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Can Supported Reduced Vanadium Oxides form H₂ from CH₃OH? A Computational Gas-Phase Mechanistic Study

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Abstract

A detailed density functional theory study is presented to clarify the mechanistic aspects of the methanol, CH₃OH, dehydrogenation process to yield hydrogen, H₂, and formaldehyde, CH₂O. A gas-phase vanadium oxide cluster is used as a model system to represent reduced V (III) oxides supported on TiO₂ catalyst. The theoretical results provide a complete scenario, involving several reaction pathways in which different methanol adsorption sites are considered, with presence of hydride and methoxide intermediates. Methanol dissociative adsorption process is both kinetically and thermodynamically feasible on V-O-Ti and V=O sites, and it might lead to form hydride species with interesting catalytic reactivity. The formation of H₂ and CH₂O on reduced vanadium sites, V(III), is found to be more favorable than for oxidized vanadium species V(V), taking place along energy barriers of 29.9 kcal/mol and 41.0 kcal/mol respectively.

TOC

1. Introduction

The dehydrogenation of methanol, CH_3OH , is of considerable interest from an academic and an industrial viewpoint due to its importance in many practical applications. CH_3OH is widely used as a fuel, solvent, and raw material for producing chemicals and other materials; in particular, the chemical transformation of CH_3OH to hydrogen, H_2 , allows considering methanol as a renewable alternative to petroleum-based hydrocarbons, thus opening the door for a possible future “methanol economy”.¹⁻⁴

On the other hand, CH_3OH has been widely studied and utilized as a smart chemical probe molecule in order to establish the fundamental structure-activity relationships for metal oxide catalysts.⁵⁻⁹ Despite its vast use, there is still a lack of understanding on the nature of the reaction mechanisms involved in the catalytic transformations, due mainly to the difficulty for obtaining representative model systems on which to carry out detailed chemical and kinetic analyses. In this context, extensive research efforts have been made both experimentally and theoretically to search for suitable catalysts to improve chemical processes concerning alcohol transformations;^{10, 11} Likewise, gas-phase experiments combined with theoretical works¹²⁻¹⁸ have provided a wealth of information of elementary steps and intermediates for various catalytic reactions,¹⁹⁻³⁷ and provides ideal model systems for local reactive sites of condensed-phase catalysts. Therefore, small transition metal oxides clusters may well be effective models of real surface species or active sites over the bulk transition metal oxides materials,³⁸ that are capable to provide a conceptual framework for modifying or controlling the chemical properties of mixed-metal oxides and for engineering industrial catalysts.

Metal oxide catalysts are more complex than conventional metal catalysts because they can terminate with multiple surface functionalities and expose cations in multiple oxidation states.³⁹⁻⁴³ In particular, vanadium oxide is an example of such complex behaviour, and several experimental and theoretical investigations have previously been carried out to quantify the number of surface active sites, understanding their structure/reactivity correlations,⁴⁴⁻⁴⁷ and also the kinetic aspects of methanol oxidation to

formaldehyde.^{34, 48-79} What all those catalytic studies have in common is a supported vanadium (V) species in which an oxidative dehydrogenation process occurs, i.e. an electron transfer from the methanol toward the catalyst takes place with concomitant reduction of V(V) to V(III). However, the influence of formal oxidation state and the reactivity of isolated functional groups that form the active sites are still unexplored on supported vanadium catalysts. In this sense, gas-phase cluster studies have been previously carried out both theoretically and experimentally concerning the role of the oxidation state in vanadium oxides towards methanol.^{25, 80} In particular, Schwarz et al. have demonstrated that the reaction of VO^+ with CH_3O yields CH_2O and H_2 along a 1,2-elimination process to produce CH_2O and H_2 .^{25, 80}

In the present study, we seek to fulfil a three-fold objective. First, to propose several reaction pathways to unravel the mechanistic aspects for the dehydrogenation process of CH_3OH to render the formation of H_2 and CH_2O on reduced vanadium oxides supported on TiO_2 catalyst. Different CH_3OH adsorption sites as well as the presence of hydride and methoxide intermediates along the reaction coordinate has been considered. Secondly, to unravel the role of the formal oxidation state of the vanadium center, V(V) vs V(III), in the reaction mechanisms by analyzing the electronic structure of the process along the reaction coordinate. Thirdly, to compare the results with those previously obtained by some of us for models containing oxidized V(V) species^{29,70, 79}, which highlight the role of electronic and geometric factors on chemical reactivity.

The remainder of the paper is organized as follows; computational details and model systems are presented in section 2. The analysis and discussion of the results are presented in section 3. The main conclusions are given in section 4.

2. Computational details and model systems

All the quantum chemical calculations were performed using the Gaussian 09 code.⁸¹ Stationary points on the potential energy surfaces (PESs) have been characterized using density functional theory (DFT) at the hybrid B3LYP⁸²⁻⁸⁴ functional level together with the 6-311G(2d,p)⁸⁵ basis set in all

atoms. Previous theoretical studies on isolated vanadates supported on titania^{72, 77} have been carried out by using the pseudo-potential on metal atoms; however, it is well-known that all-electron basis set renders more accurate results regarding energetic and geometry than the use of pseudo-potentials.^{68, 86, 87} We have already applied this level of theory to calculate molecular mechanisms on selective methanol oxidation to formaldehyde on hydrated and supported isolated vanadates;^{70, 79} and then, we are confident with the data calculated at this computing level for this type of reaction.

The local minima of the stationary structures were located and characterized performing analysis of the calculated vibrational frequencies. Thermodynamic properties were obtained for all species involved in the reaction mechanisms. The Gibbs free energy was computed using the standard equations of statistical mechanics^{88, 89} at 373 K.

Based on a similar model to that used to represent isolated vanadate species supported on titania,²⁹ our catalytic representation corresponds to a TiO₂-supported vanadium oxide, in which vanadium oxide contains a terminal vanadyl bond (V=O), and three bridging oxygen atoms (V–O–Ti sites). Two hydrogen atoms are added to the model (V–OH–Ti sites), see figure 1. The addition of the two neutral hydrogen atoms results both in a reduction of V(V) to V(III) and the formation of the V–OH–Ti hydroxyl sites. These two species are expected on the catalyst surface after methanol oxidation to formaldehyde: reduced vanadia is reported /algunas citas experimentales/ and hydroxylated vanadia species can be stabilized even at high temperature depending on the hydration and vanadia content / J.Phys.Chem.C 2011, 115, 24133–24142, *J. Phys. Chem. C*, 2013, 117 (48), pp 25535–25544 DOI: 10.1021/jp408836d /. Moreover, upon hydrogenation of V₂O₅-TiO₂ model catalysts the V–O–Ti sites are found to be more reactive than V=O or V–O–V sites // Topics in Catalysis Vol. 40, Nos. 1–4, December 2006 (_ 2006) 17 DOI: 10.1007/s11244-006-0090-x // *J. Phys. Chem. B* **2004**, 108, 15679-15685// *J. Phys. Chem. C* **2007**, 111, 6411-6417/, forming V–OH–Ti species and reducing V⁵⁺ to V⁴⁺/V³⁺.

In this model (S1) the vanadium site possesses an oxidation state of V(III) in a tetrahedral environment, and a triplet electronic ground state. Although alternative models have been proposed on supported isolated vanadate species^{67, 76} the pyramid arrangement seems to be the most generally

assumed, and therefore, we have considered it to carry out our calculations. Three different interactions between methanol and the cluster are considered, involving the interface V-O-Ti, the vanadyl V=O and the V site, as displayed in figure 2.

3. Result and discussion

3.1 Adsorption and dissociation of CH₃OH

It is well-known that the interaction of one CH₃OH molecule with the catalyst surface is favorable^{61,63} and it can be associated with weak electrostatic interactions between the vanadium site (acidic) and the oxygen atom of methanol molecule (basic).²⁹ In our gas-phase cluster model the interaction of CH₃OH with surface results in the formation of two encounter complexes (M0 and M3) with geometric parameters similar to those of separated reactants. In the M0 intermediate, this interaction takes place mainly between the hydroxyl group of methanol and V-O-Ti site, whereas in M3 it appears at the V=O bond, see figures 3 and 4. The formation of these adducts are exothermic processes by 19.0 and 16.3 kcal/mol, respectively. For the activation of CH₃OH, it is necessary a proton transfer process from hydroxyl group of CH₃OH towards either V-O-Ti or V=O, with a total (and free) energy barriers of 6.9 (7.6) and 13.2 (15.1) kcal/mol, via the transition states TS₀₋₁ and TS₃₋₄, respectively, to yield the formation of methoxide V-OCH₃ species, represented by M1 and M4, with exothermic adsorption energies of -15.2 and -32.5 kcal/mol, respectively, see figure 2. The effect of temperature at 373 K shows a quasi-equilibrated process of molecular-methanol adsorption, i.e. M0 and M3, with ΔG values of -4.6 and -3.1 kcal/mol, respectively. Therefore, the effect of the temperature results in a quasi-indistinguishable molecular adsorption site. Likewise, methanol adsorption on V-O-Ti sites can be assumed as a quasi-equilibrated process with $\Delta G = -1.2$ kcal/mol, whereas the adsorption on V=O sites is predicted significantly more exergonic ($\Delta G = -19.7$ kcal/mol). Alternatively, methanol adsorption concerning the formation of hydride-methoxy-intermediate (M7) has been also considered, see figures 2 and 6. A proton transfer from hydroxyl group of methanol toward vanadium site results in the formation of M7. This process is predicted to be exothermic by 20.4 kcal/mol and $\Delta G = -6.7$

kcal/mol, see figure 2, although this route via a hydride intermediate is kinetically less favorable than those predicted for V-O-Ti and V=O sites. The formation of M7 involves a change in the formal oxidation state of vanadium atom, V (III) $\rightarrow$ V(V), as well as a spin crossing process, being a typical two state reactivity (TSR) scenario.⁹⁰ The importance of hydride intermediates in the H₂ production from CH₃OH on transition metal atoms has been remarked by Zhou et al.⁹¹, while Schwarz et al. have reported the presence of hydride intermediates in the dehydrogenation of CH₃OH with mononuclear vanadium-oxide cations⁸⁰ with presence of V(III) oxidation state. We conclude thus that hydride intermediates might have an important role when vanadium is (partially) reduced i.e. when its formal oxidation state is lower than V(V).

To sum up, the dissociation of CH₃OH both by V=O bond and V-O-Ti sites is clearly favorable in V(III) models, whereas hydride-intermediates may not be taken into account as a feasible reaction channel since its formation is achieved along a higher energetic demand. In contrast, the formation of M7 intermediate can be not favorable according the description of the model system. However, titania-supported vanadium oxide surface undergoes dynamic changes under reaction conditions, which can involve the changes in the oxidation state between V(V) and V(III). Additional factors such as water and the effect of support can play a role in the stabilization of the vanadium oxidation state.

3.2 Exploration of reaction pathways

To understand the dehydrogenation process of CH₃OH on reduced vanadium oxide cluster supported on titania, we have explored three reaction pathways: Path A, Path B1 and Path B2, starting from the methanol and the catalyst model (S1) as reference.

In the first step along the path A, the CH₃OH adsorption process occurs at the V-O-Ti site to render the methoxy-intermediate M1. In the next stage, via TS₁₋₂, the H₂ and product-complex M2 are formed by recombination of the CH₃ of CH₃OH and OH group of the support; thus, two electrons are transferred from the CH₃OH molecule to form H₂ avoiding thus a change in the formal oxidation state of the vanadium center, while the system remains in its triplet ground state.

The formation of H₂ is predicted to have an activation energy barrier of 36.4 kcal/mol ($\Delta G^\ddagger = 38.2$ kcal/mol), while M2 is calculated to be 19.2 kcal/mol higher in energy than M1. In M2, H₂ interacts with the oxygen atom of V=O site whereas the interaction of CH₂O is mainly between the oxygen of carbonyl bond and the vanadium atom. The intermediate M2 presents two V-(OH)-Ti groups as well as a vanadyl V=O group. Finally, CH₂O and H₂ desorb with values of $\Delta E = 13.0$ kcal/mol (and $\Delta G = -7.1$ kcal/mol).

Path B1 contemplates firstly the methanol dissociation by vanadyl bond to form M4. Later, the formation of H₂ and CH₂O is reached by means of H-transfer process from the adsorbed methoxy group toward the hydrogen atom of the recently formed OH group, via TS₄₋₂. This step is associated with an activation energy barrier of 53.5 ($\Delta G^\ddagger = 55.4$) kcal/mol. The vanadyl bond is recovered in this step, leading to the product-complex M2, which is also found in Path A. M2 is 36.5 kcal/mol (and $\Delta G = 35.0$ kcal/mol) less stable than the preceding intermediate M4.

On Path B2, CH₃OH dissociation process takes place identically as it occurs along the Path B1. Then, the formation of H₂ and CH₂O is achieved by means of hydride transfer from the CH₃ group toward one of the OH group from the support via TS₄₋₅ (see figure 5). This step has an activation energy barrier of 29.0 kcal/mol ($\Delta G^\ddagger = 32.0$ kcal/mol). The product-complex M5 is predicted only 4 kcal/mol ($\Delta G = 3.8$) less stable than M4. Finally, CH₂O and H₂ desorb with $\Delta E = 20.2$ kcal/mol ($\Delta G = -0.5$ kcal/mol) leaving the catalyst as in S2, see Figure 1. Note that the final product S2 + CH₂O + H₂ is predicted to be 8.3 kcal/mol more stable than S1 + MeOH, being the conversion of S1 to S2 an exothermic process of 25.3 kcal, see Figure 1.

According to this energetic profile, Path B2 would be both kinetically and thermodynamically preferred with respect to the other mechanisms explored. Thus, it is concluded that Path B2, proceeding without vanadyl V=O groups, considerably lowers the energetic cost to obtain simultaneously H₂ and CH₂O compared to the other pathways considered.

In the present mechanistic exercise three different patterns appear depending on the adsorption and dissociation of CH₃OH. Path A leads to less stable intermediates (-19.0 kcal/mol for M0 and -15.2 kcal/mol for M1) as compared with Path B1 (-16.3 kcal/mol for M3, -32.5 kcal/mol for M4). While Path A favors the molecular CH₃OH adsorption process, the Path B1 strongly stabilizes the dissociative mode. Therefore, the activation barriers to overcome the rate-limiting step (associated with the C-H bond breaking) is higher for Path B1 (53.5 kcal/mol) as compared to Path A (36.4 kcal/mol). This implies that: i) CH₃OH likely dissociates on the surface catalyst forming methoxide and hydroxyl groups ii) the M4 intermediate will form on the catalyst surface. This is in agreement with experimental results, see below. iii) If species M1 formed, it would react more rapidly to the products than M4.

Note that both M1 and M4 intermediates contain a V atom five-fold coordinated. These species have been predicted less stable than tetrahedral ones in oxidized vanadium-supported catalysts; nevertheless, the presence of penta-coordinated V species interacting with water or methanol molecules has been detected by IR spectroscopy⁹²⁻⁹⁵. The role of five-fold coordinated V(V) species in reactivity have been analyzed in previous DFT studies.⁷⁰ Our present results indicate thus that the presence of reduced V(III) sites is thermodynamically favorable.

On the other hand, the formation of a hydride intermediate is thermodynamically favored (M7, -20.4 kcal/mol, see figure 6), however, its formation requires to overcome an energy barrier higher than those for the formation of M1 and M4 (32.4 kcal/mol) intermediates, making M7 intermediate less accessible in reactive processes.

The CH₃OH dissociation process on V(III) cluster takes place with barriers significantly lower (6.8 – 13.2 kcal/mol) than those found on V(V) systems (10.7 – 25.2 kcal/mol).⁷⁰ Consequently, the CH₃OH adsorption step varies considerably as function of V formal oxidation state, for details see Table 1; while the adsorption process is both kinetically and thermodynamically favorable at V-O-Ti and V=O sites on V(III) systems, the CH₃OH dissociation on supported vanadates species is experimentally suggested through V-O-Ti sites.^{65, 78, 96} Interestingly, the reaction is found to be more favorable for V(III)

species than for oxidized vanadium species V(V), taking place along energy barriers of 29.9 kcal/mol and 41.0 kcal/mol respectively.

The CH₃OH adsorption process at V=O sites on isolated vanadates has been discarded because it is an endothermic process yielding five-fold coordinated methoxy-intermediates.²⁹ Moreover, we have previously demonstrated that those five-fold species are found to be potentially interesting for catalytic reactivity.⁷⁰ Therefore, the formation of methoxy-intermediates in reduced V catalyst seems to be more favorable than in fully-oxidized systems. Likewise, the activation of C-H bond is significantly affected. The C-H bond activation barrier on V(V) catalyst is ~41 kcal/mol, while on V^{III} catalyst it ranges 32-55 kcal/mol. This difference in energy could be attributed to the nature of the transition state involved at the C-H activation step. On V(V) catalyst a homolytic C-H bond breaking takes place while V atom is partially reduced to V(IV). On V(III) catalyst there is not electronic transfer process between methoxide group and V metal center and therefore the C-H break must be necessarily heterolytic.

Interestingly, product M5 does not contain any V=O group, instead, a V-OH group is found together with one V-(OH)-Ti and two V-O-Ti groups. The structure M5 is predicted to be 32.5 kcal/mol more stable than M2; both structures are similar but the latter possesses a V=O group which is absent in the former. This means that reduced vanadia catalysts may not have such vanadyl groups at the exit channel, in fact, they are characteristic of oxidized V(V)-containing catalysts although recently they have been proposed to exist in polyvanadate surface species.⁴⁸ The absence of vanadyl V=O groups in reduced vanadium catalysts is supported by experimental results: vanadia-oxidized catalysts present a characteristic Raman vibration at ~1030 cm⁻¹, assigned to V=O groups. In the oxidation conditions, the vanadium species should be in majority at the fifth oxidation state, while the intensity of such Raman band strongly decreases.^{97, 98} The oxidation reaction of CH₃OH proceeds with concomitant reduction of the catalyst, which decreases the oxidation of V(V) to V(IV)/V(III), in agreement with previous theoretical results.^{68, 70-72, 79} Surprisingly, in the analysis of the products of the CH₃OH oxidation reaction only the oxidation products CH₂O, CO, CO₂ are reported⁶⁵, but not H₂. Note that catalytic systems are usually dynamic and the presence of vanadium at a different oxidation states cannot be excluded. The lack of the confirmation

of the formation of H_2 can be related to the type of the analytical technique used for a detection of the reaction products, similarly to water. Thus, our results predict the formation of H_2 as product of CH_3OH oxidation together with formaldehyde when a reduced V(III) catalyst is present.

Finally, the energy barriers for the activation of O-H and C-H bonds are not significantly altered by the temperature (373 K), nevertheless, the stability of adducts (M0, M2, M3, M5, and M6) and methoxy-intermediates (M1, M4 and M7) and their corresponding transition states are strongly affected. Thus, on V(III) catalysts, the adsorption of CH_3OH is expected to be an exergonic process on both V=O and V-O-Ti sites, yielding to the formation of five-fold coordinated methoxy-intermediates which seem to be both kinetically and thermodynamically favorable. Likewise, the H_2 and CH_2O desorption is expected to be an exergonic process.

4. Conclusions

The present theoretical work adds a new insight into the gas phase mechanisms of the dehydrogenation of CH_3OH to be compared with supported reduced vanadium oxides. The results show that the methanol adsorption on V(III) systems sites is thermodynamically favourable, while methanol dissociation gives rise to stable five-fold coordinates V(III) methoxy-intermediates. The most likely intermediate does not contain vanadyl V=O groups. As result, the role of the catalyst is first to dissociate the CH_3OH molecule and second to improve the gas-phase mechanism by stabilizing the transition state. In fact, one of the reaction pathway (Path B2) to obtain H_2 and CH_2O is found to proceed below the reference energy. The CH_3OH adsorption process may also bring about the formation of hydride intermediates, although kinetically less favourable, they may present an interesting catalytic activity. The overall methanol oxidation process is found to be more favourable over V(III) than on V(V) species.

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Notes

The authors declare no competing financial interest.

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Figure 1. Models for the reduced vanadium oxide species supported on TiO_2 catalyst. Distances in angstrom and energy in kcal/mol.

Figure 2. Structures at B3LYP/6-311G(2d,p) level for the CH_3OH adsorption process on a) V-O-Ti site b) V=O site c) vanadium site. The ΔG values are calculated at 373 K. $\Delta G^\ddagger$ and $\Delta E^\ddagger$ values correspond to the relative free activation energy and activation energy of the transition state, respectively.

Figure 3. Total energy profiles at the B3LYP/6-311G(2d,p) level for Path A relative to the entrance channel S1+ CH₃OH.

Figure 4. Total energy profiles at the B3LYP/6-311G(2d,p) level for Path B1 relative to the entrance channel S1 + CH₃OH.

Figure 5. Total energy profiles at the B3LYP/6-311G(2d,p) level for Path B2 relative to the entrance channel S1 + CH₃OH.

Figure 6. Relevant geometries obtained at B3LYP/6-311G(2d,p) level and energy profile for the CH₃OH adsorption process on vanadium site.

Table 1. Selected properties to compare V(V)/V(III) catalysts for the oxidation reaction of CH₃OH. Energies in kcal/mol. surface. TS: transition state

Oxidation State on Vanadium Atom	(III) ^a	(V) ^b	Comparison
Initial	V ^(III) O ₄ H ₂ Ti ₃ O _x (triplet) + CH ₃ OH	V ^(V) O ₄ Ti ₃ O _x (singlet), CH ₃ OH	-
Final	V ^(III) O ₄ H ₂ Ti ₃ O _x (triplet), H ₂ + CH ₂ O	V ^(III) O ₄ H ₂ Ti ₃ O _x (triplet), CH ₂ O	-
^c ΔE_{molec}	Exothermic (16-19 kcal/mol)	Exothermic (7.0 kcal/mol)	Molecular better on V ^(III)
ΔE_{ads}	Exothermic (15.2-32.5 kcal/mol)	Exothermic (17.1 kcal/mol)	Better on V ^(III) than V ^(V)
Methanol adsorption site	V=O and V-O-Ti	V-O-Ti	
Methanol dissociation barrier	6.9-13.2 kcal/mol	10.7 kcal/mol	
Methoxy-intermediate	Pentahedral methoxide, no V=O bond	Tetrahedral methoxide preferred, V=O bond present	Pentahedral stabilized on V ^(III) , V=O only stable on V ^(V)
C-H activation	By OH groups	By V=O bonds	In both cases this is the rate-limiting step
^d $\Delta E_{rls}^{\ddagger}$	36.4, 53.5 and 29.0 kcal/mol	41.0 kcal/mol	-
TS _{rls} /OSV ^e	Triplet; V ³⁺	Biracaloid (OSS) ^e ; V ^(IV)	-
Electron transfer	Two electrons: directly from methoxide group to H ₂	Two electrons: from methoxide the catalyst V ^(V) , as a consequence V ^(V) → V ^(III)	-
Spin crossing?	No, only triplet ground state	Yes, singlet → triplet	-
Formation of hydride intermediate?	Exothermic (-20.4 kcal/mol) Barrier: 32.4 kcal/mol Triplet → singlet	-	-

^aThis paper. ^bRef 70. ^cMolecular adsorption of methanol on surface. ^dActivation energy for rate-limiting step ^eOpen Shell Singlet.