanadia taken by a support. These values are presented as VO_x loading (U nm⁻² of the carrier) the third column of Table 4. It is worth to note that supports with different specific area, amount of impurities, etc. have been used to prepare the supported vanadia catalysts. Furthermore, different precursors and preparation conditions have been involved. However, as it can be observed in Table 4, the specific amount of vanadium fixed by the support is quite characteristic for a specific oxide and it could have been predicted from the theoretical data. Besides, this agreement indicates that the model of the support cluster is quite representative of the real system and that almost all the OH groups are reactive sites for the anchoring of VO_x.

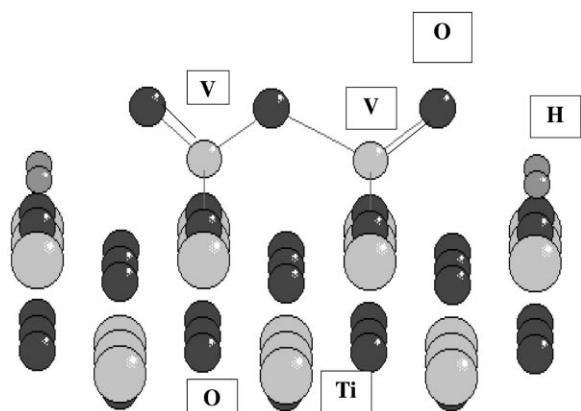


Fig. 7. Vv supported on (001) plane of TiO₂ (anatase form).

Table 4
Specific vanadia loading and VO_x area

Support	Surface area (m ² g ⁻¹)	VO _x loading (U nm ⁻²) from published data	References	VO _x area (nm ²) from modeled clusters	VO _x loading (U nm ⁻²) from modeled clusters
TiO ₂	50	8.74	[12]	0.14 (VV)	6.9 (VV) TiO ₂ (0 0 1)
TiO ₂	50	5.84	[37]		
γ-Al ₂ O ₃	180	3.6	[12]	0.24 (VV)	4.7 (VV) Al ₂ O ₃ (1 1 0)D
γ-Al ₂ O ₃	138	4.9	[21]		
SiO ₂	300	0.3	[38]	0.65 (V)	2.4 (V)SiO ₂ (1 0 0)
		0.7	[40]	1.28 (VV)	0.78 (VV) SiO (1 0 0)
		2.6	[34]	1.01 (VO)	0.99 (VO) SiO ₂ (1 1 1)

When calculating RSE for a determined V-surface structure, bond lengths and angles were varied in order to obtain the lowest energy value. Regarding V=O and V–OH bond lengths, for all the considered supports, the energy minima were obtained for values similar to those corresponding to typical inorganic compounds (1.63 and 1.78 Å for V=O and V–OH, respectively). On the contrary, the optimal V–O_s (O_s, lattice oxygen) bond lengths are strongly influenced by the oxide carrier composition. In Table 3 we have reported the optimal lengths of V–O_s bonds and in Fig. 8 the

dependence of RSE on V–O_s bond lengths is shown. As it can be observed in the Table 3, the lengths, and for consecution, the strengths of V–O_s, vary with the support composition. According to our results the trend in the strength of the bond V-surface would be SiO₂ > γ-Al₂O₃ > TiO₂. These calculations would explain the origin of the influence of the support on the catalytic pattern of VO_x catalyst supported on different oxide carriers and would be in agreement with Wachs et al. [10,12] who suggested that bridging oxygen atoms are responsible for the catalytic behavior of

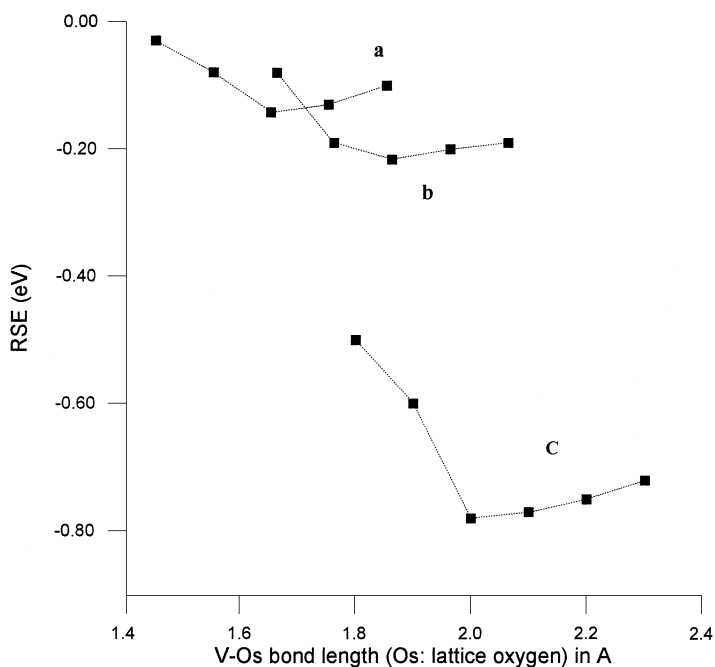


Fig. 8. RSE vs. V–O_s bond length for a V species supported on (a) SiO₂; (b) γ-Al₂O₃ and; (c) TiO₂.

supported catalysts when hydrocarbon oxidation reactions are considered. They concluded that the difference in catalytic activity (TOF) would depend on the strength of V–O_s bond and would correlate with the ease of oxygen removal from the carrier. On the other hand, some researchers have addressed the activity of supported vanadia catalysts with terminal V=O bonds [22]. This interpretation is in disagreement with our results, since this bond is not modified by the composition of the oxide carrier or by the local surrounding of the V atoms and similar catalytic pattern should be expected for vanadia supported on any of the carriers. Only for the case of VO supported on SiO₂ one could suggest that the V=O bond is active, since the only V–O_s bond is quite short; however, this supposition is quite speculative.

Temperature programmed reduction (TPR) experiments have been widely used to investigate the different types of VO_x specie present in vanadia catalyst [38,39]. The temperature of the peak maxima, T_{\max} , is observed to be a strong function of the oxide support. Although for the same kind of catalysts prepared in different laboratories, different values of T_{\max} were obtained, the whole of the reported results shows that the order of reducibility is VO_x/SiO₂ > VO_x/γ-Al₂O₃ > VO_x/TiO₂. In the light of the present theoretical calculations, this trend is easily ascribed to the difference in V–O_s length.

Other point to consider is the acidity of surface vanadia species. For the bare supports, no surface acidity has been detected for SiO₂ [40] while it was established that γ-Al₂O₃ and TiO₂ mainly possess surface Lewis acid sites and the relative strength of these sites is higher for the former than for the latter oxide. Unsupported V₂O₅ possess both Brønsted and Lewis surface acidity. When vanadia is supported on TiO₂ or γ-Al₂O₃, with the formation of a highly dispersed vanadia phase, a decrease in the number of surface Lewis acid sites and an increase in the number of surface Brønsted acid sites has been detected [40]. The diminution of Lewis acidity would be related with the fact that former uncoordinated Al and Ti cations coordinate with VO_x. The OH groups of V^h and V^{vh} would originate the augmentation of Brønsted acid sites. In contrast to the other supported vanadia catalysts, neither Brønsted nor Lewis acidity have been detected for highly dispersed vanadia on SiO₂. In this sense, the results of EH calculation can explain this

lack of acidity: V or VO specie (the most important ones on SiO₂) has no acidity, neither Brønsted nor Lewis.

3. Conclusion

The nature of the VO_x specie depends on the composition of the support. At low vanadia loading, SiO₂ surface is covered with V-monomers; for the case of γ-Al₂O₃ and TiO₂, dimeric V-structures are predominant. The composition of the support also influences the VO_x–support interaction, since the strength of V–O_s bond is altered by the nature of a given support. Taking into account the present results, the difference in catalytic behavior corresponding to the VO_x catalysts supported on silica, alumina or titania should be addressed to vanadia–support interaction.

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