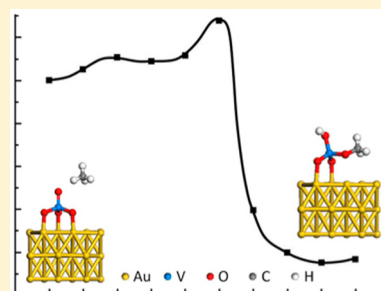


Oxidative Dehydrogenation of Methane by Isolated Vanadium Oxide Clusters Supported on Au (111) and Ag (111) Surfaces

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ABSTRACT: We use density functional theory, with the GGA-PBE functional, to investigate the ability of vanadium oxide clusters, supported on Ag or Au, to break the C–H bond in methane. We perform a thermodynamic analysis to show that the VO₄ cluster is the most likely oxidant and then proceed to calculate the energy of the dissociative adsorption of methane and its activation energy. We explain some peculiar features of the reaction path and propose that they are general for alkane activation on oxides.



1. INTRODUCTION

Catalysts consisting of metal clusters supported on oxides are widely used. Recently, a number of articles have studied “inverse catalysts” that consist of small oxide clusters supported on a metal surface.^{1–31}

In the present article we investigate the stability of isolated VO_x ($x = 0–5$) clusters in the presence of gaseous oxygen and their ability to break the C–H bond in methane. We have chosen to look at VO_x clusters because the vanadium atom has several valence states, which means that when x has the appropriate value the VO_x cluster can engage in redox reactions. Moreover, submonolayers of VO_x supported on metals may be more active for redox reactions than bulk V₂O₅, as is known to be the case when VO_x is supported on oxide surfaces.^{32,33}

The Au and Ag supports were chosen with possible methods of preparation in mind. While methods that prepare such system in ultrahigh vacuum are of great scientific interest, because of the control they allow, they cannot be scaled up for practical application. A more practical possibility is the preparation of binary metal-alloy particles, followed by calcination in oxygen. If one of the metals does not oxidize (e.g., Au) and the other one does (e.g., V), the latter diffuses to the surface, binds the oxygen, and forms the desired oxide clusters. If both metals oxidize, then calcination is likely to result in the formation of a doped oxide or of oxide clusters supported on an oxide. While such systems are interesting catalysts, they are not inverse catalysts and will not be examined here. Silver, which we also study, forms a thin oxide layer on the surface^{34–41} and is a good industrial oxidation catalyst (e.g., for ethylene epoxidation or methanol oxidation to formaldehyde), but it does not activate alkanes, which is the reaction of interest

here. Because of this, we assume that the vanadium clusters, but not the Ag surface, will activate methane.

Inverse catalysts provide us with a large class of possible catalysts because any oxide can be combined with several metal supports that are not easily oxidized. Moreover, such a system may function as “dual catalyst” by combining the catalytic properties of the metal support (e.g., Au, Pt, Ag) with those of the oxide cluster. As far as we are aware, such a possibility has not been explored. One can imagine that, for example, in the case of VO_x supported on Ag, the C–H bond in an alkane is broken by a reaction with the VO_x cluster, and the dissociation fragments undergo a mild oxidation on the Ag surface.

In this article we use density functional theory (DFT) to study the structure of VO_x clusters supported on Au (111) and Ag (111) surfaces, in the presence of oxygen, and their ability to break the C–H bond in methane. We start with a metal surface covered with a fixed number of V atoms and assume that when exposed to gaseous O₂, the V atoms will be oxidized. In principle, such a surface can be covered with naked V atoms and with all oxidized clusters from VO₁ to VO₅, in concentrations that depend on temperature and oxygen pressure. We calculate these equilibrium concentrations by using equilibrium statistical mechanics. The energies of the clusters and their vibrational frequencies are obtained from DFT. This procedure gives us the composition of the “as prepared” catalyst. To study the breaking of the C–H bond in methane, we identify the value of x for which the reaction VO_x + ¹/₂O₂ → VO_{x+1} has the lowest energy. We assume then that VO_{x+1} is the oxidant and that the oxidative dehydrogenation

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mechanism involves the reduction of VO_{x+1} by the methane, followed by the reoxidation of VO_x by gaseous oxygen. Because the rate-limiting step in methane oxidation is breaking the C–H bond, we study only the activation energy for the dissociative adsorption of methane to form a hydroxyl and a methoxide with the oxygen atoms of VO_{x+1} . We find that the activation energy is low when Au is the support, and therefore the system is a potential catalyst for methane oxidative activation.

The model used here is idealized. We assume that the clusters are isolated while it is possible that they assemble into VO_x “islands”, which might have a different reactivity. We have not considered the possibility of surface restructuring when VO_x clusters are formed, nor did we consider that the V atom might be imbedded in the top surface layer (replacing a gold atom in the lattice). Finally, we did not consider the role of steps or other “defects”.

2. COMPUTATIONAL DETAILS

The DFT calculations were performed with the VASP 4.6 program,^{42–50} employing the PAW approach, the GGA-PBE exchange-correlation functional,⁵¹ and a plane-wave basis set with an energy cutoff of 400 eV. All calculations used spin-polarized DFT but did not take into account the spin–orbit coupling. The supercell used in the calculations is shown in Figure 1.

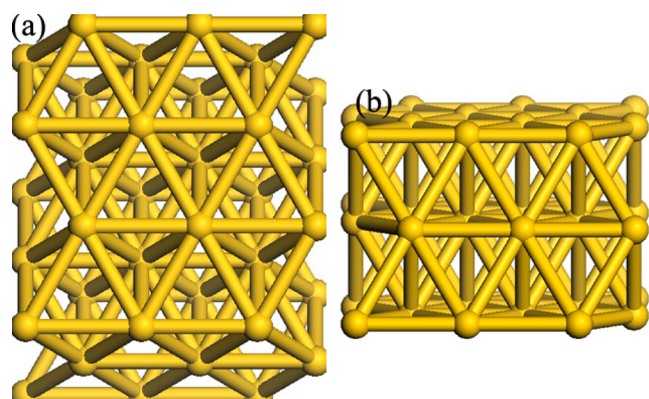


Figure 1. The supercell used in the computations (a) viewed from above (looking down to the surface) and (b) side view.

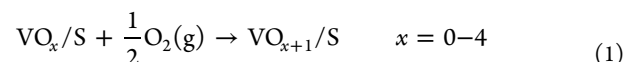
We found that the surface chemical properties are essentially unchanged when we add an additional atomic layer to the three-layer slab. The atoms in the bottom layer are frozen at the positions they have in bulk gold (or silver). All other atomic positions are optimized to minimize the total energy. Due to the large size of the supercell, we use a $2 \times 2 \times 1$ k-point mesh. The dipole correction was included.^{52,53} Atomic charges were obtained with the Bader method⁵⁴ as implemented by Henkelman et al.^{55,56}

3. RESULTS AND DISCUSSION

3.1. Structures of Various VO_x Clusters Supported on Au (111) or Ag (111) Surface. The first step in our study of VO_x supported on a metal is to determine x in VO_x . To do this, we assume that the catalyst will be prepared by calcining in oxygen small particles of vanadium–gold or vanadium–silver alloys. The temperature is sufficiently high to allow vanadium mobility in the solid, and the calcination time is long enough so that all vanadium atoms in the alloy end on the surface where

they form VO_x . Since we want to prepare isolated clusters, the ratio of vanadium to gold or silver, prior to calcination, must be chosen so that the total amount of vanadium in the alloy is smaller than the amount needed to form a monolayer. The driving force for vanadium segregation at the surface is the high energy of vanadium–oxygen bonds, compared to energy of gold–oxygen or silver–oxygen bonds. In principle, all clusters (V , VO , VO_2 , VO_3 , VO_4 , and VO_5) might be present simultaneously on the surface in proportions that are determined by the thermodynamic equilibrium conditions.

The reactions that lead to the formation of various clusters are



Here S is the Au or Ag surface, VO_x/S is the surface with a VO_x cluster adsorbed on it, and $\text{O}_2(\text{g})$ is gaseous oxygen. The equilibrium conditions for these reactions are⁵⁷

$$\mu[\text{VO}_{x+1}] - \mu[\text{VO}_x] - \frac{1}{2}\mu[\text{O}_2(\text{g})] = 0 \quad x = 0-4 \quad (2)$$

These five equations, plus a material conservation condition, connect the equilibrium coverage of each species to surface temperature and partial pressure of oxygen. One can use them to calculate the equilibrium coverage of each species, for a given temperature and pressure.

This calculation has two goals. One is to find the cluster that is most abundant on the surface under given preparation conditions. The other is to find which clusters provide a good redox couple. Since we are interested in oxidation reactions, we envision that the reductant removes one oxygen atom from VO_{x+1} to form VO_x and an oxidation product. Subsequently VO_x reacts with gas-phase oxygen to re-form VO_{x+1} . This is a Mars–van Krevelen like mechanism, using the oxide clusters as a source of oxygen. The most likely oxygen-donating cluster is one that is abundant under the working condition and for which oxygen removal requires a smaller energy than for the other clusters. One can easily foresee, for example, that given the affinity of V for oxygen, the reduction of VO to V and subsequent oxidation of V to VO is not a likely redox couple.

The chemical potentials needed when using the equilibrium conditions are calculated as follows. For gaseous O_2 we calculate the chemical potential by using statistical mechanics⁵⁸ and information provided by spectroscopy. We assume that the gas is ideal, which is a good approximation at pressures of 1 atm or less and the high temperatures studied here.^{59,60} The energy of VO_x/S and the vibrational frequencies of the cluster are calculated by DFT. To calculate the frequencies, we use the harmonic approximation. The low-frequency modes (e.g., the “frustrated” rotation and translation modes) which contribute most to the entropy are “floppy”, and the harmonic approximation is not excellent. However, since the equilibrium conditions involve differences in chemical potentials, some of the errors made in this way will tend to cancel each other. We also assume that the contributions to the chemical potentials from lattice vibrations (phonons) cancel because the equilibrium conditions depend on the difference between the chemical potentials of VO_{x+1}/S and VO_x/S . To calculate the configurational entropy of the mixture of various VO_x clusters that may be present on the surface, we use an ideal lattice gas. This widely used assumption is questionable at temperatures for which the clusters start moving along the surface. In the

limit when this motion is unhindered by barriers to diffusion (i.e., the residence time on a surface site is very short), the appropriate entropy approaches that of a two-dimensional gas. Any in-between situation would require the use of Monte Carlo simulations that cannot be performed properly unless one is willing to derive accurate classical interaction potentials for all the atoms involved. This is beyond what we are willing to do given all the other approximations involved.

We have included in the calculations only the lowest-energy clusters since the difference between the energy of the most stable isomer and the next stable one is much larger than $k_B T$ (k_B is Boltzmann constant and T is the temperature in kelvin).

The structures of the lowest-energy VO_x clusters on Au(111) are shown in Figure 2.

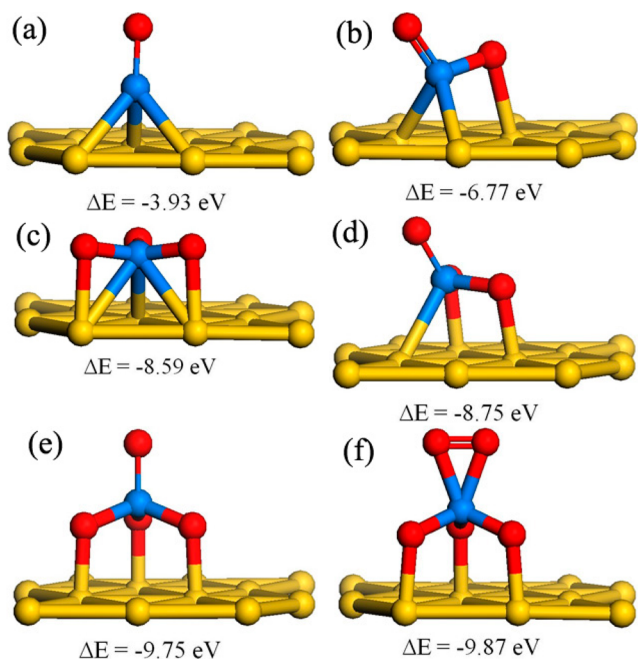


Figure 2. The lowest energy structures of the VO_x clusters supported on Au. ΔE is the energy of the reaction $V/S + (x/2)O_2(g) \rightarrow VO_x/S$, where S is Au(111), VO_x/S is the VO_x cluster adsorbed on S, and V/S is a vanadium atom adsorbed on S. The values of ΔE in the figure are the same as the ones given in Table 1. The structure of (a) VO, (b) VO_2 , (c) VO_3 , (d) an isomer of VO_3 whose energy is close to that shown in Figure 1c, (e) VO_4 , and (f) VO_5 .

The structures of the VO_x clusters bound on Ag are very similar to those on Au, and we do not show them. We use as zero of the energy, the energy of V/S (S is Au(111) or Ag(111)) plus the energy of $5/2 O_2$ molecules in the gas. The energies of the oxidized clusters with respect to this reference are given in Table 1 and in Figure 2. There is not much to say about these energies other than point out that the vanadium atom is extremely eager to bind oxygen, which is not surprising. Moreover, Ag tends to bind the clusters more strongly than Au, which one would also expect. The energies of the reactions $VO_x/S + 1/2 O_2 \rightarrow VO_{x+1}/S$ are larger on Ag than on Au. This suggests that VO_x on Au are better oxidants than VO_x on Ag. The VO_5 cluster deserves some comment since V appears to be overcoordinated. It is not: the two oxygen atoms parallel to the surface are a peroxide.

There are two isomers for VO_3 on Au that are sufficiently close in energy to be shown in Figures 2c and 2d. The energy

Table 1. $\Delta E(VO_x)$ Is the Energy (in eV) of the Reaction $V/S + (x/2)O_2(g) \rightarrow VO_x/S$, where S Is Either Au(111) or Ag(111), VO_x/S Is the VO_x Cluster Adsorbed on S, and V/S Is a Vanadium Atom Adsorbed on S; $\Delta E(VO_x \rightarrow VO_{x+1})$ Is the Energy (in eV) of the Reaction $VO_x/S + (1/2)O_2 \rightarrow VO_{x+1}/S$

x	$\Delta E(VO_x)$		$\Delta E(VO_x \rightarrow VO_{x+1})$	
	Au(111)	Ag(111)	Au(111)	Ag(111)
1	-3.93	-3.90	-2.84	-3.19
2	-6.77	-7.09	-1.82	-2.83
3	-8.75	-9.92	-1.00	-2.2
4	-9.75	-12.14	-0.12	+0.5
5	-9.87	-11.64		

of the isomers of all other structures, which we have calculated, is too high, and they will not be present on the surface, at the temperatures of interest here. We do not show their structures.

Table 2 shows the lengths of various bonds in the clusters. The absence of a number in the table indicates that the bond is not formed. We identify as a vanadyl a V–O group whose bond is shorter than the other V–O bonds and in which the oxygen atom is not bonded to the support. The V–O bond length of the vanadyl group is independent of the number of atoms in the cluster, which is rather curious. For the smaller clusters, the distance between the V atom and the Au (or Ag) surface is short enough to conclude that V is bonded to the surface. For the large clusters (VO_4 and VO_5), the distance is too large to assume that a V–support bond is present. The oxygen atoms in these larger clusters insert themselves between V and Au (or Ag) atoms. It is often assumed that the presence of such oxygen atoms (bonded to two different cations) is the feature that makes the inverse catalysts promising oxidation catalysts, since one can tune the reactivity of the oxygen by changing the cation pairs.

We did not expect the system to make a VO_5 cluster. The energy of the reaction $VO_4/S + 1/2 O_2(g) = VO_5/S$ is -0.13 eV when S is Au and 0.51 eV when S is Ag. The structure of VO_5 is similar with that of VO_4 except that the vanadyl is replaced by an O_2 “molecule”. The O–O bond length in this molecule is 1.37 Å, which is between that of O_2^- (1.21 Å) and that of O_2^{2-} (1.48 Å). This bond is longer than that of the gaseous O_2 molecule (1.21 Å) and shorter than the O–O bond in hydrogen peroxide (1.48 Å). This suggests that this “ O_2 group” in the cluster is reactive. However, the equilibrium calculations predict that it is not present in large amounts on the surface even at oxygen pressures of 1 atm, if the temperature is above 600 K. Since we expect that alkane activation occurs at higher temperatures than this, we decided not to examine the reactivity of VO_5 . However, in the case of Au, future work should examine whether this species may be more reactive than the VO_4 cluster (which is studied here).

We have also calculated the Bader valence on various atoms, which is the number of electrons lost (or gained) by an atom when it becomes part of a molecule. The Bader valence is positive when the atom donates electrons to the rest of the molecule. The results are shown in Table 3, where one can see that, in the case of Au, as x in VO_x increases the amount of charge donated by the V atom increases. When $x < 3$, the V atom binds to Au and the Au gains charge. As the amount of oxygen in VO_x increases, V–O–Au bonds are formed and the V–Au bonds are no longer present. In this case, the Au atom that binds to an O atom (to form a V–O–Au group) loses

Table 2. Length of Some of the Bonds in the VO_x Clusters

		bond length (Å)						
		V	VO	VO ₂	VO ₃ (high energy)	VO ₃ (low energy)	VO ₄	VO ₅
Au (111)	V–Au	2.59	2.61	2.59	2.74	2.69		
	O–Au			2.48	2.31	2.16	2.07	2.12
	V–O			1.66	1.70	1.74	1.79	1.94
	vanadyl		1.61	1.62		1.63	1.63	
Ag (111)	V–Ag	2.70	2.74	2.69	2.82	2.85		
	O–Ag			2.46	2.29	2.37	2.31	2.37
	V–O			1.66	1.71	1.74	1.81	1.94
	vanadyl		1.62	1.63		1.63	1.61	

Table 3. The “Bader Valence” (BV) of Various Atoms in the System^a

		Bader valence (electron)					
		V	VO	VO ₂	VO ₃ (low energy)	VO ₄	VO ₅
Au (111)	V	+0.87	+1.34	+1.61	+1.73	+1.85	+1.84
	O(bridging)			−0.60	−0.63	−0.81	−0.82
	O(vanadyl)		−0.58	−0.68	−0.69	−0.69	
	Au(V)	−0.26	−0.27	−0.27			
	Au(O)			+0.12	+0.17	+0.21	+0.22
Ag (111)	V	+0.58	+1.17	+1.49	+1.67	+1.78	+1.84
	O(bridging)			−0.78	−0.91	−0.95	−0.90
	O(vanadyl)		−0.66	−0.72	−0.73	−0.65	
	Ag(V)	−0.18	−0.20	−0.20			
	Ag(O)			+0.10	+0.18	+0.24	+0.17

^aThis is the number of electrons that an atom gains (if BV has negative sign) or loses (if BV has positive sign) when it became a part of a chemical compound. The number of electrons on a given atom in a molecule is calculated by the Bader method. Here is an example how to read the table: to make the VO₄ cluster on Au, vanadium atom donates 1.85 electrons, the oxygen atoms bridging V to Au gain 0.81 electron, the oxygen in vanadyl gains 0.69 electron, etc.

electron charge. The oxygen in the vanadyl group in the clusters having $x > 1$ does not change its charge as x increases. This suggests that the V atom, which is the main electron donor, gives the vanadyl priority and ensures that the oxygen atom in V=O is supplied with the same number of electrons no matter how many bridging oxygens are present. The Bader valence on the atoms in the VO_x/Ag system follows a similar trend as for VO_x/Au. However, the amount of electron charge donated by the V atom is always lower on the Ag support than on the Au support. This is consistent with the fact that Au is more electronegative than Ag.

3.2. Pressure and Temperature Dependence of VO_x Coverage. To calculate the equilibrium coverage of various VO_x clusters on the surface, we solve eq 2, as described in section 3.1. However, since it is difficult to obtain accurate values from DFT for the ground state energy of O₂, we do not use the DFT value for computing the chemical potential of oxygen. We could have used experimental data for this particular chemical potential, but for consistency sake, we wanted to use an all-DFT data set. To do this we use the reaction



as the source of oxygen. The equilibrium condition for this reaction is

$$2[\mu_{\text{H}_2\text{O}}(P_{\text{H}_2\text{O}}, T) - \mu_{\text{H}_2}(P_{\text{H}_2}, T)] = \mu_{\text{O}_2}(P_{\text{O}_2}, T) \quad (4)$$

This allows us to calculate the chemical potential of oxygen from that of gas-phase water and hydrogen, for which DFT gives acceptable values for energies.

Figure 3 shows the equilibrium concentration of the VO_x clusters supported on Au (111), as a function of temperature, at

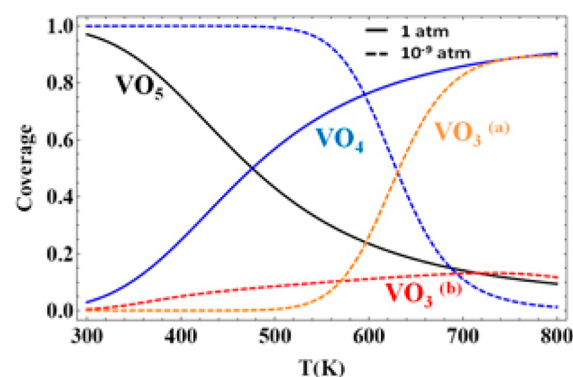


Figure 3. Equilibrium coverage of various VO_x clusters as a function of temperature for two oxygen pressures (10^{−9} and 1 atm).

two oxygen pressures (10^{−9} and 1 atm). At 1 atm, VO₄ (blue solid line) clusters predominate in the high-temperature range, with some VO₅ present. For this reason we decided to examine the ability of the VO₄ clusters to adsorb methane dissociatively. We did not exclude the possibility that the VO₅ cluster is the active species when the support is Au, and this possibility needs to be examined in future work. Similar results were obtained for Ag except that in that case the presence of VO₅ is less likely than on Au (see the energy of the reaction VO₄/Ag + 1/2O₂(g) → VO₅/Ag in Table 1).

We emphasize that the coverage under steady-state reaction conditions is determined by kinetics. In the case of oxidative

dehydrogenation, CH₄ is a good reductant and oxygen is an excellent oxidant, and the steady-state concentration of the clusters on the surface is determined by the competition between the oxidation and the reduction rates. The steady-state concentrations can be determined only by developing a complete kinetic scheme that includes the rates of formation and disappearance of every conceivable intermediate. In the present work we are only interested in the ability of the system to break the C–H bond, and the role of the thermodynamic calculation is to suggest which cluster is likely to perform this function.

3.3. CH₄ Dissociation on VO₄ Supported on the Au (111) and Ag (111) Surface. It is widely believed that the rate-limiting step in alkane activation is the dissociative adsorption of the alkane (the breaking of the C–H bond). If VO₄/Au (111) or VO₄/Ag (111) is used as catalyst, CH₄ dissociates to make a methoxide and a hydroxyl with the oxygen atoms of the VO₄ cluster. The VO₄ cluster has an oxygen atom that forms a vanadyl group, denoted here by O_v, and three equivalent oxygen atoms that form V–O–S bonds (we call these bridging-oxygen atoms and denote them by O_b). There are four possible final states for dissociative adsorption. To describe them we use the notation {CH₃–O_v; H–O_b}, which means that the methyl is bound to the O_v atom and the hydrogen is bound to one of the O_b atoms. A similar notation is used for the other three possible final states of dissociated methane.

The structures of the four possible final states are shown in Figures 4a–d. In Table 4 we report the energies of dissociative adsorption corresponding to the four reactions

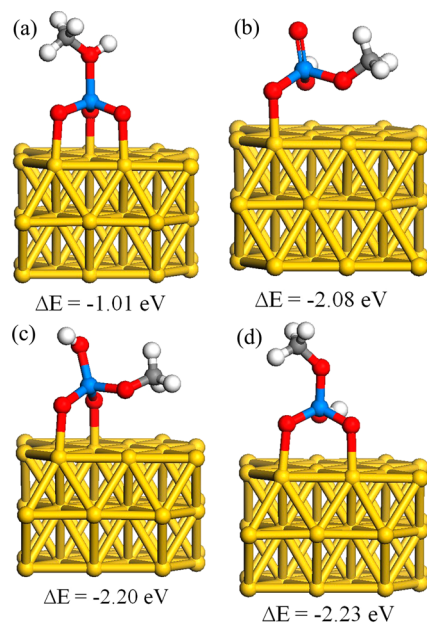
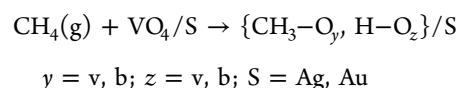


Figure 4. The four structures that can be formed when CH₄ adsorbs dissociatively on VO₄ supported on Au(111): (a) CH₃ and H bound to O_v (the oxygen in vanadyl); (b) H and CH₃ bound to oxygen atoms (O_b) that formed the V–O–Au bridge before methane dissociative adsorption; (c) H adsorbed on O_v and CH₃ adsorbed on O_b; (d) CH₃ adsorbed on O_v and H adsorbed on O_b.

Table 4. Energy (in eV) of the Dissociative Adsorption of Methane on the VO₄ Cluster Supported on Au(111) or Ag(111)^a

fragment binding	Au	Ag
CH ₃ –O _v ; H–O _v	–1.01	–0.04
CH ₃ –O _b ; H–O _b	–2.08	–0.98
CH ₃ –O _b ; H–O _v	–2.20	–1.15
CH ₃ –O _v ; H–O _b	–2.23	–1.16

^aThe symbols in the first column indicate the oxygen atoms to which the dissociation fragments are bound. O_v is the vanadyl oxygen and O_b is an oxygen atom that bridged V to Au (or Ag) before methane was adsorbed. For example, the final state for the first row is the methyl bound to the vanadyl oxygen and the hydrogen bound to an oxygen atom that was a bridging oxygen before methane adsorption.

There are two states that have the same energy (within the errors of DFT): in one the methyl is bound to O_b and the hydrogen to O_v; in the other the methyl is bound to O_v and the hydrogen to O_b. This does not mean that H and CH₃ are interchangeable: in the first two rows of the table interchanging the binding sites causes a very large variation of reaction energy. These qualitative observations are also true for methane dissociation on VO₄/Ag.

Unlike Au, silver dissociates oxygen and is covered with an “oxygen layer”.^{38–40,61} It is therefore possible that if the coverage of VO₄ is low, some oxygen atoms will be present on the Ag surface, between the vanadium oxide clusters. We suspect that these oxygen atoms will not react with methane since there is no indication that Ag is a good catalyst for oxidative activation of methane. The question is, however, whether these oxygen atoms will affect the activity of the VO₄ clusters. To answer this question, we calculated the adsorption energy of oxygen (the energy of the reaction $1/2\text{O}_2 + \text{VO}_4/\text{Ag} \rightarrow (\text{O}, \text{VO}_4)/\text{Ag}$) at various sites near and far from the VO₄ cluster. We found that the binding energy of an O atom at a Ag site near VO₄ is 0.23 eV, while the binding energy of O on Ag (without a VO₄ cluster) is –0.29 eV. The oxygen atoms on the VO₄/Ag surface prefer to bind away from the VO₄ cluster. The addition of an O atom away from the cluster causes no change in the structure of VO₄. We conclude therefore that the effect of the O atoms adsorbed on Ag, on the chemical properties of the VO₄ cluster, is negligible.

The four possible adsorption sites for fragments produced by the dissociation of methane on VO₄/Ag are shown in Figures 5a–d. We find that the dissociative adsorption on VO₄/Ag is substantially different from that on VO₄/Au in both the dissociation energy and the structures of the final states. The energies of the dissociative adsorption of methane on VO₄/Ag are given in Table 4. The ability of the VO₄ cluster to dissociate methane is diminished when the support is Ag. This reduction in the binding energy is substantial for all four possible final states. If the Bronsted–Evans–Polanyi rule^{62–75} applies, we expect the activation energy for dissociative adsorption of methane by VO₄/Ag to be larger than for VO₄/Au. In the next section we show this to be the case.

The difference in the structure of the dissociated states for VO₄/Au and VO₄/Ag can be seen by comparing Figures 4 and 5. In the case of Au, {CH₃–O_v, H–O_v} has a triangular base of three oxygen atoms that are bonded to V and to three Au atoms (Figure 4a). In the case of Ag, CH₃ and H are bonded to the oxygen atom that used to form a vanadyl (O^a in the figure). However, when this structure is formed, a V–O–Ag is broken

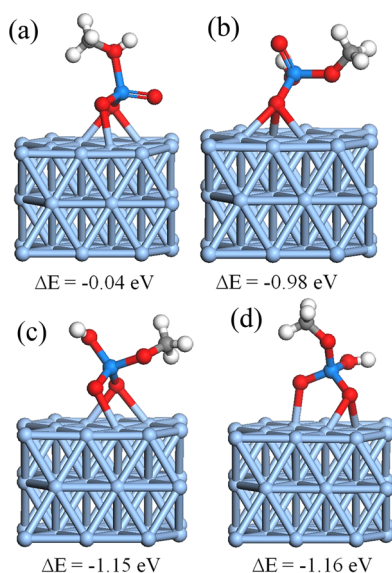


Figure 5. The four structures that can be formed when CH_4 adsorbs dissociatively on VO_4 supported on $\text{Ag}(111)$: (a) CH_3 and H bound to O_v (the oxygen atom that formed a vanadyl prior to methane adsorption); (b) H and CH_3 bound to oxygen atoms (O_b) that formed the $\text{V}-\text{O}-\text{Au}$ bridge before methane dissociative adsorption; (c) H adsorbed on O_v and CH_3 adsorbed on O_b ; (d) CH_3 adsorbed on O_v and H adsorbed on O_b .

and a $\text{V}=\text{O}$ group is formed; only two O atoms bridge the V with Ag (Figure 5a). The reaction energy in the case of Ag is ~ 1 eV lower than on Au . The structures in Figures 4b–d for Au support are similar to those in Figures 5b–d for the Ag support, except for small details (in Figure 5b). The reaction energy on VO_4/Ag is lower by about ~ 1 eV from that on VO_4/Au for all four final dissociation states. We propose that the difference in the reaction energy between VO_4/Au and VO_4/Ag is rooted in the fact that the VO_4 cluster is more strongly bound to Ag than to Au . This means that the oxygen atoms in VO_4/Ag are more satisfied with their situation (they are more stable) than the oxygen atoms in VO_4/Au . One can formulate an analog to the Sabatier principle: if one compares the same cluster (or the same active site) on different supports, the stronger a cluster (or an active site) binds to the support, the smaller the binding energy of a reactant to it. We do not have

enough examples to promote this statement to the status of a “principle”, and it is, right now, merely a suggestion to be tested by future work. If the BEP rule works for the system, one would conclude that the stronger the cluster is bound to the support, the higher the activation energy for a reaction in which a reactant binds to or dissociates on the cluster. We point out that a large energy for dissociative adsorption is not always a good thing. If the binding energy of the dissociation products is much lower than the energy of the intended final products, the catalyst will be very poor (Sabatier principle). Catalysts seem to follow a Buddhist philosophy: moderation in all steps leading from reactants to products.

3.4. Activation Energy for CH_4 Dissociation on VO_4 Supported on $\text{Au}(111)$ or $\text{Ag}(111)$ Surface. The calculation of the activation energy is very time-consuming, and because of this, we assume that the Brønsted–Evans–Polanyi (BEP) rules hold and therefore calculate only the activation energies to reach the state in which the dissociation fragments are bound most strongly. The reaction paths calculated with the nudged elastic band (NEB)⁷⁶ method are shown in Figure 6a,b. The energy barrier for CH_4 dissociation on $\text{VO}_4/\text{Au}(111)$ is about 0.7 eV, and that for the dissociation of $\text{VO}_4/\text{Ag}(111)$ is about 1.25 eV. The pictures in these figures show the initial state (the VO_4 cluster on the surface and CH_4 in gas phase) and the final state (after dissociation).

The shape of the reaction path is rather different from the one normally seen in textbooks. There seem to be two barriers and the high-energy part of the path is unusually broad (along the reaction coordinate). The two movies (see Supporting Information) explain why this happens. Intuitively, one expects that in a dissociative adsorption reaction the activation energy is determined by the fact that as one stretches the bond that is to be broken, both fragments start making bonds with the surface and this lowers the activation energy. However, in the present system (and in all oxides), the distance between a pair of neighboring oxygen atoms is much larger than the $\text{C}-\text{H}$ distance in an alkane. Because of this, it is not possible that both H and the alkyl make bonds with the oxygen atoms simultaneously (in a concerted fashion) without an inordinate stretch of the $\text{C}-\text{H}$ bond, which would require quite a large energy. Hence, the reaction has two steps, which are clearly seen in the two movies. In the first step the hydrogen in CH_4 binds to an oxygen atom in the cluster to form a hydroxyl. The

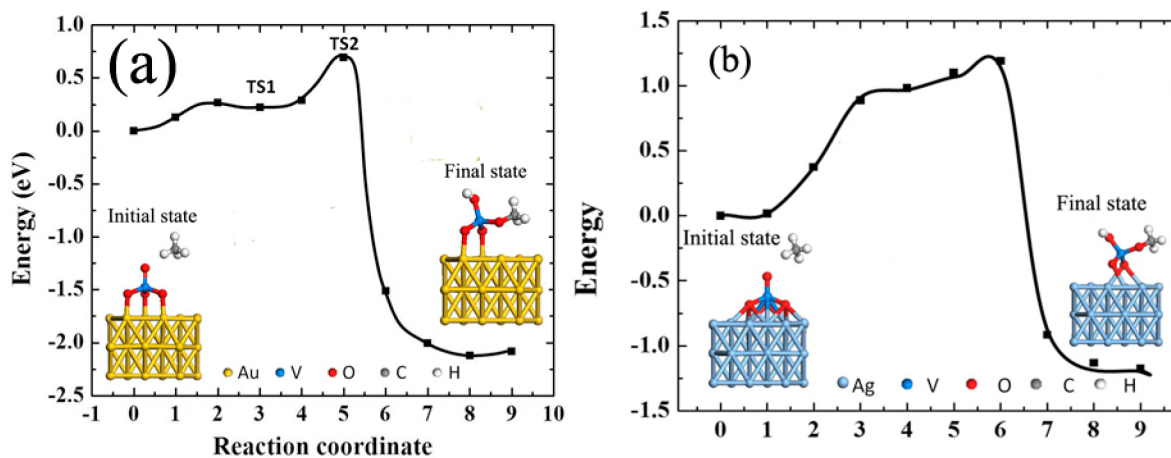


Figure 6. The reaction path calculated with the NEB method for the dissociative adsorption of CH_4 on (a) VO_4 supported on $\text{Au}(111)$ and (b) VO_4 supported on $\text{Ag}(111)$. The initial state is CH_4 in the gas. The final state is the one for which the reaction energy is largest.

methyl is left almost unbound, and it must travel to find another oxygen atom to bind to. It is this travel that gives the reaction path the large width. This also suggests that the dissociative adsorption of an alkane may result in some production of gas phase alkyls. Moreover, the ability of an oxide to bind hydrogen might be a good descriptor for the ability of the oxide to dissociate an alkane. An oxide that makes a strong bond with H will have a higher alkane dissociation energy (i.e., more exothermic) and a lower activation energy for the breaking of the C–H bond. A similar observation, from a different perspective, has been made by Sauer and co-workers.^{77–79}

4. CONCLUSIONS

It appears that isolated VO₄ clusters supported on Au (111) are promising catalysts for the first step in methane activation, the breaking of the C–H bond. We found that the support makes a substantial difference and that Au is a much better support than Ag. This probably happens because Au makes weaker bonds with the oxygen in VO₄, or, equivalently, because VO₄ binds less strongly to Au than to Ag. We propose that if one compares the activity of the same cluster on a variety of supports, then the reaction energy for the dissociative adsorption is higher when the bond of the cluster to the support is weaker. This rule needs to be tested for more systems before being accepted.

The reaction path for the dissociative adsorption of methane has an unusual shape because the reaction takes place in two steps. First, a hydrogen atom in the alkane makes a bond with one of the oxygen atoms in the cluster. This breaks the C–H bond, but the alkyl is not yet bonded to the surface. To bind to the surface, the alkyl needs to travel quite a distance to find an oxygen atom to bind to. Given the fact that on all oxides or oxide clusters the distance between two neighboring oxygen atoms is much larger than the length of the C–H bond in an alkane, we propose that this behavior is general. We have observed this behavior for other systems. We suggest (see also Sauer's work^{77–79}) that for a quick screening, of the ability of an oxide (doped or undoped) or an oxide cluster to adsorb an alkane dissociatively, one should use the energy of a hydroxyl formation. If the energy of hydroxyl formation is larger on oxide A than on oxide B, then the energy of the dissociative adsorption of the alkane on A will be larger than the energy of dissociative adsorption on B. If the BEP rules are valid, the activation energy for dissociative adsorption on A will be smaller than on B. We emphasize that these "rules" are, at this point, based on very few examples and need to be tested further.

■ ASSOCIATED CONTENT

■ Supporting Information

Animations showing methane dissociation by vanadium oxide clusters supported on silver and on gold. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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