

A combined theoretical and experimental study of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst

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Abstract

In order to investigate the nature of VO_x supported on $\gamma\text{-Al}_2\text{O}_3$ a combination of a theoretical study and experimental characterisation is carried out. A Molecular Orbital approach of the Extended Hückel type is performed to calculate the formation and the stabilisation energies of postulated VO_x species. The evaluation of these energies indicates that pyrovanadates and divanadates are plausible species. Experimental characterisation of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts was performed by TPR and Oxygen Uptake Measurements to corroborate theoretical models. Experimental results also indicate that $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst with low vanadium loading should be envisaged as supported vanadium dimers. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium supported catalysts; Extended Hückel; Catalyst characterisation

1. Introduction

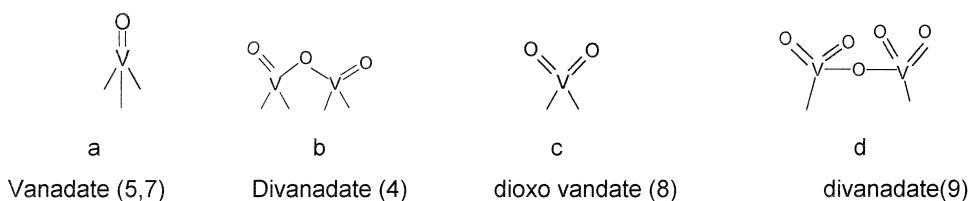
Supported vanadium oxide on different carriers is widely used as a heterogeneous catalyst for partial oxidation of hydrocarbons and for the reduction of NO with NH_3 . The highest activity and selectivity is achieved when highly dispersed species are present, rather than vanadium pentoxide crystallites [1,2].

The structure of the highly dispersed vanadia has been extensively studied and much research work has been published [3–11]. There is a

consensus regarding that, at low loading, vanadia is molecularly dispersed, whereas at higher loading, V_2O_5 crystallites are formed. However, the exact structure of the species (from now on VO_x) which constitutes the monolayer is a matter of controversy and it is interesting to note that a large variety of structures have been proposed: Monovanadates [5,7], divanadates [4,9], polyvanadates [11], etc. In Scheme 1 some of them are shown.

In fundamental studies in heterogeneous catalysis, it is desirable to establish relationships between surface structures and catalytic properties of a system. In this spirit, the determination of the actual structure of VO_x species can provide useful information leading to a better un-

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Scheme 1.

Understanding of the elementary steps of heterogeneously catalysed reactions. This paper aims to determine the exact nature of the dispersed vanadium species. In pursuing this, a combination of a theoretical study and an experimental characterisation of $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ system has been performed. As far as we know, supported vanadium oxide structures have not been analysed by a theoretical approach. In the present work, a Molecular Orbital study of the Extended Hückel type has been carried out for vanadium oxide supported on $\gamma\text{-Al}_2\text{O}_3$. Selected supported species have been modelled and their calculated energies were used to determine the plausibility of the different models.

$\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared from $\text{V}(\text{AcAc})_3$. Preparation methods using acetylacetonates compounds have been used to support several transition metal oxides on TiO_2 , SiO_2 or Al_2O_3 [12–15]. We have selected this preparation method since decomposition of the metal complex mounted on the support surface in an oxidant atmosphere yields the highly dispersed oxide, the formation of V_2O_5 crystallites being completely avoided. On the contrary, the traditional way of preparing highly dispersed vanadium catalysts by impregnating the support with a solution of NH_4VO_3 , leads to a $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ system in which highly dispersed oxide species coexist with a low concentration of crystalline V_2O_5 .

Characterisation of the $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ samples was performed by Oxygen Uptake measurements and TPR experiments in order to corroborate the existence of the species postulated from theoretical calculations.

2. Theoretical model

The theoretical studies applied to catalysis may be classified in semi-empirical and ab initio methods. Amongst the formers, an Extended Hückel modified method (EHMO) was selected to perform the quantum mechanical study of the $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalytic system.

The EHMO was widely used by Hoffman et al. [16–19] to study electronic structure of transition metal complexes and adsorbed molecules; it provides useful qualitative trends in large model system. The electronic structure and derived properties are established from electron equations for the molecular orbitals, approximated by experimental data. In this formalism, the non-diagonal elements of the Hamiltonian of the system are proportional to the overlap matrix elements. More recently, in order to improve the traditional Extended Hückel Hamiltonian some corrections were introduced by Chamber et al. [20] and Anderson and Hoffman [21].

The total energy of a selected VO_x supported on an alumina cluster is a sumatory of an attractive and a repulsive term and may be represented by the following equation:

$$E_t = \sum_i n_i E_i + 1/2 \sum_i \sum_{i \neq j} E_{\text{rep}(i,j)} \quad (1)$$

The attractive energy is related to the electrons in the valence level i with an occupancy n_i . The repulsion energy is originated between all the possible pairs nucleus i -fixed atom j .

Experimental parameters are necessary for calculations, being the EHMO a semi-empirical

Table 1
Extended Hückel parameters for V, O, Al 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
H	1s	−13.60	1.00

^aCoefficients used in the double ξ expansion of orbitals.

method. We have used reported ionization potential obtained from spectroscopic data [22]. Since for the level 4p only theoretical data are available in literature, we have taken the data of Hartree–Fock–Slater [23]. Parameters used in this work for vanadium, aluminium, oxygen and hydrogen are presented in Table 1.

The program used to calculate the energy of the different supported VO_x specie was the ICONC, originally developed by Chamber et al. [20], which take into account repulsive terms that are not originally in the EHMO. In the present work, calculations were carried out with a modified version of ICONC. This version has been tested in previous works dealing with the adsorption of metallocenes and Ziegler–Natta catalysts [24,25].

3. Modelling of $\gamma\text{-Al}_2\text{O}_3$

The cluster approach was applied to approximate the study of the real support. $\gamma\text{-Al}_2\text{O}_3$ was modeled by a portion of the infinite solid. Thus, an undesirable effect appears: the so-called dangling bonds; hydrogen atoms were used to complete the internal aluminium coordination. Another disadvantage is the importance of the missing atoms in determining the electric field at the surface. However, we have considered that a two layer alumina cluster is adequate for modelling a support crystal based on the theo-

retical work of Pisani et al. [26]. These authors have performed Hartree–Fock characterisation of $\alpha\text{-Al}_2\text{O}_3$ and they concluded that a two layer cluster is adequate for modelling an ionic crystal surface.

The model of $\gamma\text{-Al}_2\text{O}_3$ was constructed based on a tetragonally distorted defect spinel structure [27,28], with aluminium cations arranged in an approximately cubic close packed oxygen array. We have considered that the preferentially exposed planes are (100) and face C and D of the (110) plane [28,29]. Undoubtedly, other planes such as (111) may exist but they are less abundant; they are not considered in the present model.

The number of aluminium, oxygen and hydrogen atoms for each cluster analysed in our study are reported in Table 2.

4. Modelling of surface vanadium structures on $\gamma\text{-Al}_2\text{O}_3$ (VO_x)

A large number of structural configurations of supported vanadium oxide species could be envisaged; obviously, modelling all of them is a complicated task. Thus, we have restricted the present study to some selected specie based on literature data and on our own previous experience.

Taking into account the vanadium oxide structures shown in Scheme 1, we have studied a tetrahedral monoxo vanadate (Scheme 1, a) from now on named as V and a dimeric vanadate (Scheme 1, b), from now on VV. Considering that in the presence of moisture hydration of vanadium species occurs, we have also studied

Table 2
Number of Al, O and H atoms in different faces of $\gamma\text{-Al}_2\text{O}_3$

Plane	Number of O atoms	Number of Al atoms	Number of H atoms
(100)	53	12	46
(110)C	24	8	19
(110)D	28	7	42

a hydrated monovanadate (Vh) and a pyrovanadate (VVp). The representation of these supported oxide structures are shown in Table 3.

Other postulated species as structures c and d have been neglected since the oxidation number 6 for vanadium is considered chemically improbable; furthermore our previous theoretical calculations have shown that structures possessing vanadium atoms in higher oxidation states than 5 are not stable. Polyvanadate chains [11] were not modelled since they were found not to be plausible based on previous experimental data (oxygen uptake measurements, as we will see later). Besides, in order to perform energy calculations for a vanadate oligomer it is neces-

sary to model alumina cluster excessively large from a computational point of view.

The surface complexes were modelled by fitting the above mentioned structures to the three different faces of the support. Taking into account the lattice parameter of $\gamma\text{-Al}_2\text{O}_3$, the bond lengths and the bond angles of typical vanadium inorganic compound (vanadates, pyrovanadates, etc.) hydrogen atoms were removed from hydroxyl groups of a particular site and a specific VO_x structure was attached to oxygen atoms.

Finally, the formation and the stabilisation energies were calculated for each species. In order to calculate the former, a pseudo forma-

Table 3




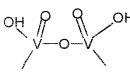
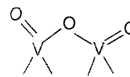
Supported Species	$\gamma\text{-Al}_2\text{O}_3$ plane	Stabilisation Energy (eV)	Formation Energy (eV)
 Vh1	100	-18.11	-0.35
	110C	-18.57	-1.10
	110D	-19.60	-3.23
 Vh2	100	-16.37	1.39
	110C	--	--
	110D	--	--
 V	100	-27.85	-2.49
	110C	-25.13	0.53
	110D	-2.75	12.92
 V Vp	100	--	--
	110C	-19.47	-19.37
	110D	--	---
 V V	100	-39.40	-10.82
	110C	--	--
	110D	-42.35	-15.51

Table 4

Sample	V (wt.%)	θ (%)	O/V (at. ratio)	H/V (at. ratio-TPR)
I	0.6	7	0.47	1.2
II	1.1	11	0.51	1.3
III	2.4	25	0.47	1.2

tion reaction between a vanadium species closely related to the anchored structure, and the support is considered. Lets take an example: for the specie V we have postulated a reaction in which $(\text{H})_3\text{V}=\text{O}$ and a specific alumina cluster react to form the supported complex and water; thus the relative formation energy is the energetic difference between products and reactants. The stabilisation energy has been calculated as the electronic energy difference between the anchored species to support and the sumatory of the energy of an alumina crystal and the specie infinitely separated from the surface.

5. Experimental

$\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ samples were prepared by reaction of $\gamma\text{-Al}_2\text{O}_3$ (Rhône-Poulenc, 120 m^2/g) with an organic solution of $\text{V}(\text{AcAc})_3$ (Aldrich, 99.99%). The preparation was performed at room temperature in anaerobic conditions. Finally, the solids were filtered and calcined in air

at 400°C for 4 h. For more details of the preparation method see Ref. [30]. The vanadium contents, determined by Atomic Absorption Spectroscopy, and the fraction of the support covered by the dispersed vanadia (θ) are reported in Table 4. θ values were calculated taking into account that each VO_x unit occupies 0.1 nm^2 [31].

Characterisation of all catalysts was performed by TPR in a conventional equipment. Samples were reduced in tubular furnace in a Ar/H_2 (5%) mixture. The flow rate was 20 cc/min and the furnace was linearly heated from room temperature to 500°C with a heating rate of 10°C/min. Then the furnace was kept isothermally at the final temperature to complete reduction. The hydrogen consumption was detected by a TCD cell and the temperatures of the peak maxima were determined as well as the total area under the peaks, a calibration of the apparatus enable a quantitative analysis of gas consumption.

Oxygen uptakes were measured in a conventional glass volumetric apparatus. Before measuring, samples were reduced in flowing hydrogen at 500°C during 3 h and outgassed for 20 h at the same temperature and cooled to 300°C. Isotherms were then determined in the 10–500 Torr; doses of chromatographic oxygen were admitted into the sample cell and the amount of oxygen atom uptake during reoxidation was measured at different equilibrium pressures. The

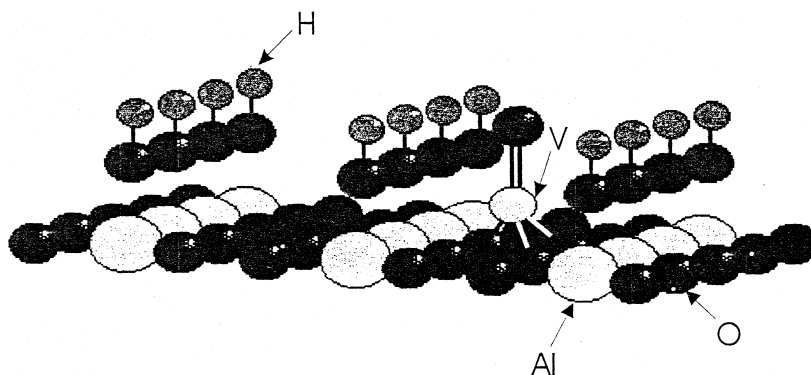


Fig. 1. V species located on (100) plane of γ -alumina.

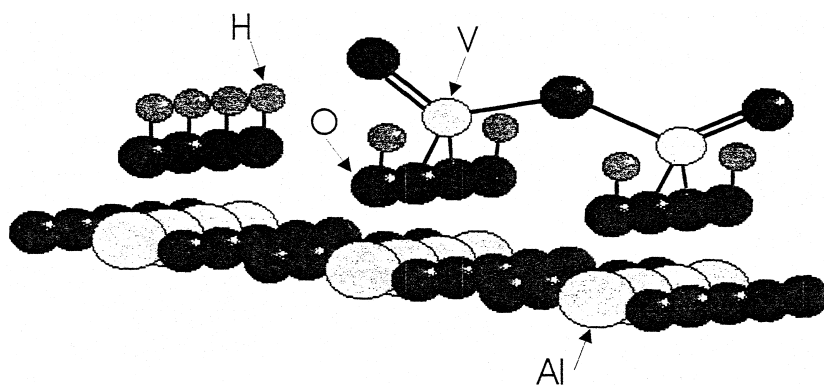


Fig. 2. VV species located on the (100) plane of γ -alumina.

O/V atomic ratio was calculated by extrapolating the isotherms to zero pressure.

6. Results and discussion

6.1. Theoretical calculations

(100) Plane. The above mentioned structures, V, Vh, VV and VVp match with the anion array of (100) face. Furthermore, the hydrated vanadate Vh could be anchored to the γ -alumina, in two different ways; the difference between both specie being the distance between oxygen atoms that bond vanadium to the support. These specie will be named as Vh1 and Vh2, with 2.4 and 3.8 as oxygen–oxygen distance respectively.

Summing up, five possible structures were modelled for (100) plane: V, Vh1, Vh2, VV and VVp; some of them are shown in Figs. 1 and 2 as ball-and-stick representation. For the sake of simplicity, not all atoms are shown.

The formation and the stabilisation energies of each structure anchored to support are reported in Table 3. The lowest formation energy corresponds to the divanadate structure VV. Furthermore, amongst all vanadium specie, VV is the most stable. These results would indicate that VV is the most plausible species on the (100) plane. However, a low concentration of V is expected, though its formation energy is not favourable (-2.49 eV), since the low value of stabilisation energy (-27.85 eV) suggests that the presence of V should not be neglected.

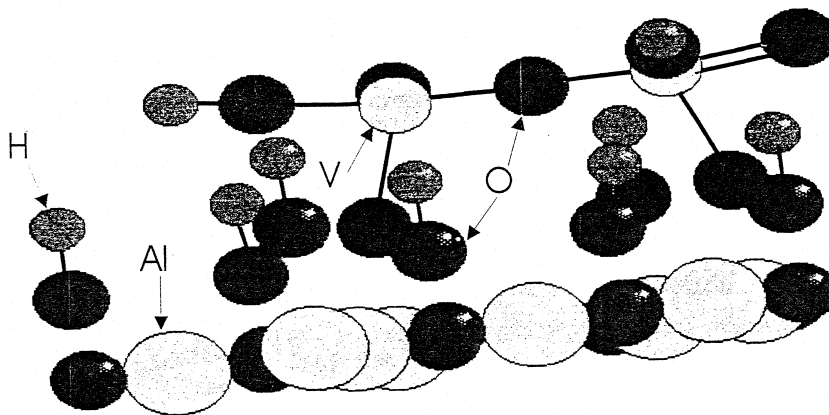


Fig. 3. VVp species located on the (110) C plane of γ -alumina.

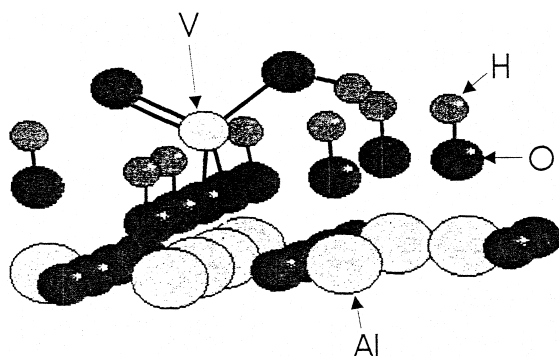


Fig. 4. Vh species located on the (110) C plane of γ -alumina.

Face C of (110) plane. V–O–V bond length in divanadate VV is too large to match with the anion array of support for the C face of (110) plane. Thus, only the specie V, VVp and one structural configuration of the hydrated vanadate, Vh1 have been modelled in this case.

According to the formation and stabilisation energy values shown in Table 3, VVp is undoubtedly the most plausible species. Surprisingly, bond lengths and angles of this supported complexes are almost the same as those of unsupported pyrovanadates. This is obviously related with its high stability. Fig. 3 shows how the VVp species is located on the alumina cluster.

We have speculated that VVp could lose hydrogen to form an ionic structure, $(V_2O_5)^{2-}$, the reaction being assisted by support. The calculated formation and stabilisation energies for

such a structure were very high: -19.57 and -20.45 eV respectively. This result indicates that the ionic pyrovanadate should be the most plausible structure on (110) C plane.

Although the formation energy of Vh1 is positive, it is highly stable. Thus, the presence of Vh1 on 110 C face should not be completely disregarded. The representation of this structure is shown in Fig. 4.

Face D of (110) plane. Based on structural consideration three structures were modelled: V, Vh1, and VV. The calculated relative energies indicate that the formation of V on this plane is completely not probable and that its stability is rather low. Both structures, Vh1 and VV are highly stabilised on the (110) D surface, but the formation of the dimeric structure VV is preferred to the formation of the monomeric hydrated vanadate. Fig. 5 shows VV anchored to D face of (110) plane.

Summing up, for each face, calculations depict the following scenario: the (110) and (110) D planes are preferentially covered by dimeric VV, while VVp (presumably as the ionic species, $(V_2O_5)^{2-}$) is predominate on (110)C face. The presence of the monomeric specie V on (100) plane, and Vh1 on both faces of (110) plane should not be completely disregarded; they would also be present on these planes, though in a lower concentration than the dimeric specie.

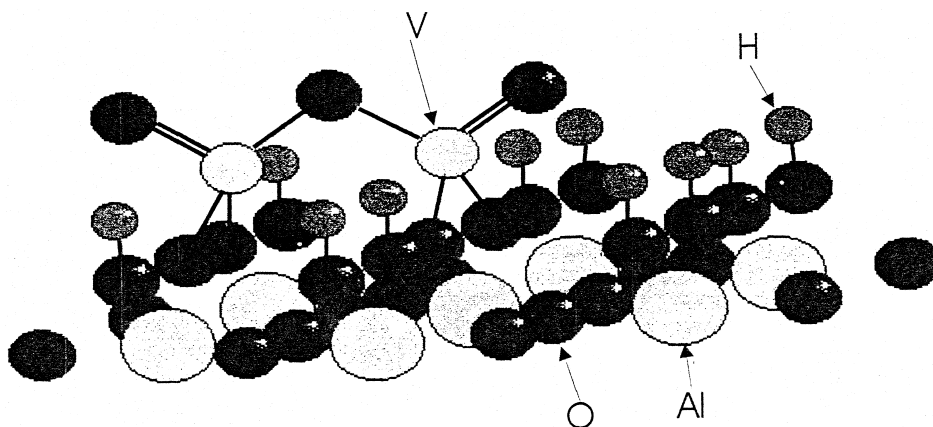


Fig. 5. VV species located on the (110) D plane of γ -alumina.

Calculations have shown, for the most part of the studied structures, high stabilisation and formation energies. This theoretical result agrees with a well known experimental fact: vanadia is highly dispersed by alumina, and at low concentration molecularly dispersed vanadium oxide is easily formed.

6.2. Catalysts preparation

Table 4 shows the vanadium concentration and the fraction of monolayer for the three $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ samples. The coverage of support by VO_x is low for all the catalysts, thus, the formation of vanadium pentoxide crystallites may be neglected.

6.3. Oxygen uptake measurements

It is important to recall that this measurement is related to the amount of oxygen uptake by previously reduced $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ samples. The temperature of the pretreatment was selected taking into account previous experiments that showed that after reduction at 773 K samples ended up in a reproducible lower valent state. The extent of reduction, and then the reoxidation, are related to the oxidation state of vanadium and the structure of the supported oxide. To label, for example, any monomeric structure possessing only one vanadium atom, i.e., structures Vh or V, would consume at least one oxygen atoms per VO_x unit during reoxidation, originating a O/V atomic ratio of unity.

As shown in Table 4, values of O/V atomic ratio ranging 0.47 to 0.51 were obtained for all samples. Within experimental error, these ratios were 0.5, indicating monovanadates specie would not be formed on $\gamma\text{-Al}_2\text{O}_3$, whatever the vanadium loading. On the contrary, the existence of any dimeric species as VV, or VVp, is in agreement with present data.

6.4. TPR experiments

The TPR profile of the three $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ samples are shown in Fig. 6. A hydrogen consumption at around 480°C is observed for all the

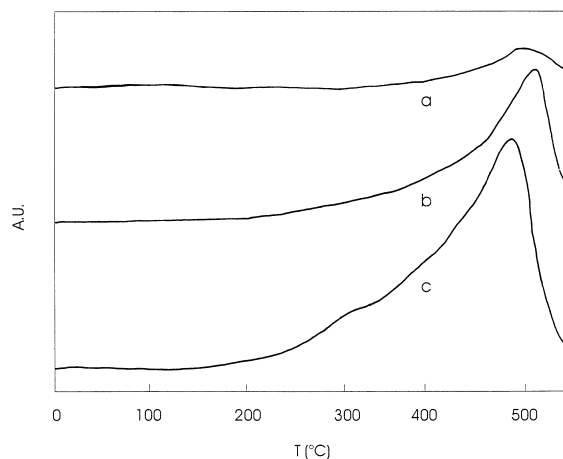
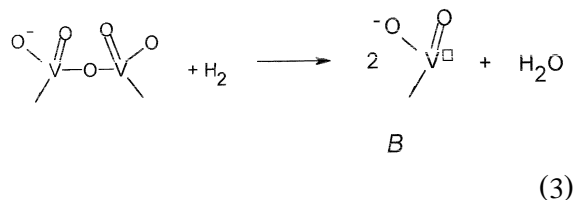
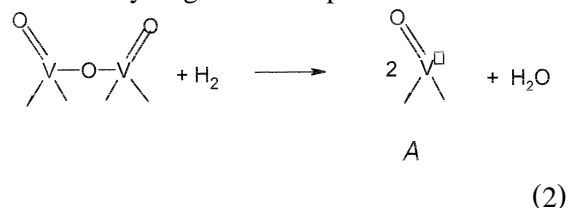


Fig. 6. TPR profiles for $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts: (a) sample I (0.6 wt.%); (b) sample II (1.1 wt.%) and (c) sample III (2.4 wt.%).

catalysts. With increasing coverage (samples II and III) a shoulder around 300°C is also detected. These results suggest that two different specie are present in samples II and III. Concerning catalyst I, we consider that vanadium low loading hamper the detection of the first peak at 300°C.

Last column in Table 4 shows the atomic ratio H/V; these values have been calculated from the integrated area of the main peak and may be considered approximately one for all the catalyst. The reaction and the specie involved in the consumption of hydrogen could not be unambiguously determined. However, keeping in mind the theoretical calculations and oxygen uptake results, we suggest that the following reactions involving dimeric structures should be related to hydrogen consumption



In both postulated reactions, vanadium atoms are reduced to the oxidation states 4, with the creation of an oxygen vacancy.

7. General discussion

For $\text{VO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts with low concentration of vanadium, theoretical calculation have shown that dimeric supported structures, as divanadates and pyrovanadates, are more likely to exist than monomeric ones.

These results are mainly confirmed by oxygen uptake measurements and are useful to explain TPR results. The amount of oxygen taken during the reoxidation of samples, expressed as the atomic ratio O/V, is approximately 0.5. This value is in agreement with the postulated existence of dimers. We could postulate that during the reduction pretreatment performed during oxygen uptake measurements, reactions 2 and 3 take place and the species a and b would be created. Then, a vanadium dimer would be formed from A or B by consumption of one oxygen atom, justifying the measured values for O/V atomic ratio.

TPR results should be discussed keeping in mind previous results; the partial reduction of dimeric specie is responsible for hydrogen consumption peaks.

The plausibility of a low concentration of V or Vh monomers is suggested by theoretical calculations. However, this fact cannot be confirmed by experimental evidence. We could argue that the low loading of monomers hinder their detection by the present experimental techniques.

From a structural point of view, dimers as well as monomers, are in a tetrahedral coordination. This fact would be in disagreement with other studies that have reported an octahedral coordination for vanadium in low loading samples, mainly based on Raman spectroscopy results [3]. However, the interpretation of Raman features is rather complicated due to the irregular coordination of vanadium in compounds

taken as Ref. [9]. Moreover it is interesting to note that all the analysed specie are anchored to the support in a strongly deformed tetrahedral coordination. For example, all V–O bond length in the specie V are different. This fact turns the interpretation of the results coming from Raman spectroscopy rather complicated.

It is interesting to note that, for reaction catalysed by vanadium supported catalysts, to our knowledge, vanadium dimers have not been considered as active sites for mechanistic speculations. Based on our present results, more realistic mechanisms should involve dimeric structures.

8. Conclusion

The combination of a theoretical study and experimental data of the characterisation of a $\text{VO}_x/\text{Al}_2\text{O}_3$ was used to analyse the structure of highly dispersed vanadia. Both results, theoretical and experimental ones, indicate that the fraction of vanadium oxide monolayer that cover alumina is constituted by dimeric structures.

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References

- [1] G.C. Bond, K. Brückman, *Faraday Discuss. Chem. Soc.* 72 (1989) 235.
- [2] H. Bosch, F. Hanssen, *Catal. Today* 2 (1986) 369.
- [3] F. Roozeboom, M. Mittelmeijer-Hazeleger, J. Moujlin, J. Medema, V. de Beer, P. Gellings, *J. Phys. Chem.* 84 (1990) 2783.
- [4] I. Wachs, R. Saleh, S. Chan, C. Cherisch, *Appl. Catal.* 15 (1985) 339.
- [5] G. Went, T. Oyama, A. Bell, *J. Phys. Chem.* 94 (1990) 4240.
- [6] H. Eckert, I. Wachs, *J. Phys. Chem.* 93 (1989) 6796.
- [7] G. Deo, H. Eckert, I. Wachs, *Symposium on Structure-Activ-*

- ity Relationships in Heterogeneous Catalysts, Am. Chem. Soc., 1990, p. 16.
- [8] R. Kozlowski, R. Pettifer, J. Thomas, J. Phys. Chem. 87 (1983) 5176.
- [9] J. Haber, A. Kozłowska, R. Kozłowski, J. Catal. 102 (1986) 52.
- [10] P. Van der Boort, M. White, M. Mitchell, A. Verberkmoes, E. Vansant, Spectrochimica Acta A 53 (1997) 2181.
- [11] J.G. Eon, R. Olier, J.C. Volta, J. Catal. 145 (1994) 318.
- [12] P. Van der Voort, K. Possemiers, E. Vansant, J. Chem. Soc. Faraday Trans. 92 (1996) 843.
- [13] S. Hauka, E. LaKoma, T. Suntola, Appl. Surf. Sci. 75 (1994) 229.
- [14] J. Kevin, M. White, M. Mitchel, Langmuir 7 (1991) 1198.
- [15] A. Van Hengstum, J.G. Van Ommen, H. Bosch, P. Gellings, Appl. Catal. 5 (183) 207.
- [16] R. Hoffmann, J. Chem. Phys. 39 (6) (1963) 1397.
- [17] R. Sumerville, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 23.
- [18] R. Hoffmann, Solids and Surfaces: A chemist's view of bonding in extend structures, CUCH, New York, 1988.
- [19] P. Hay, J. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 97 (1975) 4884.
- [20] I. Chamber, L. Forrs, G. Calzaferri, J. Phys. Chem. 93 (1989) 5366.
- [21] A. Anderson, R. Hoffmann, J. Chem. Phys. 60 (1974) 4271.
- [22] W. Lotz, J. Opt. Soc. Am. 60 (1970) 206.
- [23] A. Vela, L. Gázquez, J. Phys. Chem. 92 (1985) 5366.
- [24] M.L. Ferreira, N. Castellani, D. Damiani, A. Juan, J. Mol. Catal. A: Chemical 122 (1997) 25.
- [25] M.L. Ferreira, D. Damiani, A. Juan, Computational Material Science 9 (1998) 357.
- [26] C. Pisani, M. Causa, R. Dovesi, C. Roetti, Prog. In Surf. Sci. 25 (1987) 119.
- [27] S. Wilson, J. Mc Connell, J. Phys. Chem. 34 (1980) 315.
- [28] H. Konizinger, X. Ratnasamy, Catal. Rev. 17 (1978) 31.
- [29] T. Shay, L.-Y. Hsu, J.M. Basset, Sh. Shore, J. Mol. Catal. 86 (1994) 479.
- [30] C. Neyertz, M. Volpe, Colloids and Surfaces A 136 (1998) 63.
- [31] J. Le Bars, J. Vadrine, A. Auroux, S. Trautmann, M. Baerns, Appl. Catal. A 119 (1994) 341.