Adsorption of CH_3OH on V_2O_5
Comparative reactivity of the (100) and (010) planes

Jorge Sambeth, Luis Gambaro, Horacio Thomas *

CINDECA-UNLP, CONICET, 47 Nro 257, 1900 La Plata, Argentina

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Abstract

Methanol adsorption on the (100) and (010) planes of V_2O_5 was analysed by Extended Hückel Method (ASED). For the plane (100) two cases were considered with vanadium atoms either saturated or unsaturated with oxygen atoms. The results showed that CH_3OH adsorption on the (010) plane is more favourable than on the (100) plane for both cases. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

By studding different catalyst, many authors have shown that the oxidation of CH_3OH is structure sensitive [1–4]. Studies on the surface properties of V_2O_5 by FTIR spectroscopy suggested that the plane (010) of V_2O_5 would be much less ionic than (100), (001) and (110) planes [5]. In these planes, since the vanadiums are not saturated, strong acidic sites of Lewis type seem to exist, whereas those sites on the (010) plane should be much weaker. The (100), (001) and (110) faces are expected to be active in water adsorption and dissociation. Busca [6] postulated that the CH_3OH would be adsorbed as methoxy on these planes. According to Andersson [7] the border of the (100) plane can be formed either by $V-O_2$ or $V-O_3$ groups.

Tatibouët and Germain [8] have obtained monocrystals of orthorhombic V_2O_5 by fusion and slow recrystallisation by exposing the (001), (100) and (010) faces. The variations of activity and selectivity observed during the methanol oxidation allowed the authors to conclude that the (001) plane is responsible for methylal formation and that the (010) plane was found to be active for H_2CO and ether.

Zhanpeinsov et al. [9], using SINDO1 method, have optimised different clusters of the (010) plane of V_2O_5. They found that the increase in the number of layers causes strong changes on the geometry of the vanadium environment. They also showed that the active site is associated to the terminal oxygens O(1) (V=O groups) and that the C–H bond breakage occurs at the centres.

Witko et al. [20] working on different clusters of V_2O_5 studied the charge distribution, the total

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* Corresponding author. Fax: + 54-21-254277.

energy and the orbital population by SINDO method. With the experimental data they built the (010) plane, optimising the geometry with the distances of V=O (1.58 Å) and of V–O (1.83 Å, this being an average of all V–O bond distances). By the same method, studies on hydrogen adsorption on V_2O_5 demonstrated that the OH formed with an O(1) is strongly bound and is also responsible for H subtraction from organic species, while the other two O types (bi and tricoordinated) lead to weaker bonds that can desorb more easily [21].

Sambeth et al. [10] have conducted experimental and theoretical studies on the adsorption of CH_3OH on the (010) plane of V_2O_5. They deduced that H atoms are removed by the lattice oxygens and that methanol is adsorbed as methoxy. They showed that this removal has two effects: high surface hydroxylation and surface reduction (V + 5 → V + 4). The theoretical results confirmed both the removal of H atoms and methoxy group formation, and also revealed two possible adsorption sites of CH_3OH on V_2O_5: the terminal oxygens O(1) and the bridge oxygens O(3) on the (010) plane.

The purpose of this paper was (i) to study the adsorption of CH_3OH by Extended Hückel Method (ASED)[13] on the plane (100) of V_2O_5 as idealised by Busca et al. [5] and Andersson [7], and (ii) to compare the obtained results with
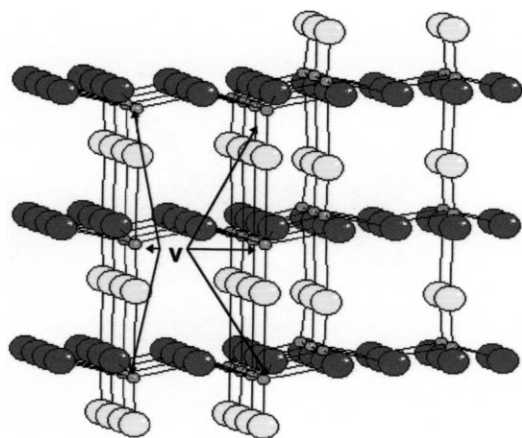

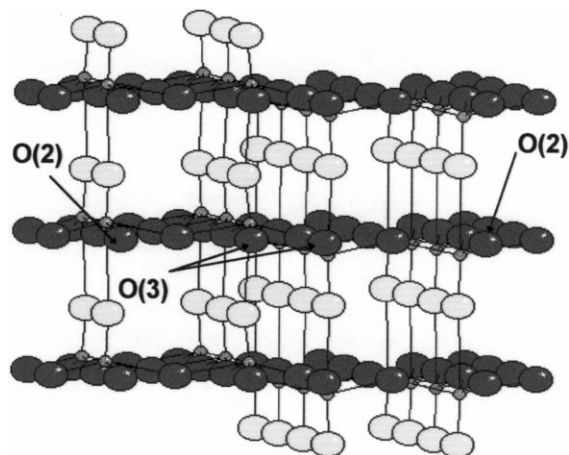Fig. 1. Representation of the (100) plane of V_2O_5 by Busca.

Fig. 2. Representation of the (100) plane of V_2O_5 by Andersson.

those of Sambeth et al. [11] on the (010) plane of V_2O_5.

2. Method and cluster models

The semi-empirical Extended Hückel Method (EHMO) is an acceptable approach to the electronic structure of a molecule that includes transition metals [12–14]. Although the method does not give representative absolute results, it predicts well the relative variations, so allowing trends to be defined with a simple calculation procedure.

The V_2O_5 crystals have three crystallographically different oxygen atoms; O(1) (V=O), O(2) and O(3) (i.e., mono, bi and tricoordinated to vanadium atoms).

The lattice was built by taking specific angles and average distances, reported in previous works [11,15,16]. The cluster was constructed with 180 atoms (134 oxygens and 46 vanadiums) in three layers.

Two lattices were built, one as proposed by Busca et al. [5] and Busca [6] with unsaturated vanadium atoms (Fig. 1) and the other as suggested by Andersson [7], where the vanadiums are saturated with oxygens (O(2) and O(3)) (Fig. 2).

For these lattices, bond lengths and angles of CH_3OH in gaseous phase [17], and the ionisa-

Table 1
Values of the orbital populations (p_z) and charge density by Witko and Hermann [16] and obtained in this work

	p_z	Q	p_z	Q
O(1)	1.581	−1.00	1.319	−1.66
O(2)	1.873	−0.90	1.945	−1.41
O(3)	1.829	−0.80	1.904	−1.33

tion potentials and Slater coefficients reported by Sambeth et al. [11] were used.

Once the lattice was built, we optimised the Wolfsberg–Helmholz parameters to obtain the net charge (Q) trend, similar to that of Witko [21] and the population of the p_z orbital for the different oxygens as well. The trend was analysed in the central zone of the cluster (Table 1).

In the model, the adsorption was carried out considering that the bond length from the H to an O of the lattice has to be in the 0.9–1.2 Å range [18]. The adsorption was studied in the central zone of the cluster to avoid border effects and the dangling boundary oxygens were saturated by H atoms.

The process was studied by calculating the relative energy of the system (E_{relative}), which included terms for both repulsion and binding
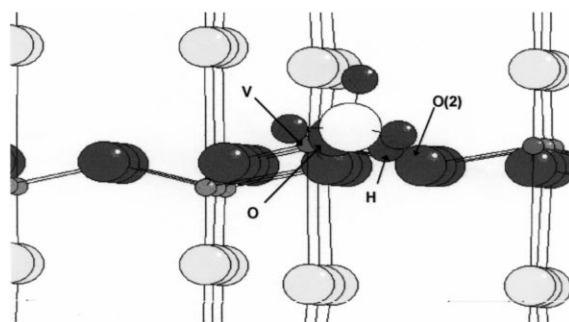

Fig. 4. Representation of the CH_3OH adsorption on the (100) plane.

energies. The relative energy was taken as zero when the adsorbate is at infinite distance from the surface.

3. Results and discussion

Once the (100) planes were built, the adsorption of CH_3OH was analysed. The minimum energy values for the adsorption of CH_3OH on V_2O_5 (Fig. 3) were found for an angle of 25° between the methanol molecule and the surface. Fig. 4 shows that the adsorption of CH_3OH from the gaseous phase involves an O(2) and
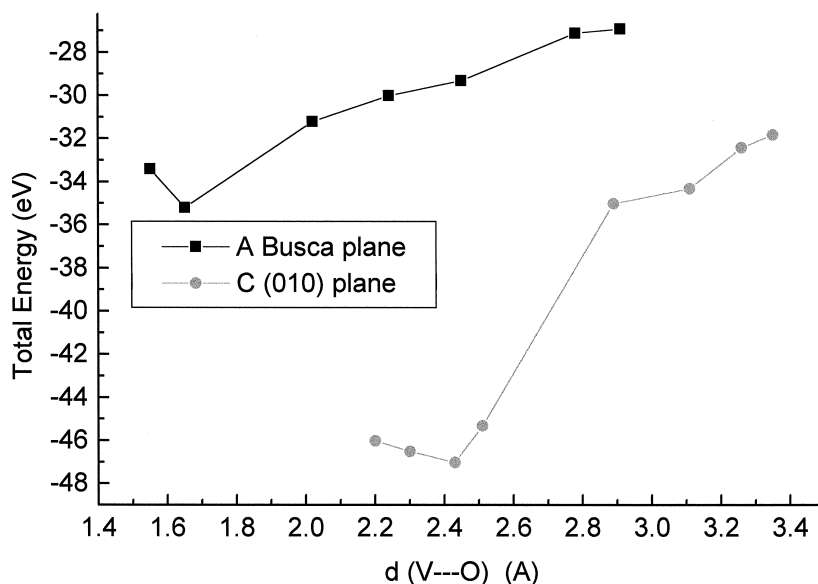

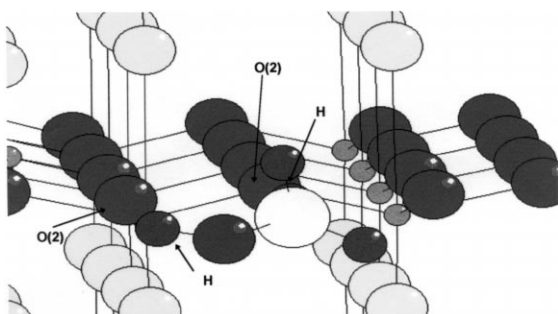Fig. 3. Total energy of the adsorption of CH_3OH on the (100) and (010) planes vs. bond lengths between oxygen (CH_3OH)–V (cluster).

Fig. 5. Representation of the CH_3OH adsorption on the (100) plane (O(1)/O(2) interaction).

the H of OH group (distance = 1.12 Å) and a vanadium atom with O of the OH group (distance = 1.65 Å).

Fig. 3 shows, in addition, the energy resulting from CH_3OH adsorption on the (010) plane [11]. Although the equilibrium distance between the oxygen (of CH_3OH) and vanadium is shorter on the (100) plane (1.65 Å) than on the (010) plane (2.27 Å) the energy is more favourable on the latter plane. The equilibrium distance is shorter on the (100) plane because the vanadium atoms are not saturated, so these atoms can

approximate considerably more on this plane than on the (010) plane. According to our results, if the plane idealised by Busca would have been developed, the catalyst should have exhibited a lower activity than the (010) plane for the adsorption of CH_3OH.

On the other hand, we also studied the adsorption of CH_3OH on the (100) plane idealised by Andersson [7]. As seen in Fig. 2, vanadium atoms are saturated so methanol cannot approach to form a O (CH_3OH)–V (cluster) bond.

Of all the positions studied, only two were found, the first favourable position was represented by CH_3OH adsorption from the gaseous phase (Fig. 5) which involves two O(2) and two H (one H of methyl group and the other H of OH group). The minimum of energy (Fig. 6, O(2)/O(2) interactions) was found for a bond lengths of 1.01 Å between the H of OH group and one oxygen of the lattice, and for 1.09 Å between the H of the CH_3 group and another oxygen of the lattice.

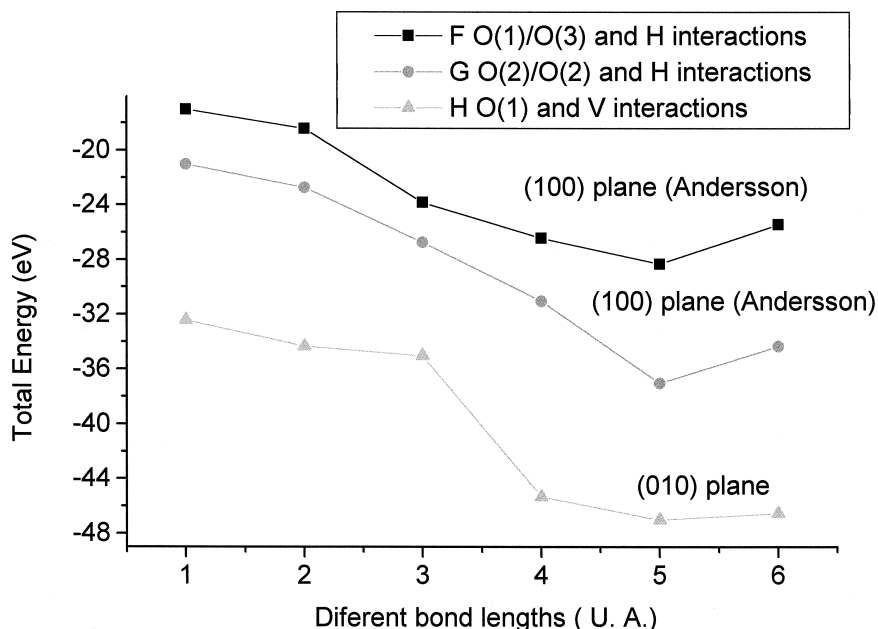Fig. 7 shows the second favourable position, the hydrogens of both OH and CH_3 groups

Fig. 6. Total energy of the adsorption of CH_3OH on the (100) and (010) planes vs. bond lengths between oxygen (CH_3OH)–oxygen (cluster) by Anderson planes, and oxygen (CH_3OH)–V (cluster) by (010) plane.
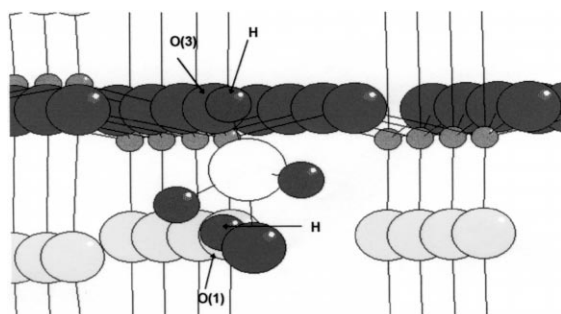
Fig. 7. Representation of the CH$_3$OH adsorption on the (100) plane (O(1)/O(3) interactions).

were released and then attached to one O(1) and one O(3), respectively. In this case, the O–H distances were 1.10 Å for H–O(1) and 1.12 Å for H–O(3).

Fig. 6 depicts the total energy curves as a function of the different bond lengths, and the adsorption energy of the CH$_3$OH obtained in a previous work [11] as well. The results show that the methanol adsorption is more favourable on the (010) plane than on the (100) plane by Andersson. These results are in agreement with the studies of Ai [19] on the CH$_3$OH oxidation on oxides of transition metals. This author has suggested that methanol would be adsorbed on acidic sites, taking an alcoholate structure and allowing H$_2$CO to be form.

According to our work, CH$_3$OH adsorption depends on the arrangement of surface atoms. Thus, to make H$_2$CO formation possible both basic (oxygen bridges) and acidic sites (vanadium atoms) should be present, regardless of the plane analysed.

4. Conclusion

The adsorption of CH$_3$OH was studied on idealised models of the (100) plane of V$_2$O$_5$ suggested by Busca et al. [5] and Busca [6] and by Andersson [7]. We used the Extended Hückel Method and compared the results with those obtained by Sambeth et al. [11] on the (010) plane. The results of the adsorption of CH$_3$OH on the (010) and (100) planes showed that the process is more favourable on the former than on the latter plane for both saturated and unsaturated vanadium atoms.

Besides, we found that independently of the minimum energy, the first step of the CH$_3$OH adsorption must lead to the formation of a carbocation (methoxy group) which involves a vanadium atom (Lewis acidic sites) and the O of the OH group, and that this interaction favours the relaxing of the O–H bond.

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