A combined theoretical and experimental study of supported vanadium oxide catalysts

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Abstract

In order to investigate the nature of VO_x species supported on SiO_2, γ-Al_2O_3 and TiO_2, a combination of a theoretical study and an experimental characterization is carried out. A molecular orbital approach of the extended Hückel type is performed to measure the plausibility of different postulated VO_x species (monovanadates, divanadates, polyvanadates, etc.). The experimental characterization is performed by TPR, oxygen uptake measurements and FTIR of adsorbed pyridine. Both theoretical and experimental results indicate that the structure of VO_x and its interaction with the support are strongly influenced by the nature of the oxide carrier. On TiO_2 and γ-Al_2O_3 dimers are the most abundant species, while on SiO_2 only monomers are formed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: VO_x catalysts; Catalyst characterization; Extended Hückel; Pyridine adsorption

1. Introduction

Vanadia supported on oxide carriers is widely used as a heterogeneous catalyst in a large number of selective oxidation reactions [1–5]. The most used supports are TiO_2, γ-Al_2O_3 and SiO_2. For low vanadium contents, vanadium oxide is molecularly dispersed on the surface of the carriers and its structure is quite unlike the corresponding to the bulk oxide. It is generally accepted that monomers or dimers are present in low loaded V samples, while polyvanadates and a two-dimensional monolayer may be present in more loaded V catalysts (from now on these species will be named as VO_x). For still higher concentration, vanadium pentoxide crystallites are formed. Numerous studies have been carried out to highlight the

nature of VO_x [6–12]. However, the specification of the structure of the monomers, dimers or of the groups forming the monolayer is not easy, and it is a topic of debate. In this context, theoretical calculations may be helpful and they should be considered as an adjunct to experimental surface studies.

The present work attempts to analyze the structure, the reducibility and acid properties of VO_x/TiO_2, VO_x/γ-Al_2O_3 and VO_x/SiO_2 by means of a combined theoretical—experimental study. For the theoretical approach, a molecular orbital study of the extend Hückel type (EHMO) is carried out in order to determine the plausibility of different structures of VO_x. Besides, samples of VO_x supported on TiO_2, γ-Al_2O_3 and SiO_2 are characterized by means of temperature-programmed reduction (TPR) and oxygen uptake at high temperature to study the nature of the supported VO_x species. The acid character of surface VO_x supported on the three carriers is

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also studied by means of FTIR spectra of adsorbed pyridine on the samples. This study is undertaken to probe the possible relationships between acidic and structural properties of supported VO_x. Theoretical results are discussed in the light of experimental data.

2. Methods

2.1. Modeling of the supports

We have constructed models of the supports, TiO_2, $\gamma\text{-}Al_2O_3$ and SiO_2 from the cluster approach. In doing so, the so-called dangling bonds appeared. For this reason, hydrogen atoms were used to complete the internal cation coordination. For the construction of the cluster, we have taken into account the X-ray crystal structure of the oxide as well as other experimental characterization data. Only some planes are preferentially exposed in the three cases, and only these planes should be the anchoring sites for the VO_x species.

For the TiO_2, we have considered the anatase form, since this material is the most used as a support for VO_x catalysts [13]. The surface of anatase consists mainly in (0 0 1) plane [14].

The model of $\gamma\text{-}Al_2O_3$ was constructed based on a tetragonal distorted defect spinel structure with cations arranged in an approximately cubic close packed oxygen array. We have considered that the preferentially exposed planes are (1 0 0) and (1 1 0) ones [15,16]. Two cation arrangements are present in the spinel lattice parallel to the (1 1 0) plane, the C and D layers. In the C layer equal number of cations are aligned in tetrahedral and octahedral interstices between rows of oxygen atoms, whereas in the D layer only cation positions in octahedral interstices occurs.

For the case of SiO_2, a structure similar to that of β-crystoballite was considered. Studies of hydroxylated silica suggest that the surface is heterogeneously

$M = Ti, Si \text{ or } Al$
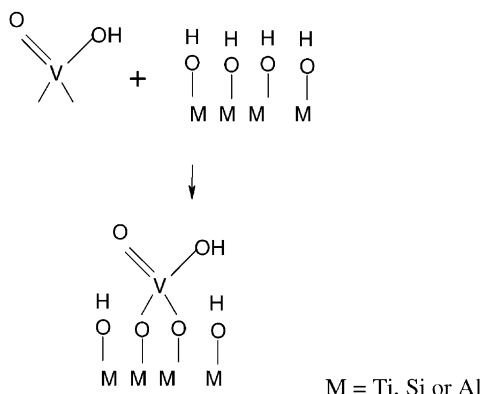
Scheme 2.

composed of (1 0 0) and (1 1 1) faces [16], the former being less abundant than the latter [17].

2.2. Modeling of VO_x/support system

Based on previous work [18,19] and from literature data, in the present work, we have studied five postulated structures. They are shown in Scheme 1.

For modeling a specific VO_x species supported on a cluster, we have removed hydrogen atoms from OH groups of a determined plane of the carrier and we have attached each of the five considered structures (see Scheme 1) to local points of the three oxides clusters, titania, alumina and silica. To label, the anchoring of **Vh** may be represented as Scheme 2 shows.

2.3. Relative energies calculations

Our calculations were performed using a modified version of the traditional extended Hückel method, implemented with the ICONC program [20]. ICONC includes repulsive terms in the energy and allows calculating relative stabilization energy (RSE) and relative formation energy (RFE). The former is calculated

Vh (13, 19, 21)   **V** (2,20)   **VO** (20)   **VV** (19, 22)   **VVh** (19,20)
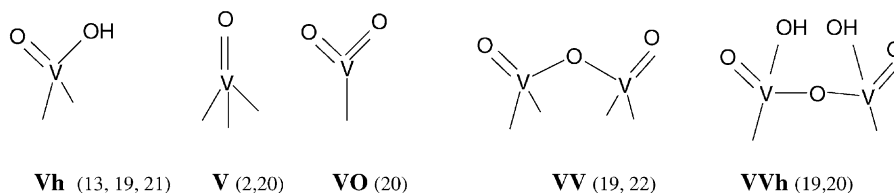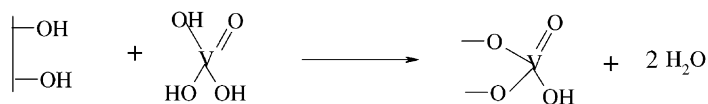
Scheme 1.

Scheme 3.

as the difference between the energy corresponding to the VO_x/support system and the summary of the energies corresponding to the VO_x moiety and the support cluster infinitely separated. RSE can be expressed as

$$RSE = E_{VO_x/support} - (E_{support} + E_{VO_x})$$

It is interesting to note that a minima of RSE may be calculated by varying the length of the bond that bridges vanadium atom to the lattice oxygen In this way, this bond length may be determined with an accuracy of $\pm 10\%$ [21]. We have also varied bond angles of supported species when searching for the lowest value of RSE. Thus, from calculation, bond lengths and structure determinations may be performed.

The RFE is the energy corresponding to a pseudo reaction between the support and a pseudo VO_x compound, with the production of water. Scheme 3 shows the formation reaction that we have considered in order to calculate the RFE corresponding to the **Vh** species.

2.4. Catalysts preparation

The samples were prepared by reaction of γ-Al_2O_3 (Rhône-Poulenc, $120\,m^2/g$), TiO_2 ($40\,m^2/g$) or SiO_2 ($210\,m^2/g$) with an organic solution of $V(AcAc)_3$ (Aldrich, 99.99%). The preparation was performed at room temperature in anaerobic conditions. After 24 h, the solids were filtered and calcined in air at 400 °C for 4 h. For more details of the preparation method see [22]. The vanadium contents were determined by atomic absorption spectroscopy.

2.5. Temperature-programmed reduction (TPR)

Characterization of all the catalysts was performed by TPR in a conventional equipment. The samples were reduced in tubular furnace in a Ar/H2 (5%) mixture. The flow rate was $20\,cm^3/min$ and the furnace was linearly heated from room temperature to 600 °C with a heating rate of 10 °C/min. A TCD cell detected the hydrogen consumption.

2.6. Oxygen uptake

Measurements were performed in a conventional glass volumetric apparatus equipped with a pumping system which allow to attain pressures as low as 10^{-6} Torr. Before measuring, the samples were reduced in flowing hydrogen at 500 °C during 3 h and outgassed for 20 h at the same temperature and cooled down to 300 °C. Subsequently, doses of chromatographic oxygen were admitted into the sample cell and the equilibrium pressures were measured with a Baratrom K instrument. The amount of oxygen atoms uptake during reoxidation was measured at different equilibrium pressures in the 10–500 Torr range were obtained. From the extrapolation of the isotherm to zero pressure, the amount of oxygen uptake by the sample was measured. The O/V atomic ratio was calculated by extrapolating the isotherms to zero pressure.

2.7. FTIR spectra of adsorbed pyridine

The supports γ-Al_2O_3, TiO_2, and SiO_2 and the corresponding VO_x-supported samples were heated in airflow at 500 °C for 1 h. Subsequently, temperature was lowered to room temperature and a nitrogen flow passed through pyridine container before contacting samples for 30 min; the solids were further flushed under N_2 at 100 °C during 1 h. Then, FTIR spectra were recorder in a FTIR 520 Nicolet-Instrumet, with a resolution of $4\,cm^{-1}$ and 10 scans.

3. Results and discussion

3.1. Relative energies calculations

Before carrying out the calculation of the energies corresponding to the five proposed VO_x-supported species, structural consideration of the anion array of the support were performed. Regarding the exposed planes of alumina and titania and the (1 0 0) plane of
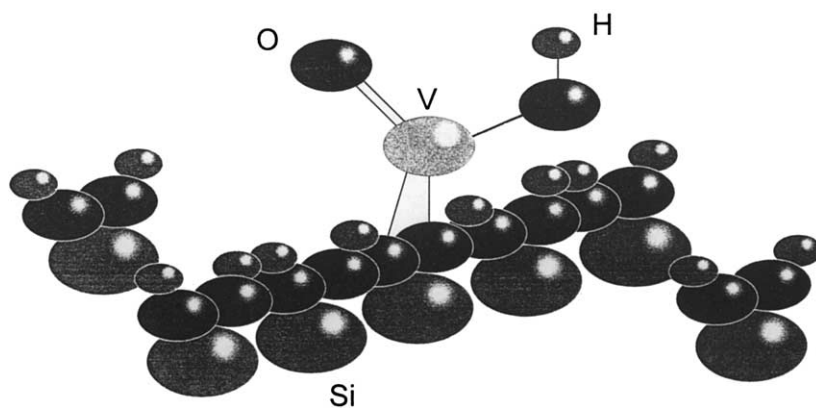
Fig. 1. **Vh** on SiO$_2$(1 0 0).

silica, the five above mentioned structure, **VO**, **V**, **Vh**, **VV** and **VVh** match with the oxygen array the supports surfaces. However, for the most abundant plane of silica, the (1 1 1) plane, only **VO** species can be attached to the oxygen atoms of the carrier. Figs. 1–5 show how some VO$_x$ structures are attached to the oxide carriers. For the sake of simplicity, not all the atoms involved in calculations are shown.

The formation and the stabilization energies (RSE and RFE) of each supported structure are reported in Tables 1–3. Both, RSE and RFE determine the plausibility of a given VO$_x$ species. The negative values indicate the favorable situation. To allow general comparison between the three oxide carriers, all energy values were referred to the lowest calculated value of -91.08 eV, corresponding to **VVh** on TiO$_2$.
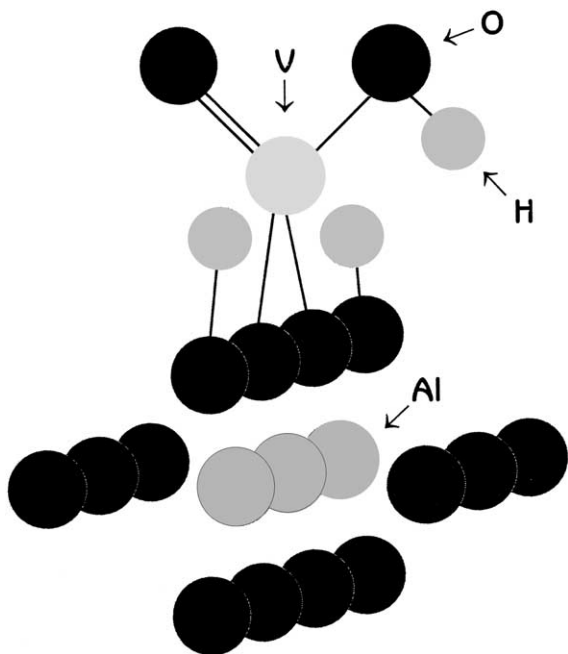
Fig. 2. **Vh** on γ-Al$_2$O$_3$(1 1 0)C.
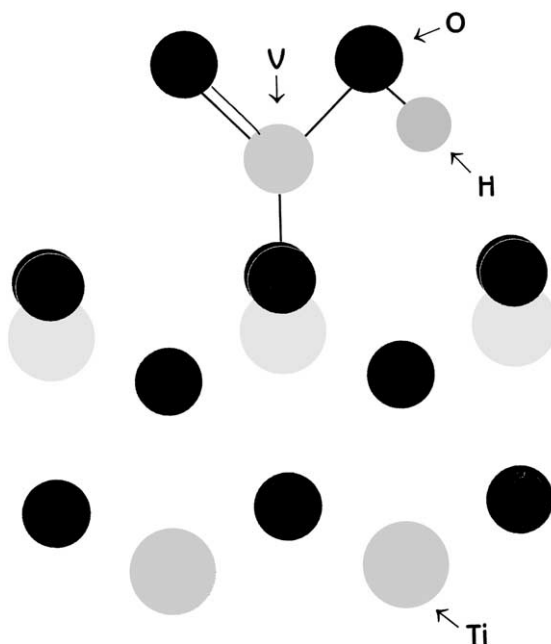
Fig. 3. **Vh** on TiO$_2$(1 0 0).
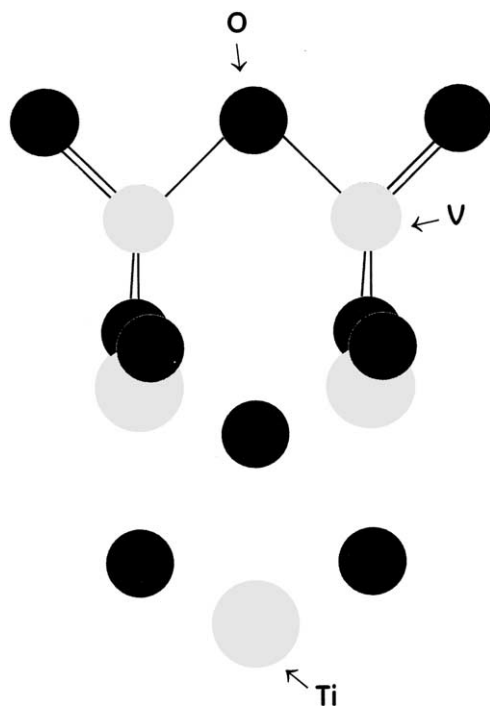
Fig. 4. **VV** on TiO$_2$(1 0 0).

Let us evaluate the RSE and RFE values for titania and alumina. For all the planes, dimeric species were more plausible than monomeric ones. This results would indicate that, when low loaded catalysts are considered, VO$_x$/γ-Al$_2$O$_3$ and VO$_x$/TiO$_2$ mainly consist of dimeric **VVh** and **VV** species. The presence of V-dimers on vanadia catalysts have been proposed by some researchers [4,5].

Since RSE and RFE corresponding to monomeric species **Vh** and **V** on alumina and titania were relatively low, monomeric species should not be completely disregarded, and a low concentration of these species on titania and alumina should be expected.

On the other hand, monomeric species were the most plausible species for both planes of silica. **VO** and **V**, in (1 1 1) and (1 1 0) planes, respectively would be the most abundant species when VO$_x$/SiO$_2$ catalysts are considered. Dimeric-supported vanadia species were not probable at all. Thus, calculations revealed that no surface vanadia monolayer could be formed on SiO$_2$, since VO$_x$ units do not polymerize on the surface of silica. This theoretical result is in agreement with experimental evidence [12].

Taking into account the whole of the RSE and RFE values shown in Table 2, the following scenario must
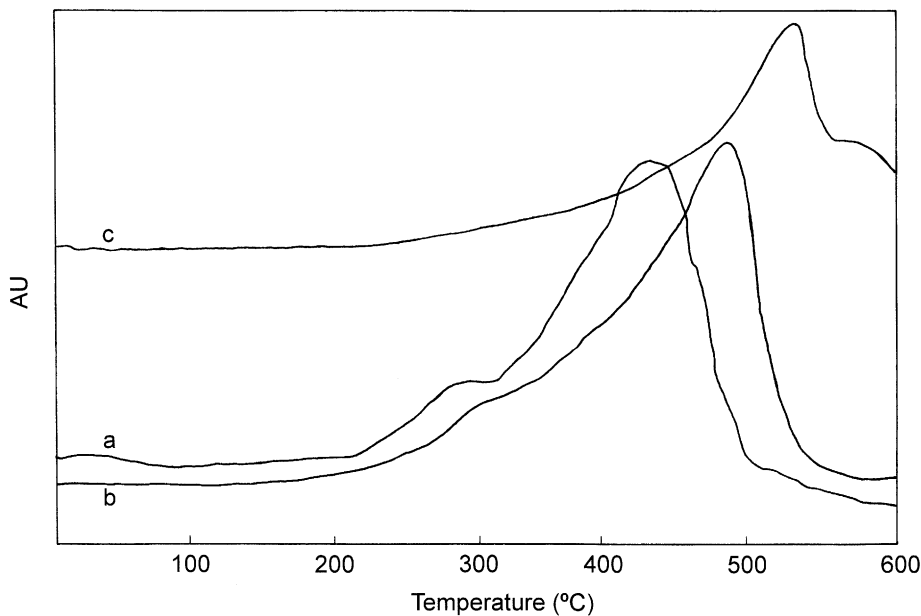

Fig. 5. TPR profiles for (a) VO$_x$/TiO$_2$; (b) VO$_x$/γ-Al$_2$O$_3$; (c) VO$_x$/SiO$_2$.

Table 1
RSE, RFE and V–O$_s$ bond lengths for the postulated VO$_x$ species on TiO$_2$

Exposed plane	VO$_x$ species	RSE (eV)	RFE (eV)	V–O$_s$ length (Å)	V–O–V length (Å)
TiO$_2$(0 0 1)	**V**	−0.78	−0.84	2.01	–
	Vh	−0.49	−0.59	1.98	–
	VO	+0.123	+0.087	1.34	–
	VV	−0.86	−0.98	2.01	3.78
	VVh	−0.88	−1.00	2.11	3.52

Table 2
RSE, RFE and V–O$_s$ bond lengths for the postulated VO$_x$ species on γ-Al$_2$O$_3$

Exposed plane	VO$_x$ species	RSE (eV)	RFE (eV)	V–O$_s$ length (Å)
Al$_2$O$_3$(1 0 0)	**V**	−0.306	−0.027	1.80
	Vh	−0.199	−0.003	1.85
	VO	+0.208	+0.005	1.40
	VV	−0.433	−0.119	1.85
	VVh	–	–	–
Al$_2$O$_3$(1 1 0)C	**V**	−0.276	+0.006	1.82
	Vh	−0.204	−0.010	1.85
	VO	+0.312	+0.021	1.52
	VV	–	–	–
	VVh	−0.214	−0.213	1.85
Al$_2$O$_3$(1 1 0)D	**V**	–	–	–
	Vh	−0.216	−0.035	1.86
	VO	+0.123	+0.009	1.43
	VV	−0.470	−0.172	1.86
	VVh	−0.210	−0.210	1.81

be envisaged: alumina and titania surfaces are preferentially covered by dimeric **VV** and **VVp**. A low concentration of the monomeric species **V** and **Vh1** would also be present, mainly on titania. Uniquely monomers, **V** and **VO** are present on SiO$_2$ surface.

Table 3
RSE, RFE and V–O$_s$ bond lengths for the postulated VO$_x$ species on SiO$_2$

Exposed plane	VO$_x$ species	RSE (eV)	RFE (eV)	V–O$_s$ (Å)
SiO$_2$(1 0 0)	**V**	−0.208	–	1.40
	Vh	−0.14	−0.017	1.61
	VO	–	–	–
	VV	−0.14	−0.134	3.25
	VVh	0.03	−0.10	3.20
SiO$_2$(1 1 1)	**V**	–	–	–
	Vh	–	–	–
	VO	−0.146	−0.07	1.30
	VV	–	–	–
	VVh	–	–	–

From these results it was deduced that the nature of the support strongly influences the structure of the vanadium-supported complexes.

Another interesting point is the bond lengths corresponding to the supported VO$_x$ complexes. As commented above, the bond lengths were varied in order to obtain the minima in RSE for each VO$_x$ complex. The bond length values are reported in Table 2. For all the complexes, notwithstanding the nature of the support, the V=O bond lengths were found to be 1.68–1.65 Å, while for **Vh** and **VVh** complexes the V–OH bond length were 1.78–1.80 Å. These values are similar to the bond lengths corresponding to known inorganic vanadium compounds (metavanadates, decavanadates, etc.) [23].

On the other hand, the lengths corresponding to V–O$_s$ (O$_s$=: lattice oxygen) bond were strongly influenced by the nature of the carrier. Thus, for all the plausible species on titania, approximately 2 Å was the value for the V–O$_s$ bond; for the VO$_x$

Table 4

Vanadium loading, fraction of monolayer and oxygen uptake of VO_x samples

Catalyst	V (wt.%)	θ (%)	O/V atomic ratio
$VO_x/\gamma\text{-}Al_2O_3$	2.4	25	0.47
VO_x/TiO_2	1.5	45	0.52
VO_x/SiO_2	2.0	12	0.72

supported on alumina the length was approximately 1.8 Å, while when silica was considered the complexes were bonded with the shortest lengths: 1.3–1.4 Å. Summing up, the length and then the strength of V–O_s bonds were specific of the oxide support. In partial oxidation reactions VO_x-supported catalysts have been found to have different catalytic behavior depending on the support, TiO_2, γ-Al_2O_3, SiO_2, MgO [24,25]. These differences have been ascribed to the nature of catalyst–support interaction and from the present theoretical calculations, it seems as they would be directly related with V–O_s bond strength.

3.2. Experimental characterization

In Table 4, the vanadium loading of all the samples is reported. Assuming that vanadium was well dispersed on the carrier surface and that each VO_x unit occupies $0.1\ nm^2$ [26], the fraction of the support covered by the dispersed vanadia (θ) was calculated and is also shown in Table 4. It can be observed that for all samples submonolayer coverage was achieved.

3.3. Temperature-programmed reduction (TPR)

TPR with hydrogen is a widely used technique for the characterization of reducible solids. The reduction profile is specific of a determined system. On this account, TPR experiments would shed light into the reducibility patter of VO_x catalysts.

Fig. 6 shows the TPR profiles for the three samples. It can be observed that different reduction pattern were obtained for the catalysts supported on different oxide carriers. For VO_x/SiO_2 a main peak at 530 °C and a shoulder at 550 °C were observed. Both TPR spectra corresponding to VO_x/γ-Al_2O_3 and VO_x/TiO_2 samples showed a main consumption in the 450–480 °C range and a small peak around 300 °C. Consumption peaks arised at lower temperature for titania (300 and 440 °C) than for alumina (300 and 480 °C).

We may consider the assignment of a determined VO_x species to a consumption peak taking in mind
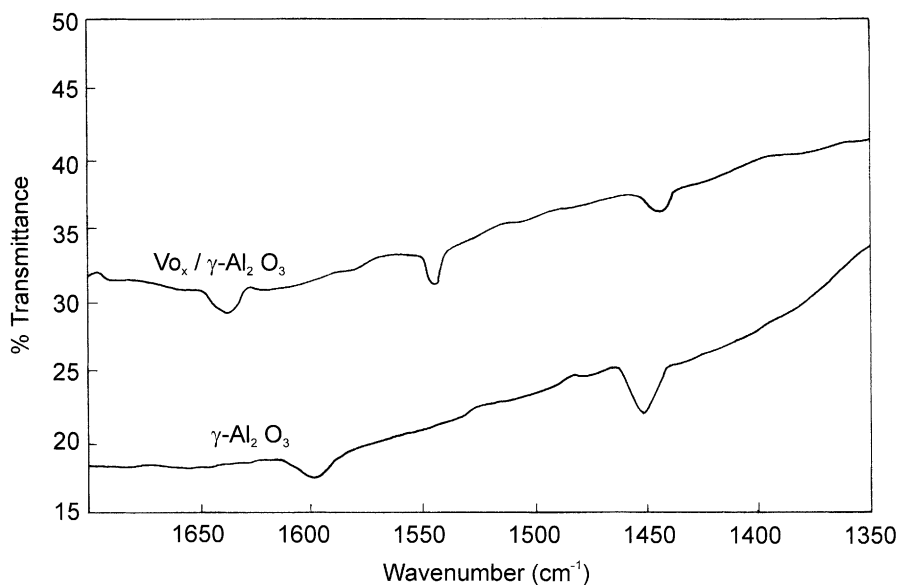

Fig. 6. FTIR VO_x/γ-Al_2O_3 and γ-Al_2O_3 with adsorbed pyridine.

previous theoretical calculation and literature information. It is expected that surface-type species would be reduced at lower temperature than polymeric and bulk like vanadia [27,28]. Thus, for the silica-supported sample the peak at $510\,^\circ$C would be ascribed to the reduction of monomeric **VO** or **V** species. The peak at higher temperature would be related with the reduction of bulk V_2O_5. When titania- and alumina-supported samples were considered, the peak at low temperature would be due to the reduction of monomeric VO_x species (**Vh** or **V**). This consumption was rather meager since the concentration of monomeric vanadates was expected to be low according to theoretical predictions. The peak at higher temperature would be associated with dimeric vanadates.

When comparing the TPR results for all the samples we could establish the following order for the reducibility of the different VO_x species: monomeric vanadate on TiO_2 < monomeric VO_x on γ-Al_2O_3 < dimeric VO_x on TiO_2 < dimeric VO_x on γ-Al_2O_3 < monomeric VO_x on SiO_2 < bulk like species.

Let us try to establish a relation between the reducibility of a determined VO_x species and the nature of the VO_x–support interaction. Let us paid attention to the V–O_s lengths of all the postulated species (Table 2, last column). As commented above, this length is quite typical of the support. Besides, the shortest is the bond the more difficult is the reduction of the VO_x species. Thus, the order of reducibility, as established from TPR results, could be explained in the light of the calculated bond lengths. The **VO** and **V** monomers supported on silica, possessing the strongest V–O_s bond need the highest temperature to be reduced, while dimers supported on titania, with more weak bonds to the support, are more easily reduced.

TPR experiments have been widely used to investigate the reducibility of vanadia catalysts [4,7,27–29]. An universal comparison of the whole of those results is quite difficult since the catalysts were prepared with different vanadium loading, with supports with different amount of impurities, in different laboratories and they were characterized using different experimental conditions. However, a general trend may be observed for VO_x catalysts supported on silica, alumina and titania: the order of reducibility is VO_x/SiO_2 > VO_x/γ-Al_2O_3 > VO_x/TiO_2. Thus, our results would be in agreement with previous works.

3.4. Oxygen uptake

It is important to recall that this measurement is related to the amount of oxygen uptake by previously reduced solids. The extend of reduction, and in consecution the extend of the reoxidation are related to the oxidation state of vanadium and the structure of the VO_x-supported complex [18].

The specific amount of oxygen consumed for the three samples is reported on Table 4, as atoms of oxygen consumed per atom of vanadium on the sample. We observed that similar O/V ratio was obtained for VO_x/TiO_2, 0.52 and VO_x/γ-Al_2O_3, 0.47. The straightforward conclusion was that the same species were involved in the uptake of oxygen. Taking into account that dimers would be the species supported on alumina and titania, we could speculate that the reaction shown in Scheme 4 took place during the reduction pretreatment of VO_x/TiO_2 and VO_x/γ-Al_2O_3. The partially reduced species uptaked one oxygen atom to constitute the dimeric species. The stoichiometry of this reaction would account for the O/V values of 0.5.

Regarding silica-supported sample, the O/V value was quite higher than those corresponding to the other catalysts. Then, the nature of the VO_x species involved in the reduction–oxidation processes was different from the corresponding to vanadia supported on titania or alumina. We suggest that the reactions shown in Scheme 5 were responsible for the O/V values. These reactions would account for a O/V value of the unity, but we speculate that VO_x surface species on silica are hard to be reduced (see TPR profiles) and that not the whole of vanadia was reduced
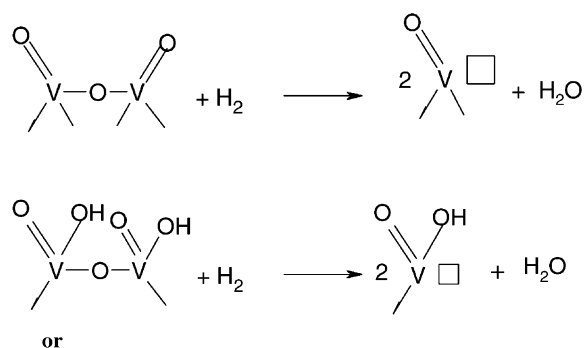
Scheme 4.
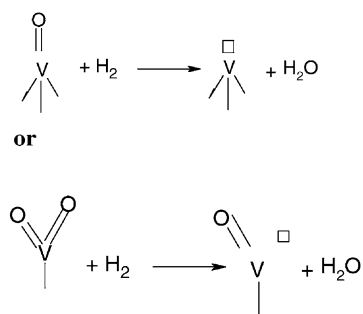
Scheme 5.

during the pretreatment, giving rise to oxygen consumption lower to the expected value (0.78 instead of 1).

3.5. FTIR of adsorbed pyridine

Chemisorption of pyridine followed by FTIR studies is a useful probe for the presence of surface Lewis and Bronsted acid sites [30,31]. The adsorption of pyridine on catalysts surface gives rise to different adsorbed species [32]: pyridine coordinately bonded to Lewis acidic cations, pyridinium cation and hydrogen-bonded pyridine. Two vibrational modes of adsorbed pyridine (19b and 8a) are the most used in IR studied; they are observed at 1440–1450 and

$1580–1600 \, cm^{-1}$ for hydrogen-bonded pyridine, at 1540–1550 and about $1640 \, cm^{-1}$ for pyridinium ion and at 1450–1465 and $1580–1635 \, cm^{-1}$ for pyridine [33]. coordinatively bonded to Lewis acid sites. It is important to note that the hydrogen-bonded pyridine is weakly held to the surface sites and it can be removed by evacuation or by long treatment at low temperature. The samples studied in the present work have been heated before performing FTIR spectra. Accordingly, one do not expect to observe hydrogen-bonded pyridine on the surface of the samples.

The FTIR spectra of chemisorbed pyridine on the bare γ-Al$_2$O$_3$ and the VO$_x$/γ-Al$_2$O$_3$ catalyst are shown in Fig. 7. For the bare support, a pyridine vibration (the most intense one) at $1450 \, cm^{-1}$ and other one at $1595 \, cm^{-1}$ were observed. These bands were detected in the frequency range corresponding to the 8a and 19b modes of vibration of the pyridine coordinatively bonded to Lewis acidic cations (coordinatively unsaturated aluminium cations, Al^{3+} cus). These data are in substantial agreement with the literature values [26,34]. Although hydroxy-groups on the surface of alumina are potentially Bronsted acid, they are not sensed by pyridine [30,32,34]. Accordingly, no bands associated with this type of acidity were detected. On the VO$_x$/γ-Al$_2$O$_3$ catalyst the intensity of the bands corresponding to Lewis
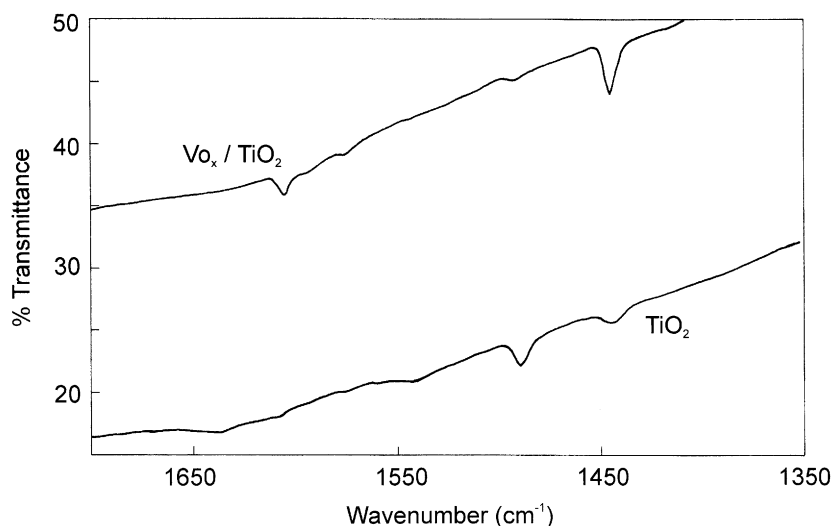

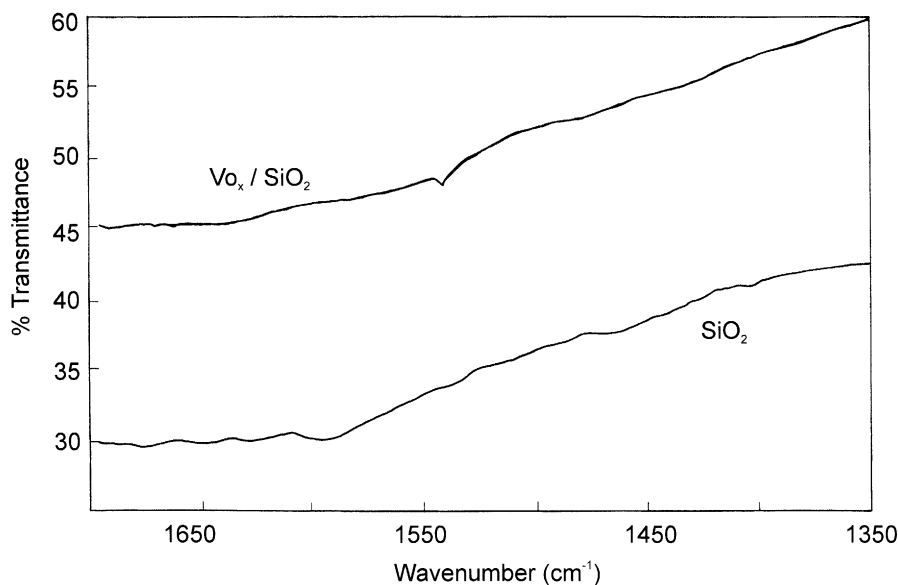Fig. 7. FTIR VO$_x$/TiO$_2$ and TiO$_2$ with adsorbed pyridine.

Fig. 8. FTIR VO_x/SiO_2 and SiO_2 with adsorbed pyridine.

sites decreased. The depletion of these bands would be related to the anchoring of vanadates on Al^{3+} cus. Besides, when vanadia was supported on alumina, vibrations mode at 1544 and $1637\,cm^{-1}$ arisen; they could be ascribed to Bronsted acid sites. Taking in mind that calculations indicated that the most plausible species on alumina were divanadates and in a lesser extend monovanadates, one could speculate that the Bronsted type acidity is related to the hydroxyl ligands of the **VVh** and **Vh** complexes. The acid strength of the hydroxyl groups of VO_x was higher than the corresponding to the OH of the alumina, thus, they could be sensed by pyridine adsorption.

The spectra of the VO_x/TiO_2 and the bare titania are shown in Fig. 8. The same trends as those observed for alumina were found. For the case of TiO_2, the bands at 1452 and $1603\,cm^{-1}$ would be related with the Lewis-type acidity. Both bands appeared at higher frequencies than those corresponding to γ-Al_2O_3. The shift would be related with the fact that the relative strength of Lewis sites was higher for the alumina than for the titania. Regarding VO_x/TiO_2, once again the bands corresponding to the vibration of pyridine adsorbed on Lewis acid sites were diminished due to the

anchoring of VO_x. The presence of Bronsted acidity was revealed by the new bands at 1640 and $1543\,cm^{-1}$ which were also ascribed to hydroxyl belonging to divanadates.

The FTIR spectra of adsorbed pyridine on SiO_2 and on the corresponding vanadia catalyst are shown in Fig. 8. No significant bands appeared on the spectrum corresponding to the probe molecule adsorbed on the bare support. When interpreting this result it is important to recall that, Lewis type acidity sites are not present on silica surface; the only way to generate Lewis acid sites in silica is to pretreat the samples at temperatures higher than $500\,^{\circ}C$ [35] which is not the case of the samples studied in the present work. Due to the high concentration of OH on the exposed planes of silica, Bronsted acidity could be expected. However, it is generally accepted that no bands associated to pyridine adsorbed on protonic acid are noted by the examination of the infrared spectra of adsorbed pyridine [30,35]. On the spectrum corresponding to VO_x/SiO_2, no important modifications have arisen due to the incorporation of vanadia. The minor band at $1540\,cm^{-1}$ could be assigned to pyridinium ion, resulting from the reaction of pyridine with the less abundant **Vh**.

4. General discussion

Theoretical calculations show that the structure, the coordination and the VO_x–support interactions of VO_x species are notably influenced by the nature of the support. These results are corroborated by experimental facts. Let us first discuss the case of SiO_2. By the evaluation of calculated stabilization and formation energies, the presence of dimers can be ruled out for this support, while **VO** and **V** are the most plausible species. Accordingly, O/V atomic ratio, as calculated by Oxygen uptake experiments, indicate that VO_x-supported complexes are constituted by only one V atom. Besides, **VO** and **V** complexes do not posses OH groups associated with vanadium. Thus, one should not expect an augmentation of Bronsted acidity upon the introduction of VO_x to silica. FTIR of adsorbed pyridine are in agreement with this theoretical fact, since only a low amount of Bronsted acidity arises when vanadia is supported on silica. When VO_x–support interaction are considered, calculations of $V–O_s$ bond lengths suggests that a strong attachment of VO_x complexes to the support should be expected. This fact is reflected by TPR which indicates a relatively high reduction temperature of VO_x.

According to calculations, the main difference between silica and alumina or titania is that dimers were the most plausible VO_x species on the latter supports. These predictions are confirmed by Oxygen uptake measurements, which were consistent with the fact that VO_x complexes are constituted by two V atoms.

Taking into account the calculated $V–O_s$ bond lengths, the interaction of dimers with alumina would be slightly higher than VO_x with titania. The analysis of the reduction temperature, as measured by TPR, were in agreement with this, since VO_x supported on TiO_2 are easier to reduce than **V** species on alumina. Different structures for these dimers are possible: **VVh** and **VV**. Without data obtained from structural spectroscopic studies, it is hard to discriminate between the postulated structures for dimers. However, FTIR spectra of adsorbed pyridine on VO_x/TiO_2 and VO_x/Al_2O_3 show an interaction of this probe molecule with Bronsted acid site (associated with OH groups belonging to VO_x complexes). These results assure the existence of **VVh** complex. Summing up, **VVh** dimers are the most abundant species on the surface of alumina and titania.

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