Catalytic oxidation of CH_3OH to $HCOOCH_3$ on V_2O_5: A theoretical study

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Abstract

In a previous work, the CH_3OH adsorption–oxidation process on V_2O_5 was studied by mass spectrometry analysis of the reaction atmosphere. The following partial oxidation products were reported: H_2CO, CO, CO_2, $(CH_3O)_2CH_2$ (methylal), CH_3OCH_2OH (hemimethylal) and $HCOOCH_3$. The data so obtained allowed a reaction pathway to be proposed. In the present work, we used models of the plane (010) of V_2O_5 and of CH_3OH, to test whether the pathway proposed in this work as well as alternative ones presented by other authors were energetically favorable or not. With this purpose, the variation of the total system energy was computed in each step by extended Hückel-type calculations (ASED, atom superposition and electron delocalization). The results showed, on the one hand, that the pathway proposed in this work is better than alternatives pathways, and on the other hand, the possible existence of other equally-favorable adsorption sites in which bridge oxygen may take part.

1. Introduction

From structural spectroscopic and theoretical studies, many authors [1–5] have found that the terminal oxygen (M=O, M: Mo, V) takes part in the oxidation of hydrocarbons. Other authors, as Deo and Wachs [6] have suggested that the bridge oxygens participate in the oxidative dehydrogenation of alcohols.

Using an ab initio method, Witko and Hermann [7] have studied the hydrogen adsorption on different oxygens of the plane (010) of vanadium pentoxide and the subsequent OH re-
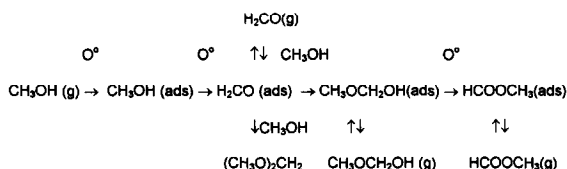
moval. They concluded that the V=O oxygens form very stable bonds with the hydrogens. In the nucleophilic oxidation of hydrocarbons those oxygens would extract hydrogens from the organic molecules. Besides, they indicated that the hydrogen–oxygen 'bond' placed as a bridge between vanadiums is easily removable as OH.

Weber [8], using the extended Hückel method (EHMO) has studied the dehydrogenation of CH_3OH in a Keggin structure, using bridge oxygens (V–O–V) and, sometimes, terminal groups (V=O). The author highlighted the fact that the oxidative dehydrogenation process involves hydrogen transfer to catalysts while its electron goes to an antibonding orbital formed

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by the interaction between CH orbitals and the HOMO (highest occupied molecular orbital) of the cluster. Therefore, the addition of electrons to the V–O–V bond weakens it, so the bridge oxygen becomes more reactive in this process.

In a previous work in our laboratory, the adsorption–oxidation of CH_3OH on pure V_2O_5 was experimentally studied by mass spectrometry and gas chromatography [1,9–11]. The reaction products found were H_2CO, CO_2, CO, H_2O, CH_3OCH_2OH, $(CH_3O)_2CH_2$ and $HCOOCH_3$. From such data, the reaction mechanisms of organic chemistry and the considerations of Wach et al. [12] and Louis et al. [13] about intermediate products in the methanol oxidation to $HCOOCH_3$, the following reaction pathway was postulated
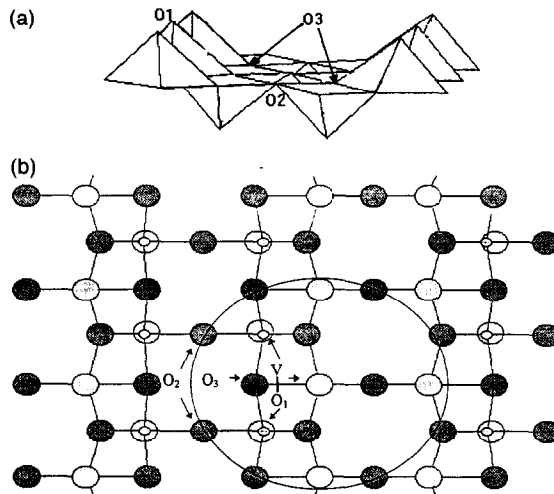

Fig. 1. Geometric structure of the vanadium pentoxide, (010) surface. (a) Perspective view of the (010) surface plane. (b) Central zone of the cluster (–). Different types of oxygen atoms.

$$H_2CO(g)$$

O° O° ↑↓ CH_3OH O°

CH_3OH (g) → CH_3OH (ads) → H_2CO (ads) → CH_3OCH_2OH(ads) → $HCOOCH_3$(ads)

↓CH_3OH ↑↓ ↑↓

$(CH_3O)_2CH_2$ CH_3OCH_2OH (g) $HCOOCH_3$(g)

The object of the present work is to analyze theoretically the different reaction pathway based on out own experimental data also other two pathways previously proposed by Liu et al. [4] and Ai [15]. The study also considers alternative ways for the adsorption–oxidation of the different species on the plane (010) of V_2O_5. The analysis is based on calculations of the variation of the system total energy by the extended Hückel-type method ASED.

2. The method and cluster model

The semiempirical extended Hückel method is an acceptable approach to the electronic structure of a molecule when transition metals are involved. It was developed by Hofmann [16] and improved by Anderson (ASED) [17] and Calzaferri (ICONC) [18], who included the repulsion energy terms in their calculations. Al-

though the method does not give representative absolute results, it predict well the relative variations, which allow trends to be defined with a simple calculation method.

From literature data [7,19], the plane (010) of the V_2O_5 lattice was constructed. It has three different types of oxygen (O_1) monocoordinated (V=O), (O_2) bicoordinated and (O_3) tricoordinated to Vanadium atoms (Fig. 1), that differ both in charge and orbital population. According to several authors they are responsible for the vanadium oxide activity in the oxidation reactions of organic molecules [20–22].

The lattice was built with 83 atoms (62 oxygens and 21 vanadiums) by taking the specific angles and the average distances for $V–O_2$ and $V–O_3$ bonds (1.81 Å) and for the $V–O_1$ species (1.57 Å) [23]. All dangling bonds were saturated with H.

We have employed bond lengths angles of the CH_3OH in gaseous phase [24]. The alcohol molecule was rotated along the C–O, axis and the rotational energy difference found was less than kT (~ 0.1 eV).

The adsorption–oxidation process was studied through calculations of the total energy of the system (E_{total}). This energy include terms

Table 1
Parameters employed in the extended Hückel calculations

Atom	s		p		d				
	H_{ii}	exp	H_{ii}	exp	H_{ii}	exp_1	$coef_1$	exp_2	$coef_2$
V	−8.81	1.300	−5.52	1.300	−11.00	4.750	0.475	1.700	0.705
O	−26.90	2.163	−12.10	2.175					
H	−13.60	1.000							
C	−15.10	1.554	−9.80	1.457					

The Wolfsberg–Helhmotz constant = 2.40

for both the repulsion and binding energies. The total energy was taken as zero when the adsorbate is at infinite distance from the surface. Values of the ionization potential and Slater coefficients used in the calculations are presented in Table 1.

3. Results and discussion

Once the lattice was built, the parameter values were optimized until the net charges (Q) and orbital populations (P_z) for the different atoms of the structure, were similar to those reported by Witko et al. [23]. The tendencies were analyzed in the central cluster zone to avoid border effects (Fig. 1b). The net charge and orbital population values for the three types of oxygen are presented in Table 2.

3.1. Experimental pathway (pathway 1)

3.1.1. Adsorption of CH_3OH and oxidation to H_2CO

They have selected several chemically-favorable positions to study the CH_3OH adsorp-

tion. When the alcohol molecules are adsorbed on those positions allow the bond length from the H to an O of the lattice to fall within the range 0.90–1.20 Å. As indicated by Petelenz and Broclawik [25], this range is acceptable for calculations. From information reported by Anderson [20] and Ai [21], the $V–O_1$ were proposed as the sites involved in the mechanism. The first position studied was represented by CH_3OH adsorption from the gaseous phase (Fig. 2a and b), which involves an O_1 and one H of the methyl group, and a vanadium atom (with a double bond facing inwards) with the O of the

Table 2
The net charge (Q) and orbital populations (P_z) values for the three types oxygen

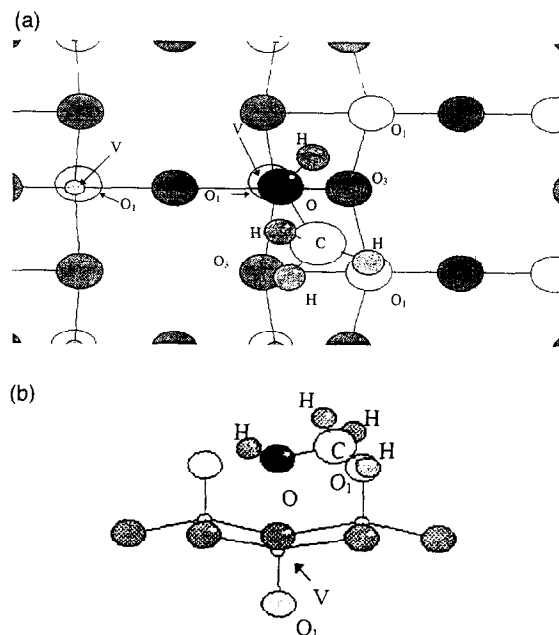|	Witko [23]		This work	
	P_z	Q	P_z	Q
O_1	1.581	−1.00	1.319	−1.66
O_2	1.873	−0.90	1.945	−1.41
O_3	1.829	−0.60	1.904	−1.33

Fig. 2. Representation of methanol adsorption (interaction $CH_3OH–V/O_1$): (a) View from the (010) surface plane; (b) View from the (001) surface plane.

OH group. The minimum of energy was found when the angle between the methanol molecule and the surface was 30°. Besides, we found a second, chemically-favorable adsorption position where a bridge oxygen (O_3) takes part (Fig. 3a and b).

Fig. 4 shows the E_{total} curve as a function of the V–OHCH$_3$ distance. It can be observed that the minimum energy values for both positions are of the same order of magnitude.

In both sites the CH$_3$OH forms a carbocation $(H_2C^{\delta(+)} - {}^{\delta(-)}OH)$ which, according to the proposed pathway [1] should be an intermediate for H$_2$CO formation.

In the first position, the C–O bond distance (1.43 Å in methanol and 1.21 Å in formaldehyde [26]) was shortened and, at the same time, the H–O distance of the OH group relaxed until the H was attached to the O_1 site.

In the second position (Fig. 3), the hydrogens of both OH and CH$_3$ were released and then attached to one O_1 and one O_3, respectively. In both positions, the system tend to be more stable, as observed in Fig. 5.
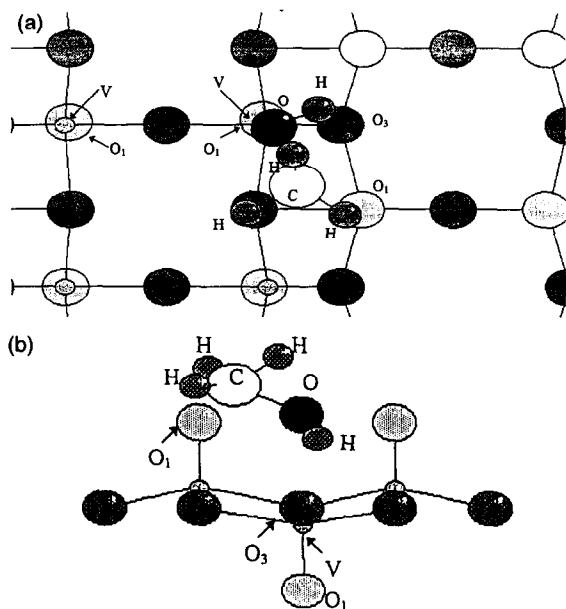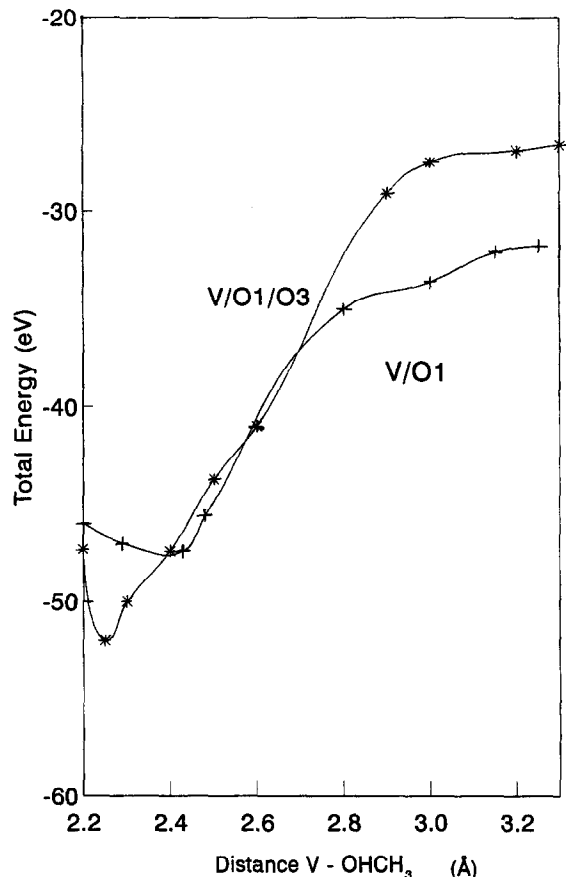

Fig. 4. System total energy curve as a function of the V–OHCH$_3$ distance.

3.1.2. Hemimethylal formation

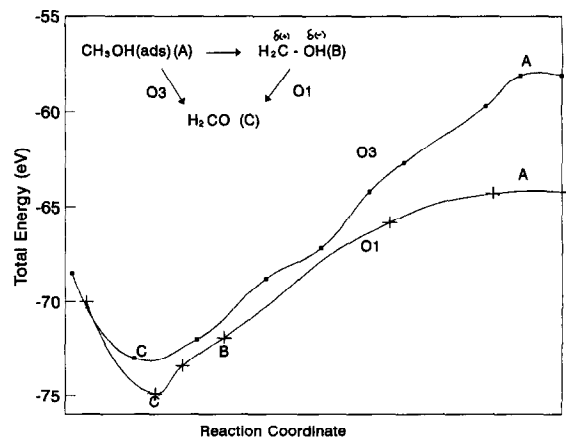Louis et al. [13], have indicated that the hemimethylal can possibly be an intermediate

Fig. 3. Representation of methanol adsorption (interaction CH$_3$OH–V/O$_1$/O$_3$): (a) View from the (010) surface plane; (b) View from the (001) surface plane.

Fig. 5. System total energy curve. CH$_3$OH oxidation to H$_2$CO.

product in the oxidation of CH_3OH to $HCOOCH_3$, for which they proposed a reaction between an adsorbed metoxi group and an adsorbed carbocation.

Sambeth et al. [1] have obtained the first experimental evidence of such species (hemimethylal) under catalytic oxidation. This authors expressed that its presence is related to a time period during which the superficial density of the adsorbed methanol molecules is high.

In the present work, the oxidation reaction of CH_3OH to $HCOOCH_3$ was studied by considering the methanol adsorption, the subsequent formation of a carbocation and the reaction between the latter and a second CH_3OH molecule.

The carbocation formed in the first position has got a spatial disposition which is adequate enough to allow reaction with other methanol molecules.

On the contrary, the carbocation formed in the second position does not have this possibility, so it can only form formaldehyde.

The analysis was focused on those different sites where a second molecule of CH_3OH could loose the H of the OH group. The oxygen can
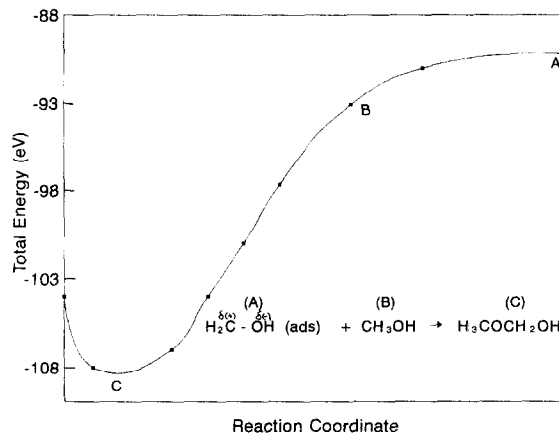

Fig. 7. System total energy curve for the hemimethylal formation.

attack the carbon of an adsorbed carbocation. To proceed with the former, we took into account that the C–O distance had to be within the order of the bond distance of the same atoms in the hemimethylal (1.47 Å). The adsorption position of the second CH_3OH can be observed in Fig. 6. We found the minimum energy of the system (Fig. 7) for a bond length of 0.97 Å between the V=O and the H of the OH group, and for 1.55 Å in the C–O bond.
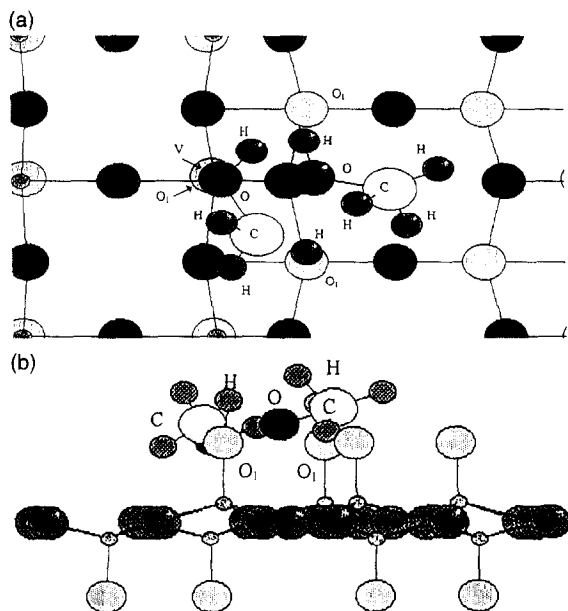

Fig. 6. Representation of H_3COCH_2OH formation: (a) View from the (010) surface plane; (b) View from the (001) surface plane.
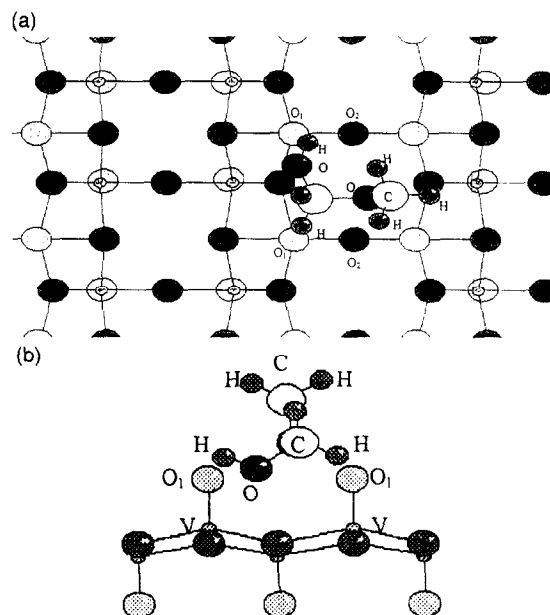

Fig. 8. $HCOOCH_3$ formation. Interaction H/O_1: (a) View from the (010) surface plane; (b) View from the (001) surface plane.

3.1.3. HCOOCH₃ formation

In order to study the oxidation of CH_3OCH_2OH to $HCOOCH_3$, the first action was to rotate the former molecule so that the H of the OH and one of the H of the CH_2 were both included on the same plane. Once the rotation concluded, the C–O bonds were shortened. Two positions were encountered for hydrogen removal, (i) the terminal oxygens and (ii) the bicoordinated ones, as observed in Fig. 8a and b and Fig. 9. We have found only slight differences of energy between those positions (Fig. 10).

3.2. Alternative pathways

Until now, we have described a proposed reaction pathway based on experimental results and analyzed by the extended Hückel method. In this section, other two possible reaction pathways will be studied. As indicated by Louis et al. [13], these pathways, together with that proposed in the present work, are the three routes by which the formation of $HCOOCH_3$ can be explained. The purpose of this section is to evaluate the relative validity of the reaction scheme proposed in this work.

3.3. Pathway 2

The first of the alternative pathways studied is that in which $HCOOCH_3$ is formed by a reaction between a formate species and a
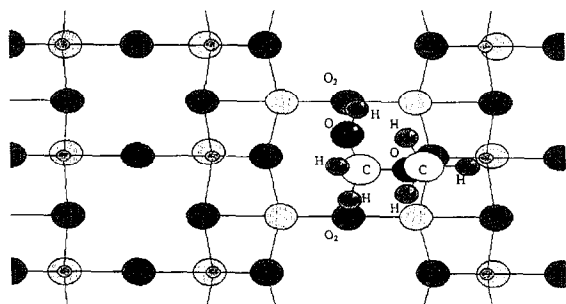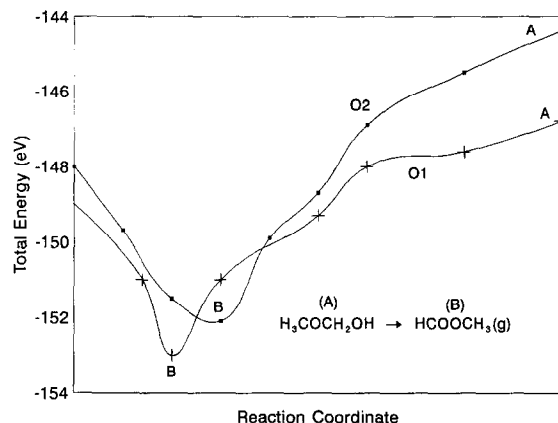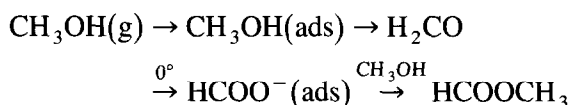

Fig. 9. HCOOCH₃ formation. Interaction H/O₂.

Fig. 10. System total energy curve; HCOOCH₃ formation (pathway 1).

CH_3OH molecule. This route was proposed by Liu et al. [14]

$$CH_3OH(g) \rightarrow CH_3OH(ads) \rightarrow H_2CO$$

$$\xrightarrow{0°} HCOO^-(ads) \xrightarrow{CH_3OH} HCOOCH_3$$

3.3.1. Formation of HCOO⁻ species

In the first place, we analyzed whether the transformation of an adsorbed CH_3OH molecule into $HCOO^-$ was sterically possible, and the result was that it is not favored with respect to bond lengths and molecular geometry. For this reason, we proceeded by studying $HCOOCH_3$ formation from adsorbed CH_3OH, its desorption as H_2CO, the adsorption of the last product and the formation of $HCOO^-$.

By experiment, Sambeth et al. [1] have found that the H_2CO exerts an important partial pressure in the reaction atmosphere, because of which a formaldehyde molecule may absorb on other site and react.

$HCOO^-$ formation was possible from the separation of one of the H of H_2CO and the interaction between the C and an O_1 of the V=O group.

The energy minimum was found when interacting an H with bridge oxygen (O_3) at a bond length of 1.02 Å between the atoms. From this position, the H–C bond was gradually stretched
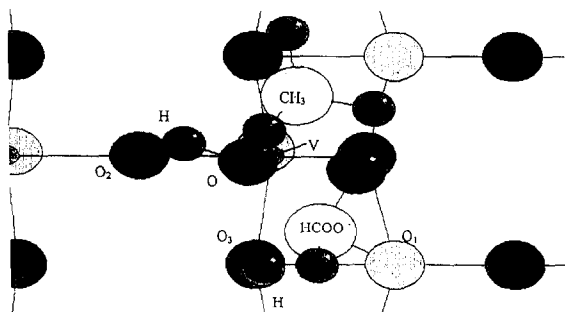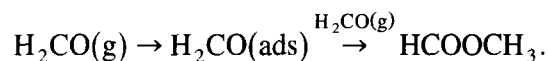
Fig. 11. Representation of HCOOCH₃ formation (pathway 2).

Reaction Coordinate

Fig. 12. System total energy curve. HCOOCH₃ formation (pathway 2).

to facilitate the interaction between the C and the O_1, and the energy minimum was obtained at a distance of 1.48 Å.

3.3.2. HCOOCH₃ formation

Once the formate species was formed, we analyzed two mechanisms to make it react with a CH_3OH molecule. In the first, a Langmuir–Hinshelwood mechanism was followed while, the second complied with the Eley–Rideal mechanism. The first situation was found more energetically stable; in it, the H of the OH from the new CH_3OH molecule interacts with an O_2 (distance 1.13 Å), and the O of the OH group with a V having its double oxygen bond facing inward the network (distance 1.62 Å). Finally, as the $C-O_1$ bond distance of the formate was shortened, the $C=O$ bond (of the formate) was stretched, so linking this last O with the CH_3 group of the adsorbed methanol (Fig. 11). As seen in the Fig. 12, the energy minimum was found for a C–O bond distance of 1.52 Å.

3.4. Pathway 3

The second alternative reaction pathway is based on Cannizzaro's deproportionation, and was suggested by some authors such as Ai [15] and Elmi et al. [27].

$$H_2CO(g) \rightarrow H_2CO(ads) \xrightarrow{H_2CO(g)} HCOOCH_3.$$

Several different positions were tested for the adsorption of a H_2CO molecule so as to favor the removal of one of the H of the molecule by
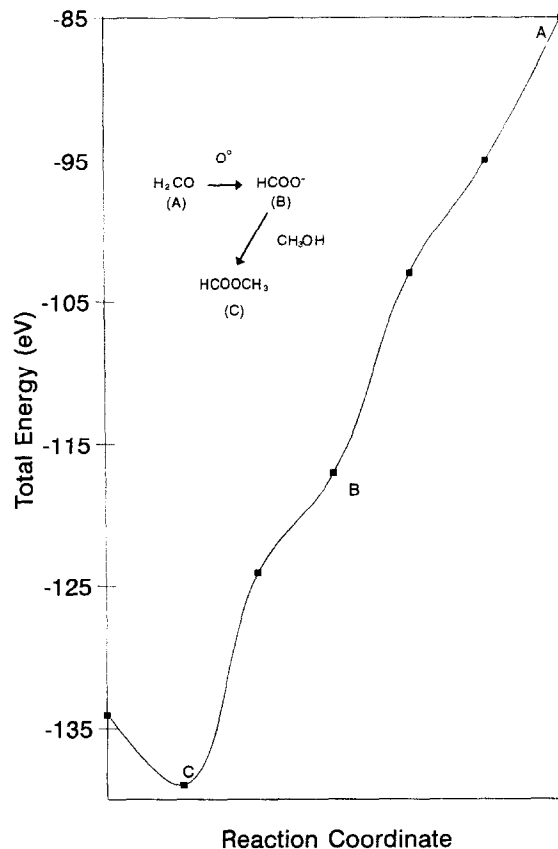
an oxygen of the network. The energy minimum was achieved for a distance of 1.12 Å between such H and an O_3.

To adsorb the second formaldehyde molecule, we looked for an angle such that, on adsorbing, the distance between the atoms of both molecules were adequate to allow the interac-
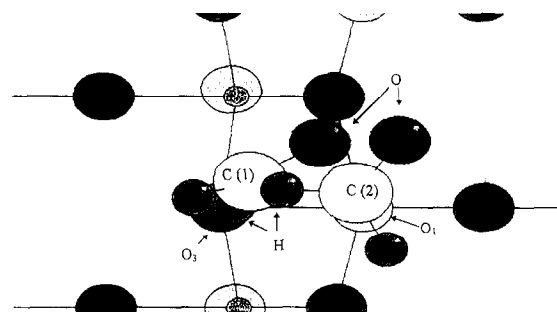
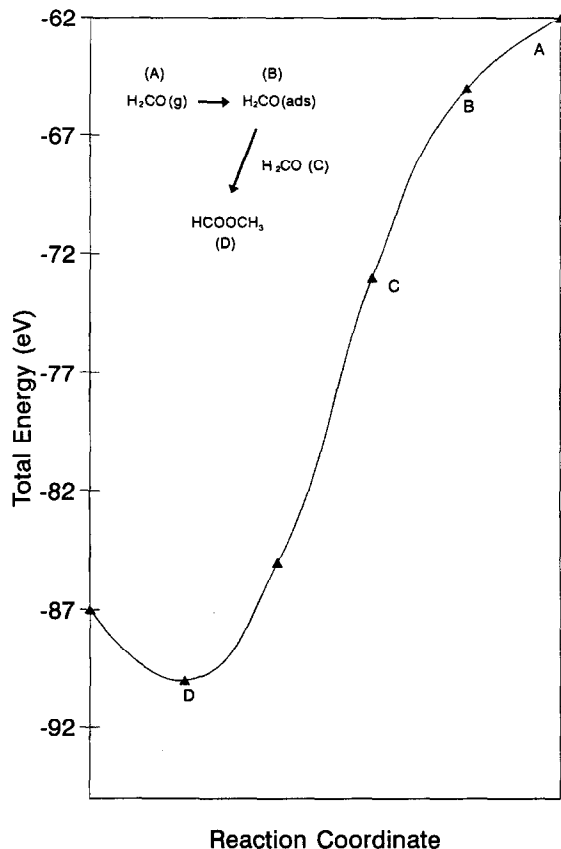

Fig. 13. Representation of HCOOCH₃ formation (pathway 3).

Fig. 14. System total energy curve. HCOOCH$_3$ formation (pathway 3).

tion between the O of the first H$_2$CO with the C of the second (bond distance 1.47 Å [24]), and the C of the first with a H of the second molecule (distance 1.09 Å [24]).

The optimum angle between the C=O axis and the cluster surface was of 5°, and at the energy minimum, the distances obtained for the C–O and C–H bonds were of 1.53 and 1.14 Å respectively (Figs. 13 and 14).
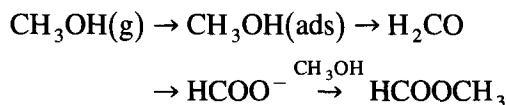
The three reaction pathways studied by the extended Hückel method are presented in the following scheme, together with their corresponding energy minima.
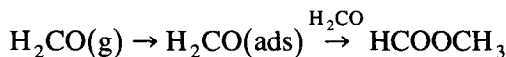
Pathway 1

$$CH_3OH(g) \rightarrow CH_3OH(ads) \rightarrow H_2CO$$
$$\overset{CH_3OH}{\rightarrow} CH_3OCH_2OH \rightarrow HCOOCH_3$$
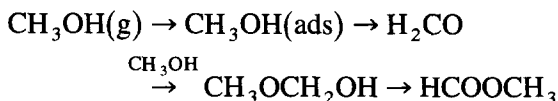
(Minimum system energy = − 153 eV).

Pathway 2

$$CH_3OH(g) \rightarrow CH_3OH(ads) \rightarrow H_2CO$$
$$\rightarrow HCOO^- \overset{CH_3OH}{\rightarrow} HCOOCH_3$$

(Minimum system energy = − 139 eV).

Pathway 3

$$H_2CO(g) \rightarrow H_2CO(ads) \overset{H_2CO}{\rightarrow} HCOOCH_3$$

(Minimum system energy = − 90 eV)

Comparing the minimum energy values of the different pathways, we found that the reaction route proposed experimentally by Sambeth et al. [1] was the most favorable. It must be pointed out that the two pathways (1 and 2) involving reaction intermediates were those that presented the lower system energies.

4. Conclusions

The previous experimental study of CH$_3$OH adsorption–oxidation on V$_2$O$_5$ [1] allowed a possible reaction pathway to be proposed.

From a model of the plane (010) of V$_2$O$_5$ and of the CH$_3$OH molecule, the proposed pathway was analyzed together with two alternative pathways for HCOOCH$_3$ formation.

The results showed that:

(i) There is an acceptable correlation between the proposed pathway (pathway 1) and the variation of the total system energy in each step of the mechanism.

(ii) The way in which a molecule is adsorbed affects the reaction mechanism (formation of a carbocation that reacts with a second methanol molecule).

(iii) In the alternative mechanisms studied we found, in agreement with previous reports by other authors [6–8], that the bridge oxygens may actively participate in the nucleophilic oxidation process of organic molecules.

(iv) The three reaction pathways studied were compared, and the result was that the mechanism proposed by Sambeth et al. [1] was the

most favorable (pathway 1). Besides, it was found that the mechanisms allowing the formation of intermediates ((CH_3OCH_2OH, pathway 1), ($HCOO^-$, pathway 2)) favored a decrease in the reaction energy.

Acknowledgements

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