

Oxidation of Methanol to Formaldehyde Catalyzed by V_2O_5 . A Density Functional Theory Study

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The adsorption of methanol on V_2O_5 and its mild oxidation to formaldehyde has been studied applying density functional theory. The model used throughout is a cluster model saturated by hydrogen atoms. It is shown that the adsorption of methanol is energetically favored if the cluster is partially reduced (i.e., protonated because of the dissociative adsorption of water). Methanol behaves as a soft base and adsorbs as a methoxonium cation. The proposed mechanism is based on two steps, the first being the dissociation of methanol to form a methoxy group on the surface. This dissociation occurs between the oxygen and the carbon atoms of methanol. Finally, for the second step, which corresponds to the desorption of formaldehyde, the calculations show that filling of the vanadyl oxygen vacancy created by formaldehyde desorption is crucial to cope with an energetically feasible reaction pathway.

I. Introduction

The catalytic oxidation of methanol has been the subject of intensive studies because of its importance for the production of basic chemicals such as formaldehyde and formic acid. Formaldehyde is industrially mainly produced by direct oxidation (oxidative dehydrogenation) of methanol over a mixed molybdenum oxide (MoO_3)–ferric molybdate ($Fe_2(MoO_4)_3$) catalyst.¹ Other oxidic materials that are highly selective for methanol oxidation are molybdenum oxide (MoO_3) and vanadium pentoxide (V_2O_5). Tatibouët and Germain² obtained formaldehyde with a selectivity amounting to 97% on pure vanadia catalyst. These authors also showed^{2–4} that formaldehyde selectivity depends on the exposed face, provided that the conversion rate in methanol is low. They suggested that the (100) face is involved in the formation of the methylal molecule whereas the (010) face is responsible for the formation of formaldehyde and dimethyl ether.

Based on FT-IR studies, Busca et al.⁵ proposed a mechanism for the oxidation in which methanol adsorbs dissociatively on the surface forming methoxy groups. However, it has also been observed⁶ by FT-IR study that methanol has the ability to adsorb without dissociation on the surface.

This work reports a density functional theory study on the adsorption of methanol on the (010) face of V_2O_5 , a comparison between experimental IR spectra and theoretical ones, and the elaboration of a mechanism for the conversion of methanol into formaldehyde.

II. Computational Background

Density functional theory^{7,8} (DFT) calculations have been performed both at the local spin density (LSD) approximation, using the VWN⁹ functional, and the generalized gradient approximation (GGA) using Becke's functional¹⁰ for exchange and Perdew's one¹¹ for correlation (BP86). All energies reported in the present work are GGAs, whereas geometries of clusters containing four vanadiums are optimized only at the LSD level. For the study of the adsorption of methanol on V_2O_5 , the linear combination of Gaussian-type orbitals—model core potential (LCGTO–MCP-DFT) DeMon-KS package¹² has been used. The basis sets are of triple- ζ plus polarization and diffuse functions quality, the contractions being V(63321/531*/41+), O(5221/411/1), C(5221/411/1), and H(41/1). Both the electron density of the system and the exchange–correlation potential are fitted with a Gaussian-type basis set called the auxiliary basis set. These basis sets are (5,5;5,5) for vanadium atom, (5,2;5,2) for oxygen and carbon atoms, and (5,1;5,1) for hydrogen atom.

Concerning the study of the oxidation mechanism of methanol, the ADF99 program¹³ has been used. The basis sets are built on Slater-type orbital primitives. A set of triple- ζ has been chosen for our study (basis set IV according to ADF notation). These basis sets include polarization functions on C, O, and H atoms.

III. Surface Model: Choice of Clusters

Whatever the selected model, the slab or the cluster model, it is known that the major difficulty in surface studies is to correctly describe the properties of the surfaces.^{14–16} We have chosen the cluster model. Although it has been claimed that there is no major influence on the properties of the material,¹⁷ dangling bonds have been saturated by hydrogen atoms.

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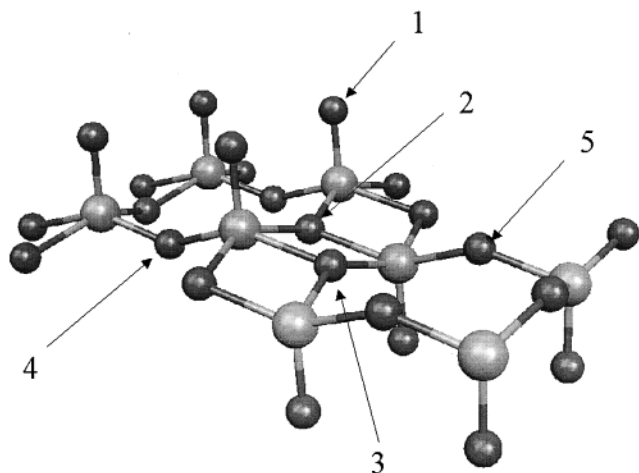


Figure 1. Oxygen types in V_2O_5 : (1) vanadyl oxygen atoms; (2,3) capping oxygen atoms; (4,5) bridging oxygen atoms.

The crystal lattice structure of vanadium pentoxide, V_2O_5 , has been widely described in the literature in the past.^{8,19} The (010) face of V_2O_5 exhibits five chemically different oxygen atoms, but only three are structurally distinguishable (see Figure 1).

The vanadyl oxygen atoms (labeled 1 in Figure 1) are bonded to a single vanadium atom by a double bond. Structurally equivalent atoms 2 and 3 are capped. Those oxygens are shared by two squared pyramids; they are thus bonded to three adjacent vanadium atoms. Finally, oxygens 4 and 5 are bridged between two vanadium atoms.

We have selected four kinds of clusters to model the local active site of the surface for the adsorption of methanol, so as to consider the three nonequivalent oxygen atoms (labeled 1, 2, and 3 in Figure 1) among the five ones. As previously

mentioned, these clusters are saturated with hydrogen atoms, thus forming OH groups of atoms in the periphery of the clusters. The clusters are depicted in Figures 2 and 3. Nine clusters have been chosen to model the adsorption of methanol. The clusters **1'** ($[(VOH)(VO)O(OH)_6]^-$), **2'** ($[(VOH)(VO)O-(VO)(OH)_7]^+$), **3'** ($[(VOH)O(VO)(VO)(OH)_7]^+$), and **3''** ($[(VO)-(OH)(VO)(VO)(OH)_7]^+$) are the protonated forms of clusters **1** ($[(VO)(VO)O(OH)_6]^{2-}$), **2** ($[(VO)(VO)O(VO)(OH)_7]$) and **3** ($[(VO)O(VO)(VO)(OH)_7]$). It is well-known that the catalyst is covered by hydrogen atoms originating from slight reduction of the surface by dissociative adsorption of water molecules. Consequently, the adsorption of methanol on such a reduced surface has also been considered. The protonation of clusters **3** can occur either on the vanadyl oxygen, which affords cluster **3'**, or on the capping oxygen, which gives cluster **3''**. Clusters **2** and **3** are structurally equivalent, but the bridging oxygen atoms are chemically different. Finally, cluster **2** exhibits oxygen atoms of type 1 and 2 and cluster **3** exhibits oxygen atoms of type 1 and 3 (Figure 1).

Structures **4** ($[(VO)_4O_4(OH)_8]^{4-}$) and **4'** ($[(VOH)(VO)_3-O_4(OH)_8]^{3-}$) (Figure 3) are the largest clusters studied in this work. They have been used to study both the adsorption of MeOH and its reactivity on vanadate-type oxygen atoms (i.e., protonated vanadyl oxygen atoms).

To obtain pertinent adsorption energies of methanol, partial optimization of both methanol and clusters has been performed. As the methanol approaches the clusters, the positions of the vanadyl oxygen atoms or those of vanadate groups were geometrically relaxed. The positions of both vanadium atoms and surrounding OH groups were kept frozen. It is to be emphasized that, in the cases of reduced clusters, structures for the adsorption of methanol were obtained from a guess structure in which methanol interacts with clusters. In particular, the

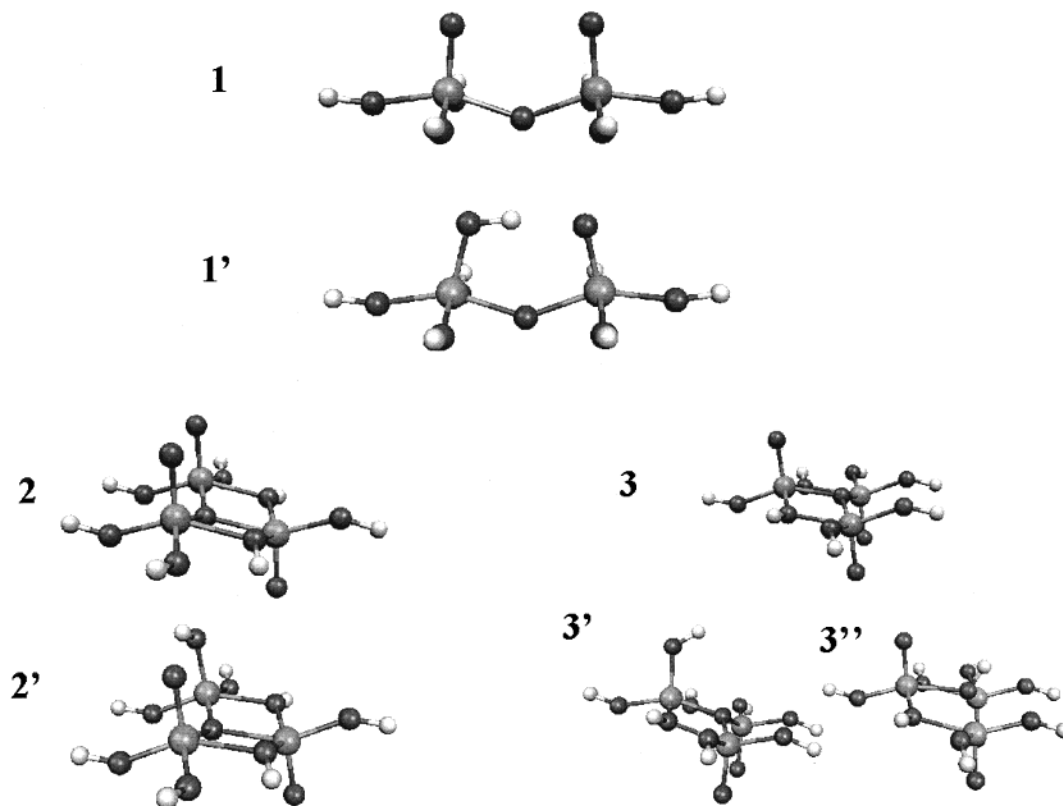


Figure 2. Model clusters in V_2O_5 : (1) $[(VO)(VO)O(OH)_6]^{2-}$; (1') $[(VOH)(VO)O(OH)_6]^-$; (2) $[(VO)(VO)O(VO)(OH)_7]$; (2') $[(VOH)(VO)O(VO)-(OH)_7]^+$; (3) $[(VO)O(VO)(VO)(OH)_7]$; (3') $[(VOH)O(VO)(VO)(OH)_7]^+$; (3'') $[(VO)(OH)(VO)(VO)(OH)_7]$.

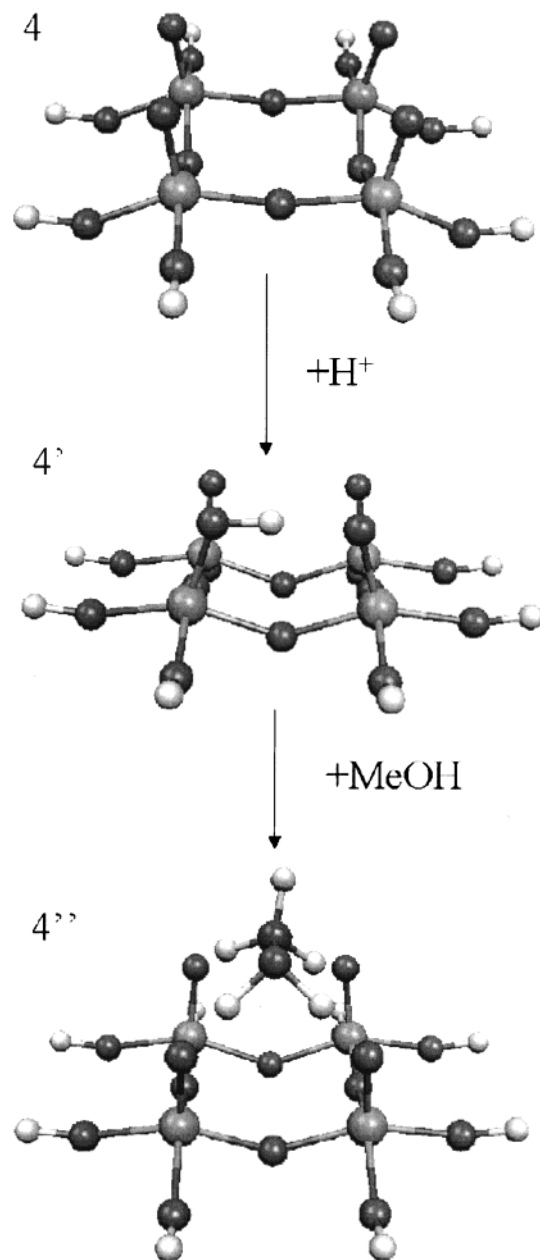


Figure 3. Adsorption of methanol on $[(\text{VOH})(\text{VO})_3\text{O}_4(\text{OH})_8]^{3-}$: (**4**) $[(\text{VO})_4\text{O}_4(\text{OH})_8]^{4-}$; (**4'**) $[(\text{VOH})(\text{VO})_3\text{O}_4(\text{OH})_8]^{3-}$; (**4''**) $\text{MeOH}/[(\text{VOH})(\text{VO})_3\text{O}_4(\text{OH})_8]^{3-}$.

protonation of methanol results from migration of the proton from the cluster to the sorbate.

Finally, the basis set superposition error (BSSE) has been estimated to correct the adsorption energies using the counterpoise method of Boys and Bernardi.²⁰ Because the basis sets used in the calculations are quite large, the BSSE corrections amount to only 1.5–3.0 kcal mol⁻¹, depending on the structure.

Finally, as clusters **1'**, **2'**, **3'**, and **3''** are charged, very crude a posteriori correction due to the artificial electrostatic contribution has been brought to the adsorption energy of methanol. This term is calculated from the expression

$$E_{\text{electrostatic}} = \sum_i^A \sum_j^B \frac{q_i q_j}{r_{ij}}$$

where A and B are the number of atoms in the adsorbate and the support, respectively, q is the Hirschfeld charge²¹ of the

TABLE 1: Geometrical Parameters of the Naked Clusters and Protonated Clusters

structures	description	distances (Å)
1^a	VO	1.619/1.619
1'^a	VO(H)	1.764
	OH	1.022
	H...O(V)	1.778
	VO	1.642
2^a	VO	1.589/1.589
2'^a	VO(H)	1.726
	OH	0.997
	H...O(V)	2.380
	VO	1.594
3^a	VO	1.592
3'^a	VO	1.747
	OH	0.986
3''^a	VO	1.580
	OH	0.990
4^b	VO	1.611/1.611/1.612/1.612
	VO ^c	1.601/1.603
	VO	1.646
	VO(H)	1.748
	OH	1.047
	H...O(V)	1.618

^a Structures are depicted in Figure 2. ^b Structures are depicted in Figure 3. ^c VO bonds opposite to VOH.

corresponding atom, and r is the distance between the atoms. Hirshfeld charges are provided by the ADF code and are less basis set dependent than Mulliken charges. The accuracy of this correction is definitely poor, because it involves a point charge model to estimate the contribution. It is, however, necessary to use such a correction to “normalize” adsorption energies.

IV. Results and Discussion

A. Geometries and Adsorption Energies. The structures of the clusters used in this study are depicted in Figure 2. Some geometrical parameters are presented in Table 1. For structure **1**, the VO bond lengths amount to 1.62 Å. These values are close to those previously published²² from a theoretical investigation of the V₂O₅ surface using periodic DFT calculations (1.61 Å). They are indeed significantly larger than the bulk VO bond lengths (1.54 Å).²³ It is noteworthy that VO bonds are systematically lengthened for clusters containing three vanadium atoms (structures **2** and **3** in Figure 2), whereas for the cluster containing four vanadium atoms (structure **4** in Figure 3), VO bond lengths amount to 1.61 Å. At this stage, no clear explanation for those behaviors can be given.

For structures **1'** and **2'** in Figure 2 and **4'** in Figure 3, the trivial consequence of protonation is the elongation of the VO bond lengths and the formation of hydrogen bonding interactions with adjacent vanadyl oxygen atoms (see Table 1).

Structures of the adsorbed methanol are depicted in Figures 3 and 4. For the sake of completeness, some geometrical parameters are presented in Table 2 but will not be discussed in detail. It can be seen that in the case of the reduced clusters (structures **4''**, **5'**, **6'**, and **7''**), the methanol molecule forms hydrogen bonds with the cluster. It is therefore expected that adsorption energies should be higher in these cases. This trend is clearly seen in Table 3, except for structure **5'** for which the adsorption energy is about twice lower than that of structure **5**.

As shown in Figures 3 and 4, adsorption of methanol on large reduced clusters (i.e., clusters containing at least three vanadium atoms) leads systematically to a protonated methanol species,

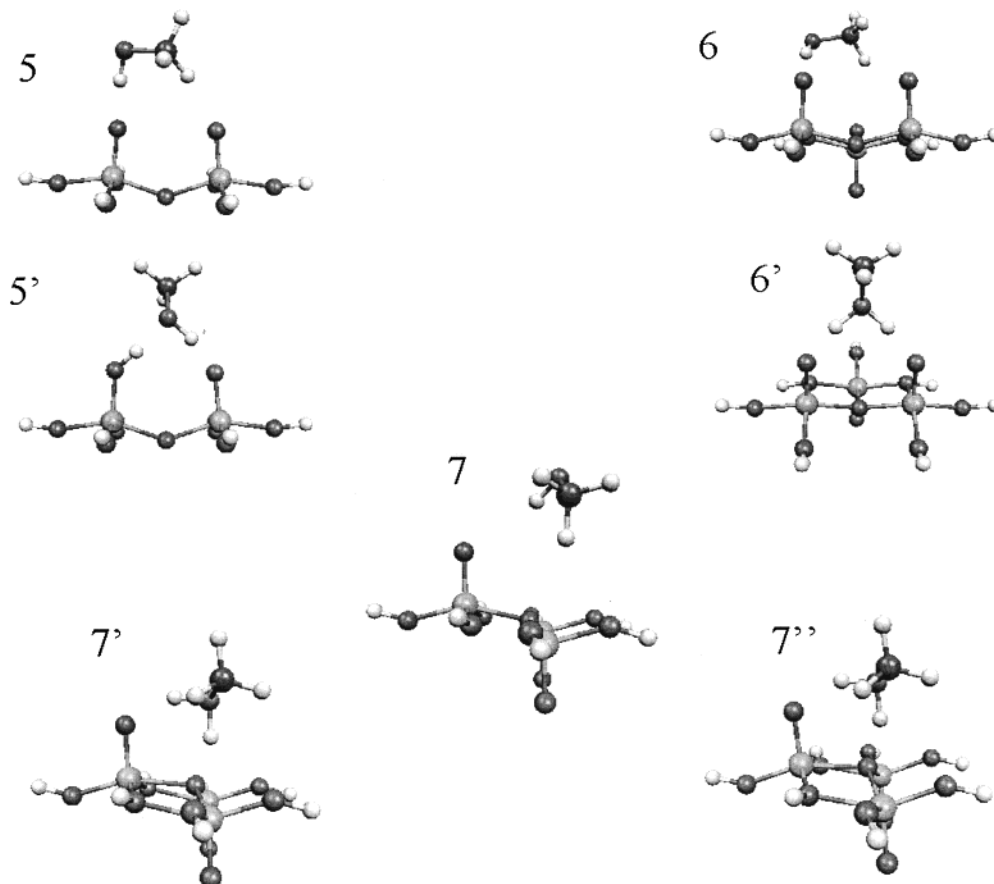


Figure 4. Adsorption of methanol on various clusters: (5) $\text{MeOH}/[(\text{VO})(\text{VO})\text{O}(\text{OH})_6]^{2-}$; (5') $\text{MeOH}/[(\text{VOH})(\text{VO})\text{O}(\text{OH})_6]^-$; (6) $\text{MeOH}/[(\text{VO})(\text{VO})\text{O}(\text{VO})(\text{OH})_7]$; (6') $\text{MeOH}/[(\text{VOH})(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^+$; (7) $\text{MeOH}/[(\text{VO})\text{O}(\text{VO})(\text{VO})(\text{OH})_7]$; (7') $\text{MeOH}/[(\text{VOH})\text{O}(\text{VO})(\text{VO})(\text{OH})_7]^+$; (7'') $\text{MeOH}/[(\text{VO})(\text{OH})(\text{VO})(\text{VO})(\text{OH})_7]^+$.

that is, a methoxonium ion. This trend can be explained by the Brønsted's acid/base principle. Because methanol behaves as a soft base, it can be protonated upon adsorption on a reduced surface. The methanol molecule can therefore abstract a hydrogen from the surface to facilitate the process of adsorption. This behavior has indeed been evidenced in a previous theoretical investigation of the adsorption of methanol on the chabazite zeolite.²⁴ From dynamics, it has been shown that the proton can easily migrate back and forth between the zeolite and the methanol, forming a methoxonium ion.

On the basis of these results, we conclude that clusters **1** and **1'** are too small to describe properly the process of methanol adsorption. Consequently, for the subsequent study of the reaction mechanism, we have used clusters containing at least three vanadium atoms.

B. Reaction Mechanism for the Oxidation of Methanol.

Important features of the reaction mechanism emerging from experimental studies are as follows: (1) Methanol adsorbs on V_2O_5 and dissociates to form methoxy groups adsorbed on the surface.^{5,25} (2) A hydrogen atom is removed from the methoxy group facilitating the desorption of formaldehyde. This step is supposed to be the rate-limiting step of the reaction.^{26–28} (3) According to the Mars–van Krevelen mechanism,²⁹ the oxygen vacancy is filled by an oxygen atom originating from the lattice. (4) During the process, water is formed as a byproduct.

To elucidate which oxygen atoms are responsible for the different steps of the reaction, we first studied the formation of an adsorbed methoxy group on the surface and then the desorption of formaldehyde. For this purpose, we have used two types of clusters: **2** ($[(\text{VO})(\text{VO})\text{O}(\text{VO})(\text{OH})_7]$) (Figure 2) and **4** ($[(\text{VO})_4\text{O}_4(\text{OH})_8]^{4-}$) (Figure 3). These clusters have been

protonated on a vanadyl oxygen atom to mimic a partially reduced reactive site. The resulting clusters are **2'** ($[(\text{VOH})(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^+$) and **4'** ($[(\text{VOH})(\text{VO})_3\text{O}_4(\text{OH})_8]^{3-}$).

To calculate the reaction path, we have used, throughout this work, a method that consists of performing a linear transit calculation from the reactant, which is either the adsorbed methanol for the first step or the adsorbed methoxy group for the second step of the reaction, to the product, which is either the methoxy group or formaldehyde, respectively. More precisely, one bond is linearly incremented and kept frozen, whereas the positions of the remaining atoms are relaxed, the V_xO_y skeleton corresponding to the bottom of the cluster being kept frozen in its geometry optimized in the naked cluster. It should be noted that this procedure gives only a very crude estimate of the energetic barrier for each step.

1. Dissociative Adsorption of Methoxy Groups. For the modeling of the first step, we assumed that the oxygen of the adsorbed methoxy group originates from vanadia. This assumption is in agreement with experimental findings. Dissociation of the methanol molecule is expected to occur between the carbon and oxygen atoms. A good candidate for the breaking of the CO bond is the methoxonium form of methanol. Both structures **4''** in Figure 3 and **6'** in Figure 4 can be used to model this process. It can be assumed that upon stretching the CO bond the methyl group has to be stabilized by the cluster, otherwise the energetic barrier will be too high. The reaction paths have been calculated using clusters **6'** and **4''**, as depicted in Figures 5 and 6, respectively.

Following the reaction coordinates (Figure 5), which correspond to the shortening of the $(\text{V})\text{O}\cdots\text{C}(\text{H}_3)$ distance, we can see that the adsorbed methanol first rearranges to form a more

TABLE 2: Geometrical Parameters of Adsorbed Methanol

structures	description	distances (Å)
4''^a	VO ^c	1.669/1.674
	(V)O...H(O)	1.226/1.250
	OH	1.144/1.165
	VO ^d	1.610/1.610
	(V)O...H(C)	2.036/2.084
5^b	VO(...HO)	1.636
	VO(...HC)	1.619
	O...H(O)	1.695
	O...H(C)	2.308
	OH	1.080
5''^b	VO(H)	1.738
	VO	1.643
	(V)OH	1.040
	(V)O...H	1.517
	(O)H...O(C)	1.545
6^b	HO(C)	1.031
	VO	1.592/1.601
	O...H(O)	2.110
	O...H(C)	2.365
	OH	0.978
6''^b	VO	1.632/1.633
	(V)O...H(O)	1.471/1.474
	OH	1.048/1.048
7^b	VO	1.600
	(V)O...H(O)	2.612
	OH	0.979
7''^b	VO	1.620
	(V)O...H(O)	1.678
	(VO...HO)	1.019
	OH(...OV ₂)	1.067
	H...O(V ₂)	1.521
7''^b	VO	1.584
	O _{capped} ...H(O)	1.720
	(O _{capped} ...HO)	1.020
	OH	1.089

^a Structure is depicted in Figure 3. ^b Structures are depicted in Figure 4. ^c VO bonds near to the alcoholate group. ^d VO bonds near to the methyl group.

TABLE 3: Adsorption Energy of Methanol on Various Clusters

structures	BP86 adsorption energy (kcal mol ⁻¹)
5 , MeOH/[(VO)(VO)O(OH) ₆] ^{2-a}	-16.8
6 , MeOH/[(VO)(VO)O(VO)(OH) ₇] ^a	-1.4
7 , MeOH/[(VO)O(VO)(VO)(OH) ₇] ^a	-2.2
5' , MeOH/[(VOH)(VO)O(OH) ₆] ^{1-a}	-7.7
6' , MeOH/[(VOH)(VO)O(VO)(OH) ₇] ^{+a}	-22.1
7' , MeOH/[(VOH)O(VO)(VO)(OH) ₇] ^{+a}	-9.7
7'' , MeOH/[(VO)(OH)(VO)(VO)(OH) ₇] ^{+a}	-12.9
4'' , MeOH/[(VOH)(VO) ₃ O ₄ (OH) ₈] ^{3-b}	-20.9

^a Structures are depicted in Figure 4. ^b Structure is depicted in Figure 3.

stable adsorbate (from the first structure to the second one, the latter one corresponding to structure **6'** in Figure 4). The stabilization energy amounts to 12.5 kcal mol⁻¹. Then, the system crosses a high barrier (52.5 kcal mol⁻¹) to give the methoxy group adsorbed on the cluster. The water molecule released during this process remains adsorbed on the cluster, the lone pair orbitals of the oxygen atom interacting with the d orbitals of the third vanadium atom. The V—O(H₂) distance amounts to 2.75 Å. According to this reaction path, the dissociation of methoxonium is endothermic by 14.0 kcal mol⁻¹. Whereas the endothermicity in this step is not dramatic, the energetic barrier is much too high to be overcome at experi-

TABLE 4: Calculated IR Spectrum of Adsorbed Methoxy Species^a

vibration mode	calcd (cm ⁻¹)	expt ^{5,30}
$\nu_{as}(\text{VO})$	955, 983	950
		:
$\nu_s(\text{VO})$	971	1020
$\nu(\text{CO})$	1045	1070
$\delta(\text{CH}_3 \text{ "wagging"})$	1089	
$\delta(\text{CH}_3 \text{ "rocking"})$	1115	1155
$\delta(\text{CH}_3 \text{ "umbrella"})$	1367	
$\delta_{as}(\text{CH}_3)$	1376	1435
$\delta_s(\text{CH}_3)$	1410	1448
$\nu_s(\text{CH}_3)$	2857	2830
$\nu_{as}(\text{CH}_3)$	2949	:
$\nu_{as}(\text{CH}_3)$	2953	2930

^a The structure corresponds to the last cluster in Figure 6 (excluding the water molecule).

mental temperature (about 520 K), therefore ruling out this cluster for the dissociation of methanol.

Figure 6 shows the reaction path for the first step using structure **4''** as the active site. The reaction coordinate corresponds to the CO bond stretching. Upon stretching the CO bond, the methoxonium crosses the barrier, which amounts to 17.5 kcal mol⁻¹. The intermediate structure is a partially dissociated methoxonium ion in which the methyl group interacts with the vanadyl oxygen atom of the cluster. This stabilizing interaction is counteracting toward destabilization due to the dissociation. The balance justifies the much lower barrier as compared to that of the previous mechanism. Once the barrier is crossed, the methyl group is adsorbed on the surface forming a methoxy group and the water molecule is released, adsorbed on two vicinal vanadyl oxygen atoms. The product obtained by this reaction is more stable than the reactant by 4.7 kcal mol⁻¹. Finally, at the end of the process, a water molecule adsorbed on the cluster is formed. The distances of the adsorbed water molecule to the cluster are 1.664 and 1.904 Å for both O...H interactions, which lie exactly in the range of typical hydrogen bonds.

The theoretical IR spectrum of the adsorbed methoxy group has been calculated. The results are summarized in Table 4. Note that the vanadyl bands are calculated at 955 and 983 cm⁻¹ for the asymmetric modes and 971 cm⁻¹ for the symmetric one. This is in very good agreement with experimental observations.^{5,30} For the CO stretching frequency of the methoxy group, the difference between experiment and theory amounts to only 35 cm⁻¹. Concerning the CH₃ bending and stretching modes, the deviation from experimental observations is slightly bigger. However, the mean absolute deviation in percentage (2.5%) remains in the commonly admitted range of errors (4%).

In conclusion, both energetic and IR calculations show that the formation of methoxy groups adsorbed on the surface may result from the breaking of the CO bond of an adsorbed methoxonium species. The agreement between the calculated and observed IR spectra suggests that this kind of methoxy groups is probably the most abundant one on the surface of the catalyst.

2. Desorption of Formaldehyde. The second step of the mechanism deals with the desorption of the methoxy group previously formed. This desorption occurs via dissociation, because a methyl hydrogen atom must be transferred onto the surface.

To study this step, the structure depicted in Figure 7, [(VOCH₃)(VO)O(VO)(OH)₇]⁺, has been used. It corresponds exactly to the same adsorption site for the methoxy species as in the previous step.

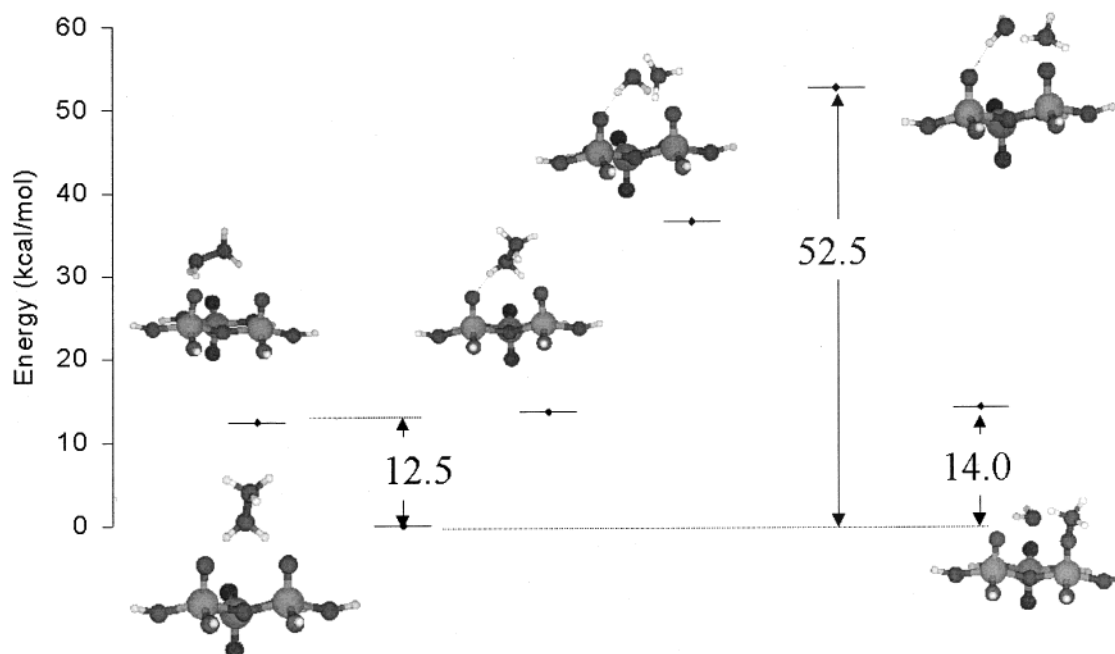


Figure 5. Reaction path for the first step of the mechanism. The starting structure is **6'**, $\text{MeOH}/[(\text{VOH})(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^+$. The reaction coordinate corresponds to the shortening of the $(\text{V})\text{O}\cdots\text{C}(\text{H}_3)$ distance.

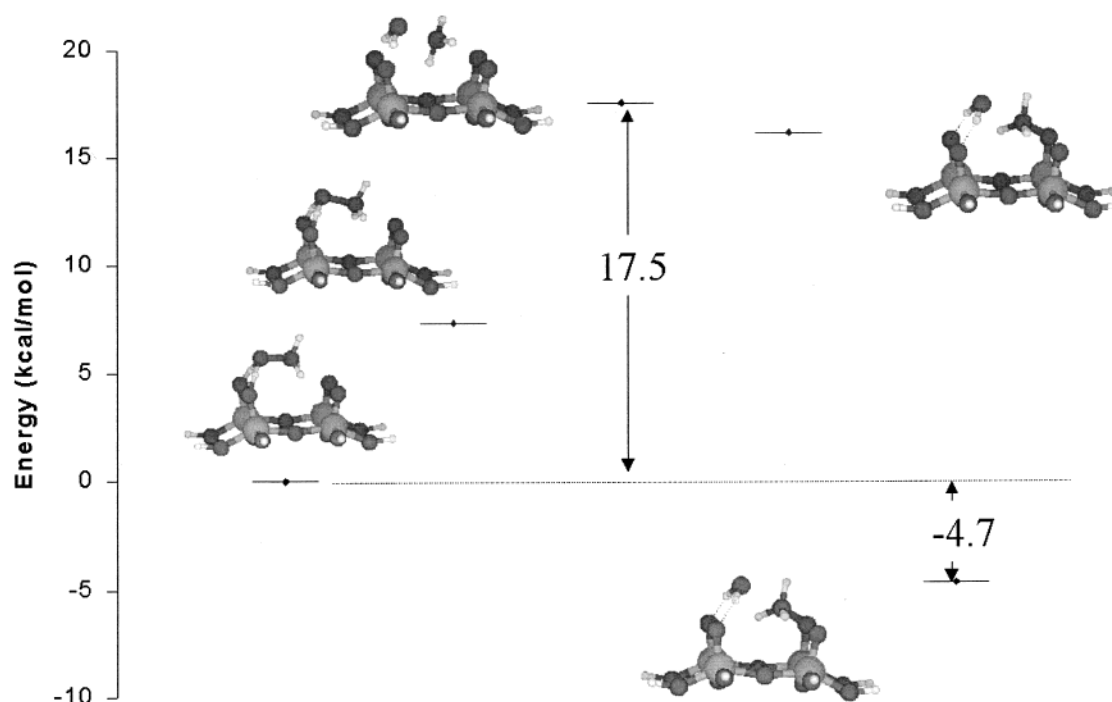


Figure 6. Reaction path for the first step of the mechanism. The starting structure is **4''**, $\text{MeOH}/[(\text{VOH})(\text{VO})_3\text{O}_4(\text{OH})_8]^{3-}$. The reaction coordinate corresponds to the stretching of the CO bond.

The calculation has been carried out for the reaction path in which the reaction coordinate corresponds to a linear combination of both the C–H and V–O bond stretching. The reaction path for this step is depicted in Figure 8. It can be seen that the energy of the system is steeply rising along the path to reach a peak at $72.0 \text{ kcal mol}^{-1}$. The estimated barrier is much too high and rules out this mechanism. Furthermore, the fully relaxed product (last structure in Figure 8) shows the following: (1) Formaldehyde readsorbs on the cluster. This demonstrates that vanadyl oxygen-type vacancies are very unstable and must be filled spontaneously. This trend has already been seen in previous works.^{31,32} (2) The step is highly endothermic. This

means that the whole reaction is endothermic too, which disagrees with experimental observations.

As a consequence, new assumptions have been made concerning this step. According to the Mars–van Krevelen mechanism, oxygen vacancies are filled with the dissociative adsorption of gas-phase oxygen molecules. This creates some oxygens in the lattice of the catalyst that move from site to site. For the step with which we are concerned, we have seen that the vanadyl vacancy has to be filled spontaneously, and possibly, we can assume a concerted mechanism. On the basis of this hypothesis, we have optimized the position of a lattice oxygen near the active site. According to the structure of the

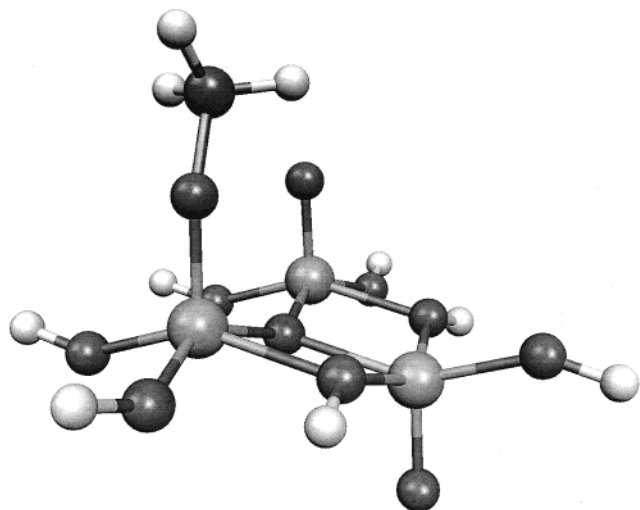
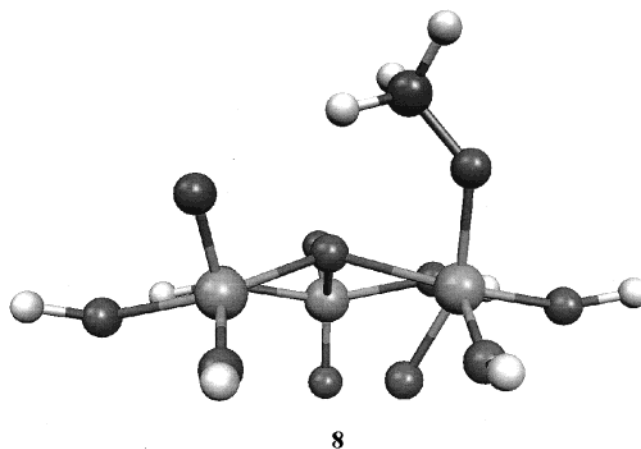


Figure 7. Cluster $[(\text{VOCH}_3)(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^+$ used to study the desorption of formaldehyde.

catalyst, the oxygen should be bonded to a vanadium atom under the medium plane of the surface. The corresponding cluster is depicted in Figure 9, and the stoichiometry is **8** $[(\text{OVOCH}_3)(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^-$. The lattice oxygen is bonded to the vanadium atom forming a distorted octahedral site around V. The VO bond distance amounts to 1.716 Å, which is, as expected, slightly larger than a vanadyl bond (ca. 1.62 Å). A consequence of the distortion is that the capping oxygen is pushed out of the surface, whereas the lattice oxygen tends to replace it. In other words, the capping oxygen moves further away from the medium plane of the surface, while the lattice oxygen gets closer to it.

From structure **8**, a reaction path for the desorption of formaldehyde has been calculated. The results are depicted in Figure 10. Along the reaction coordinate, which corresponds



8

Figure 9. Optimization of the position of a lattice oxygen for the regeneration of the vanadyl oxygen vacancy. The stoichiometry of the structure is $[(\text{OVOCH}_3)(\text{VO})\text{O}(\text{VO})(\text{OH})_7]^-$.

to a linear combination of the bending of the $\text{O}_{\text{capping}}\text{VO}(\text{CH}_3)$ angle and the stretching of the CH bond, it can be seen that, while the capping oxygen is moving toward the methoxy group, the lattice oxygen is spontaneously migrating toward the initial position of the capping oxygen. As the system reaches the top of the barrier (31.8 kcal mol⁻¹), both the oxygen and the methyl hydrogen atom occupy an intermediate position (structure **8a**). Once the barrier is crossed, the methoxy group desorbs and is substituted by the capping oxygen atom, which, in turn, is replaced by the lattice oxygen (structure **8b**). In a subsequent pathway, the methyl hydrogen is removed from the methoxy group, which adsorbs on the surface (structure **8c**). This step requires only 2.7 kcal mol⁻¹. Finally, formaldehyde is desorbed from the surface (structure **8d**) leading to a structure that is 39 kcal mol⁻¹ more stable than the reactant (structure **8**). Once the formaldehyde molecule has been released and the oxygen

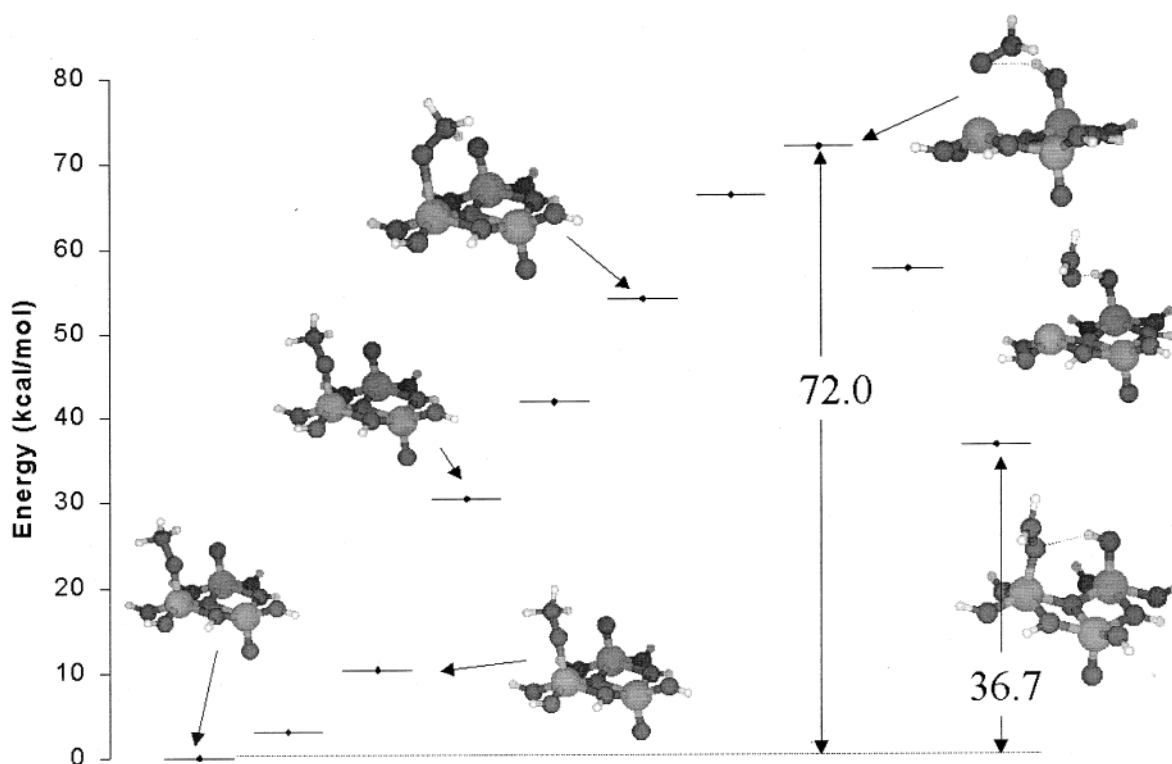


Figure 8. Reaction path leading to the desorption of formaldehyde. The reaction coordinate corresponds to a linear combination of the C-H bond stretching and the V-O bond stretching.

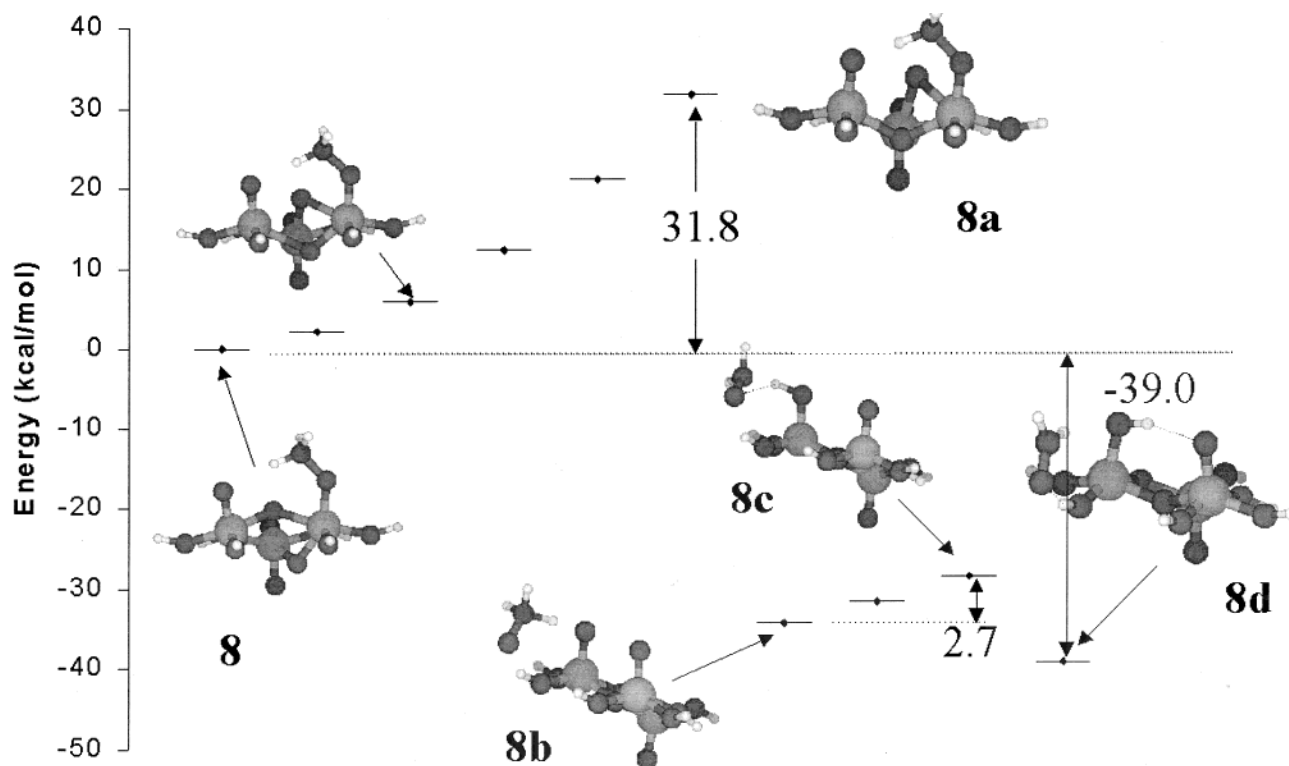


Figure 10. Reaction path for the desorption of formaldehyde mediated by a lattice oxygen. The reaction coordinate corresponds to a linear combination between the bending of the $\text{O}_{\text{capping}}\text{VO}(\text{CH}_3)$ angle and the stretching of the C–H bond.

vacancy has been filled, we obtain the same cluster as the one we have used as a starting point, that is, the catalytic cycle has been closed. It is worth mentioning that the potential energy surface (PES) seems to undergo a sharp discontinuity between structures **8a** and **8b**. This behavior is caused by the choice of the step for the reaction coordinate. The step between **8a** and **8b** results in the break of the VO bond and hence in a deep modification of the geometry, although both structures are partially optimized. A smaller step for the reaction coordinate would lead to a smoother description of the PES in this region. However, as already mentioned, this technical procedure to explore the PES gives crude estimates of energetical barriers, and we therefore did not repeat this expensive calculation with a smaller step.

For this reaction path, we have demonstrated that the energetics and the mechanism agree well with both experimental results and Mars–Krevelen reaction steps. We therefore assume that the kind of mechanism that we propose is among the most probable ones.

V. Conclusion

We have studied theoretically the adsorption of methanol on V_2O_5 and proposed a complete mechanism for the mild oxidation of methanol to formaldehyde. Methanol has been shown to adsorb preferentially on a partially reduced surface because it can form some hydrogen bonds. On a sufficiently large cluster (at least three vanadium atoms), methanol acts as soft base and adsorbs as a methoxonium cation.

The proposed mechanism is based on two steps, the first one being the dissociative adsorption of methanol to form a methoxy group on the surface. The dissociation of the methoxonium ion occurs between C and O. The methyl group adsorbs on a vanadyl-type oxygen atom thereby forming a methoxy species and releasing a water molecule. The theoretical frequency of the vibrational bands of the corresponding methoxy species are

in agreement with experimental results. The order of magnitude for the energetic barrier is ca. 20 kcal mol⁻¹.

The second step concerns the formation of formaldehyde. We have shown that unless the vanadyl oxygen vacancy is spontaneously filled the mechanism is not possible. According to our concerted mechanism, the energetic barrier is ca. 30 kcal mol⁻¹, which corroborates experimental suggestion that this step of the reaction should be the limiting one. On the other hand, because the mechanism is energetically too demanding in absence of lattice oxygen, we may assume that the limiting step could be the diffusion of oxygen atoms in the vanadia lattice. As expected, the global reaction is exothermic ($\Delta H \approx -45$ kcal mol⁻¹), and the estimated activation barriers are acceptable from an experimental point of view. Finally, the overall proposed mechanism is a Mars–van Krevelen one. Indeed, we have shown that a non-Mars–van Krevelen mechanism is thermodynamically unlikely to occur on the surface.

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