

A Theoretical Investigation of the Selective Oxidation of Methanol to Formaldehyde on Isolated Vanadate Species Supported on Silica

Anthony Goodrow and Alexis T. Bell*

Department of Chemical Engineering, University of California, Berkeley, California 94720-1462

Received: April 3, 2007; In Final Form: June 8, 2007

A theoretical analysis has been conducted on the selective oxidation of methanol to formaldehyde catalyzed by isolated vanadate species supported on silica. The active site was represented by a V=O group substituted for a Si-H group in the corner of silsesquioxane, Si₈O₁₂H₈. Calculations of ground and transition states were carried out using density functional theory, whereas statistical mechanics and absolute rate theory were used to determine equilibrium constants and rate coefficients for each elementary step. The formation of formaldehyde was found to involve two key steps. The first is the reversible adsorption of methanol, which occurs by addition across one of the three V-O-Si bonds of the active site. The rate-limiting step is the transfer of a hydrogen atom from the resulting V-OCH₃ species to the V=O bond of the active center. The release of formaldehyde and water from the active center leads to a two electron reduction of the vanadium atom in the center. Rapid reoxidation of the reduced vanadium can occur via adsorption of O₂ to form a peroxide species and subsequent migration of one of the O atoms associated with the peroxide across the surface of the support. The predicted heat of adsorption and equilibrium constant for methanol adsorption are in good agreement with those found experimentally, as is the infrared spectrum of the adsorbed methanol. The apparent first-order rate coefficient and the apparent activation energy are also in very good agreement with the values determined experimentally.

Introduction

Experimental studies have demonstrated that VO_x/SiO₂ is an active catalyst for the selective oxidation of methanol to formaldehyde even when the vanadium is present as isolated vanadate species.^{1–9} Experimental studies using XANES, EXAFS, and Raman spectroscopy have shown that isolated VO₄ units supported on silica have a distorted tetrahedral geometry containing three V-O support bonds and one V=O vanadyl bond.^{3,10} The intrinsic kinetics of methanol oxidation to formaldehyde measured at low methanol conversion are first order in methanol and zero order in oxygen suggesting that the majority of the V atoms in the catalyst are present as V⁵⁺ under reaction conditions. This conclusion is also supported by in situ Raman observations.³ Experimental studies have determined the apparent activation energy, apparent rate constant, and turnover frequency (TOF) for the formation of formaldehyde.^{3,4,8,9} These studies have also suggested that the adsorption of methanol to form V-OCH₃ species is reversible and that the rate-limiting step in the formation of formaldehyde is the transfer of a hydrogen atom from this species to an oxygen atom associated with the catalyst,^{2,4,8} possibly to the V=O bond of the active center.³

Two theoretical studies have been reported dealing with the oxidation of methanol on isolated vanadate species supported on silica. Khaliullin and Bell¹¹ represented the active center by a cluster comprised of O=V(O-)₃ bonded to three Si atoms, each of which was terminated by three hydroxyl groups. Density functional theory (DFT) was used to determine the thermodynamics of methanol adsorption and to assess the energetics for formaldehyde for a reaction mechanism based on experimental

evidence. The calculated heat of methanol adsorption and the fractional occupancy of vanadium centers by methanol were in good agreement with experimental observation. The apparent activation energy for formaldehyde formation was found to be 26.8 kcal/mol, in reasonable agreement with experiment,^{1,2} but the calculated pre-exponential factor for the apparent first-order rate coefficient was 2 orders of magnitude smaller than that observed. More recently, Sauer and co-workers¹² have reported the results of a very thorough DFT study of methanol adsorption and oxidation occurring on isolated sites of vanadia supported on silica. In this study, the active sites were represented by a cluster produced by substituting a V=O group for one of the Si-H groups in silsesquioxane, Si₈O₁₂H₈. Methanol adsorption was shown to occur by cleavage of a V-O-Si bond. Two different chemisorbed species were proposed, both containing a methoxide group bonded to vanadium. The thermodynamically preferred structure is one in which hydrogen bonding occurs between the vanadyl oxygen and the silanol group. The rate-limiting step was taken to be the transfer of a hydrogen atom from an adsorbed methoxy group to the vanadyl oxygen atom, and the activation energy for this process was determined to be 37 kcal/mol. Since the transition state for this reaction is biradicaloid, its structure and energy were calculated using the broken-symmetry approach. The apparent first-order rate coefficient for the oxidation of methanol was taken to be the product of the equilibrium constant for the reversible adsorption of methanol in its lowest energy configuration and the rate coefficient for the rate-limiting step. By this means, the apparent activation energy for methanol oxidation was estimated to be 27 kcal/mol, in reasonable agreement with the observed values.^{1,2} On the other hand, the calculated value of the apparent

* Author to whom correspondence should be addressed. E-mail: alexbell@berkeley.edu.

first-order rate coefficient was 4 orders of magnitude smaller than that measured experimentally at 503 K.^{1,2}

Thus, while previous theoretical studies have found that density functional theory can describe the reaction energetics involved in the formation of formaldehyde correctly, a proper description of the pre-exponential factor for the apparent first-order rate coefficient has not yet been achieved. There are also two other issues not addressed by these studies. The first is the fate of the species formed upon desorption of formaldehyde from the active site and the means by which V^{3+} species are formed upon the release of formaldehyde. Thus, there is a need to establish that the rate coefficients for these processes are large and, hence, that these processes are not kinetically relevant. The second issue concerns the mechanism and kinetics of reoxidation of the reduced vanadium center produced upon the release of formaldehyde and water. Particularly intriguing is the question of how isolated vanadate centers are reoxidized by O_2 , since one molecule of O_2 is needed to reoxidize two reduced vanadate centers. The present study was undertaken with the specific aim of identifying the pathway by which the thermodynamically preferred configuration of adsorbed methanol is formed on isolated vanadate sites supported on silica, the changes in Gibbs free energy for all elementary processes involved in the oxidation of methanol to formaldehyde at such sites, and the processes involved in the reoxidation of such sites once they are reduced.

Theoretical Methods

Models of the surface of amorphous silica, containing two to eight Si atoms and different ring structures, were examined in an effort to find a suitable representation. The criteria used for selecting the best representation were that the geometry and vibrational frequencies determined for the model silica surface and for the vanadate species attached to such a surface should be consistent with those found experimentally. A further criterion was that the computational costs for carrying out transition-state searches for elementary reactions should not be prohibitive. Clusters isolated from the low-index surfaces of β -cristoballite^{13–16} were examined as well as silsesquioxane ($Si_8O_{12}H_8$), the model for a silica surface used by Sauer and co-workers.¹² Of the several clusters considered, silsesquioxane was found to be the best for capturing the physical properties of silica with a reasonable expenditure of computational effort. VO_x/SiO_2 was modeled by replacing one of the eight Si–H groups in the silsesquioxane cube by a vanadyl group, $V=O$. The resulting silica-supported VO_4 species has a distorted tetrahedral geometry containing three $V-O-Si$ support bonds and one $V=O$ vanadyl bond, as seen in Figure 1.

Density functional theory (DFT) was used to compute the optimized structures, vibrational frequencies, and thermodynamic properties of all species. Geometry optimization with full relaxation of all atoms was performed using the B3LYP functional and the 6-31G* basis set within Gaussian 03.¹⁷ After structural optimization, a more accurate estimate of the energy was calculated using the LACV3P**++ basis set in Jaguar 6.5.¹⁸ The electronic structure of vanadium was described using the LANL2DZ basis set, which treats the inner core of electrons separately from the valence electrons. Calculated frequencies were scaled by 0.9614 to account for the overestimation of vibrational frequencies determined at the B3LYP/6-31G* level of theory.¹⁹ The growing string method (GSM)²⁰ was used to find an initial estimate for transition-state geometries, also using the B3LYP/6-31G* level of theory. The estimated transition-state geometry was then refined using the transition-state search

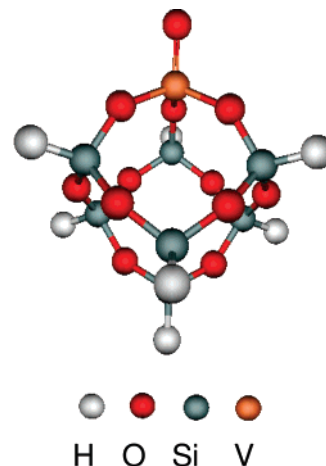


Figure 1. A silsesquioxane model of the VO_x/SiO_2 active catalytic site.

(TSS) in Gaussian 03, which uses the Beryn optimization algorithm to update the Hessian matrix and trust radius.^{21,22} The final value of the transition state energy was calculated using the LACV3P**++ basis set for all atoms except V, which was described using the LANL2DZ basis set. These calculations were carried using Jaguar 6.5.

The broken symmetry approach^{23,24} was used to calculate the energy of the transition state for reactions involving multiple spin states, which have a biradicaloid electronic structure. The unrestricted open shell B3LYP functional was used to perform these electronic structure calculations. Multireference treatment was used to calculate the projected low spin energy, $E(ls)$, of the transition state by using the energy from the broken symmetry calculation, $E(bs)$, and from the triplet calculation, $E(t)$, according to the following formula:²⁴

$$E(ls) = E(t) + 2 \frac{E(bs) - E(t)}{2 - \langle S^2 \rangle} \quad (1)$$

In eq 1, $\langle S^2 \rangle$ is the average spin–spin coupling, ranging from 0 when the valence electrons are paired to 1 when the valence electrons are unpaired.

The Gibbs free energy for each ground- or transition-state structure was calculated using standard relationships from statistical mechanics.^{25–29} These calculations were done for 650 K, the temperature at which the selective oxidation of methanol to formaldehyde was studied experimentally. The standard state for all gas-phase species was taken to be 1 atm and the standard state for all vanadia species was taken to be a mole fraction of 1. The symbol ΔG° is used to refer to the Gibbs free energy under these standard state conditions. The partition functions for translational, rotational, and vibrational degrees of freedom used in the calculations of Gibbs free energies were calculated explicitly. This approach avoids treating the translational and rotational partition functions for species involving the cluster as gas-phase species, the approach used in Gaussian 03 and other quantum chemical codes.²⁵ In calculating the partition functions for adsorbed species it was assumed that such species have no degrees of translational or bulk rotational freedom. Internal rotations of adsorbed species were considered and the scaled values of vibrational frequencies (see above) were used in the calculation of the vibrational partition function, and for species involving the cluster the number of degrees of vibrational freedom was decremented by the number of degrees of internal rotational freedom.^{26–29} No change in procedure was needed

TABLE 1: Comparison of the Properties of Isolated Vanadate Species on SiO₂ Determined Theoretically and Experimentally

	theory	experiment
$r(\text{V}=\text{O})$	1.58 Å	1.58 ± 0.03 Å ^{a,b}
$r(\text{V}-\text{O})$	1.76 Å	1.79 ± 0.02 Å ^{a,b}
$\nu(\text{V}=\text{O})$	1035 cm ⁻¹	1030–1040 cm ^{-1 a,b-d}
$\nu(\text{Si}-\text{O}-\text{V})$	991 cm ⁻¹	980 cm ^{-1 a,e}
D ₁ band	506 cm ⁻¹	495 cm ^{-1 f-h}
D ₂ band	611 cm ⁻¹	606 cm ^{-1 f-h}
$r(\text{Si}-\text{O})$	1.71 Å	1.608 Å ^{h,i}
$r(\text{O}-\text{O})$	2.87 Å	2.626 Å ^{h,i}
$r(\text{Si}-\text{Si})$	3.50 Å	3.077 Å ^{h,i}

^a VO_x/SiO₂ catalyst at low weight loading, <1 V/nm². ^b Reference 3. ^c Reference 1. ^d Reference 2. ^e Reference 30. ^f Reference 31. ^g Reference 32. ^h Amorphous SiO₂. ⁱ Reference 15.

for the electronic partition function which is just the electronic spin multiplicity for each species.²⁵

Results and Discussion

Comparison of Calculated and Observed Properties of VO_x/SiO₂. Table 1 lists the geometries and vibrational frequencies for the model of VO_x/SiO₂ used in this study together with values observed experimentally for isolated vanadate species supported on silica and silica itself. It is evident that the bond lengths and vibrational frequencies associated with the vanadate species are in very good agreement with the corresponding values found experimentally.^{3,30} Good agreement is also observed in the frequencies of the D₁ and D₂ bands associated with vibrations of the four-membered rings of silica.^{31,32} Deviations between theoretical calculations and experimental observations are observed, though, in the Si–O and O–O bond distances in silica, which tend to be 0.1 Å longer in the model of silsesquioxane than in amorphous silica.

Adsorption of Methanol. Methanol adsorption onto isolated VO₄ sites, species **1**, can occur via alcoholysis of a V–O–Si linkage, leading to either a V–OCH₃/Si–OH or a V–OH/Si–OCH₃ pair.^{1–3} Experimental evidence shows that V–OCH₃ is a necessary precursor to the formation of formaldehyde,^{3,7–9} whereas Si–OCH₃ is a precursor to the combustion of methanol to CO and H₂O.³ Figure 2 indicates two possible geometries for the V–OCH₃ species, species **2** and **2'**. The difference in adsorption energies between **2** and **2'** is 4.7 kcal/mol, in reasonable agreement with the value of 2.4 kcal/mol reported previously.¹² Species **2'** is more stable than **2** because of the strong hydrogen-bond formed between the vanadyl oxygen and silanol group. The Gibbs free energy change for methanol adsorption, $\Delta G^\circ_{\text{ads}}$, is positive for both **2** and **2'**; however, the

TABLE 2: Comparison of the V=O and V–O–CH₃ Vibrational Frequencies for Species **2 and **2'****

vibrational modes	theory (species 2)	theory (species 2')	exp ^a
$\nu(\text{V}=\text{O})$ cm ⁻¹	1017	1034	1030
$\nu(\text{V}-\text{O}-\text{C})$ cm ⁻¹	1052	1071	1070

^a Reference 3.

formation of **2'** is more favorable than the formation of **2** by 9.0 kcal/mol. Further evidence for the preferential formation of **2'** is provided by Raman spectroscopy. As shown in Table 2, the experimentally observed vibrational frequencies for V=O and V–OCH₃ are fully consistent with **2'** but not with **2**.³

While **2'** is favored thermodynamically, **2** is expected to form upon the initial adsorption of methanol. The activation barrier for methanol adsorption as **2** is 9.6 kcal/mol. The activation barrier for the direct conversion from **2** to **2'** is high, 48.3 kcal/mol, due to the highly strained geometry of the transition-state and, hence, this process is unlikely to occur under reaction conditions. An alternate route for conversion of **2** to **2'** is shown schematically in Figure 3. In this case, a second molecule of methanol adds to **2** to form a species containing two V–OCH₃ groups. Rotation around the remaining V–O–Si bond followed by the desorption of a molecule of methanol yields the energetically preferred species, **2'**. The indirect conversion of **2** to **2'** is projected to be facile at reaction conditions, since the activation energy for this process is only 6.7 kcal/mol.

As noted above, methanol adsorption can also occur so as to produce a methoxide group bonded to silicon rather than vanadium. A comparison of the thermodynamics for forming V–OCH₃ versus Si–OCH₃ groups is shown in Figure 4. As noted in Figure 4 the Gibbs free energy of adsorption is less favorable for the formation of a Si–OCH₃ group than the formation of a V–OCH₃ group by 4.0 kcal/mol.

A comparison of the calculated and observed frequencies for the symmetric and asymmetric C–H vibrations associated with V–OCH₃ to Si–OCH₃ species is shown in Table 3. With the exception of the symmetric C–H stretching vibrations for methoxide groups bonded to vanadium, the calculated and observed vibrational frequencies agree to within 5–6 cm⁻¹. The 17 cm⁻¹ difference between the calculated and experimental value for the symmetric C–H stretch for the methoxide groups bonded to vanadium is very likely due to a higher degree of hydrogen bonding in the model system between the vanadyl oxygen and the hydrogen atom of the silanol group.

The extent of methanol adsorption at 650 K to form V–OCH₃/Si–OH versus V–OH/Si–OCH₃ pairs was computed

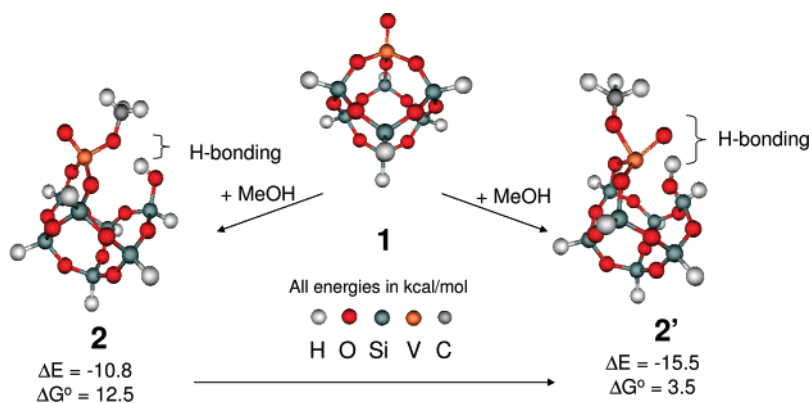


Figure 2. Proposed structures **2** and **2'** from methanol adsorption onto **1**. ΔE and ΔG° are shown in kcal/mol at 650 K. ΔE and ΔG° are shown in kcal/mol at 650 K.

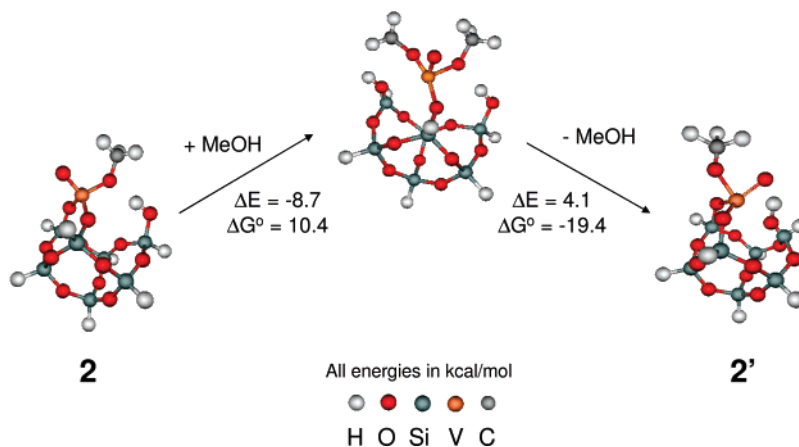


Figure 3. Conversion between **2** and **2'** via adsorption of additional methanol. ΔE and ΔG° are shown in kcal/mol at 650 K.

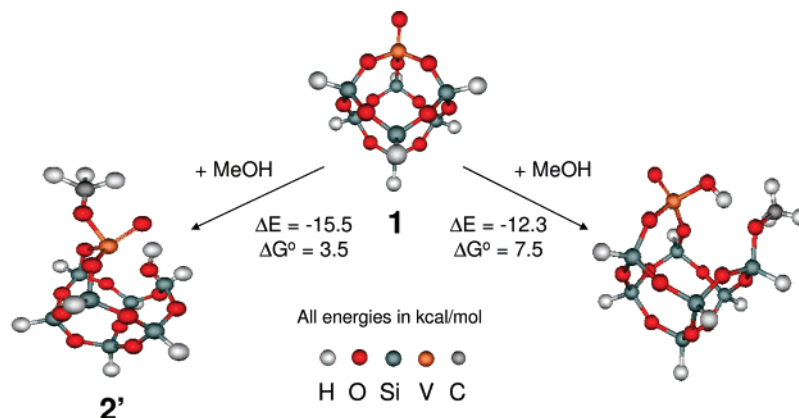


Figure 4. Adsorption of methanol onto **1** to form a V-OCH₃ or Si-OCH₃ group. ΔE and ΔG° are shown in kcal/mol at 650 K.

TABLE 3: Comparison of the Vibrational Frequencies for C-H Bond Stretches in V-OCH₃ and Si-OCH₃ Species

adsorbed species	vibrational mode	theory (cm ⁻¹)	exp (cm ⁻¹) ^a
V-OCH ₃	symmetric C-H	2847	2830
	asymmetric C-H	2925	2930
	V=O	1034	1030
Si-OCH ₃	symmetric C-H	2855	2860
	asymmetric C-H	2954	2960
	V=O	1058	

^a Reference 3.

from the ratio of adsorption equilibrium constants to form V-OCH₃/S-OH versus V-OH/Si-OCH₃ pairs, assuming that the structure for the first of these pairs is **2'**. By this means the relative surface concentration ratio of V-OCH₃ to Si-OCH₃ is estimated to be 1.2, or 55% V-OCH₃/Si-OH pairs and 45% V-OCH₃/Si-OCpairs. These values agree quite well with those computed from experimental Raman spectra,³ 60% V-OCH₃/Si-OH pairs and 40% V-OCH₃/Si-OCH₃ pairs, using computed Raman scattering cross sections.

Catalytic Cycle. The mechanism of methanol oxidation to formaldehyde can be envisioned to occur in two parts as shown in Figures 5 and 6. In the first part of the cycle, methanol adsorption is followed by the transfer of a hydrogen atom from the methoxide group of **2'** to the vanadyl group of this species to form a vanadium hydroxyl group **3**. This step is identical to that considered in the theoretical work of Khaliullin and Bell¹¹ and Sauer and co-workers.¹² An alternative to this scenario would be direct hydrogen atom transfer to the vanadium atom itself to form a metal hydride. While it had been suggested that a vanadium hydride species should be stable,³³ the presence of

a metal hydride attached to a vanadium atom that is also bonded to oxygen (V=O) was found to be unfavorable. Examination of both scenarios showed that energy change for the transfer of the hydrogen atom to the vanadyl group is lower than that to form a vanadium hydride species by over 20 kcal/mol. The resulting structure **3** has a weakly bound formaldehyde and a hydroxyl group. The value of ΔG° for this step at 650 K is 37.7 kcal/mol and the associated activation energy is 39.8 kcal/mol. The activation energy for this step was found by performing a broken symmetry calculation because the spin state of vanadium changes from a singlet in the reactant state **2'** to a triplet in the product state **3** upon transfer of the hydrogen atom. Specifically, upon adsorption of methanol, vanadium is formally V⁵⁺ with no d electrons but following the hydrogen-transfer step, the valence of vanadium reduces to a formal V³⁺ with two unpaired d electrons.

The formaldehyde molecule associated with **3** can readily desorb, since the change in Gibbs free energy for this process is $\Delta G^\circ = -2.8$ kcal/mol, a result that is in agreement with experimental observation.³⁴ The remaining two hydroxyl groups associated with species **4**, one attached to vanadium and the other to silicon, react to form water and reform a support V-O-Si bond (the reaction of **4** to form **5**). The activation barrier for this process is 14.5 kcal/mol, and the Gibbs free energy of reaction, $\Delta G^\circ = -25.9$ kcal/mol, is highly favorable. The pathway for the formation of formaldehyde shown in Figure 5 differs from that examined by Sauer and co-workers,¹² even though the initial structure **3** is identical. In that study it was reported that the direct desorption of formaldehyde was endothermic by 22.6 kcal/mol and, hence, was thought to be unfavorable. An alternative pathway was proposed in which the

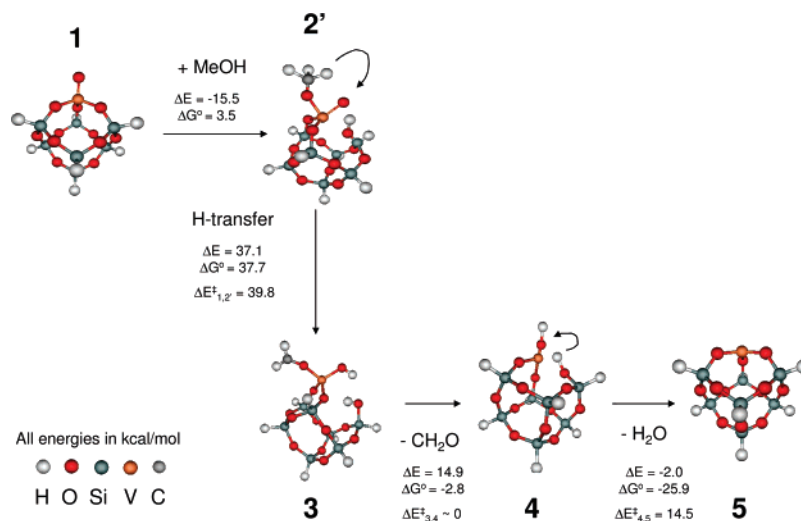


Figure 5. Selective oxidation of methanol to formaldehyde over vanadate species **1**. Vanadium is reduced to V^{3+} in species **5**. ΔE and ΔG° are shown in kcal/mol at 650 K.

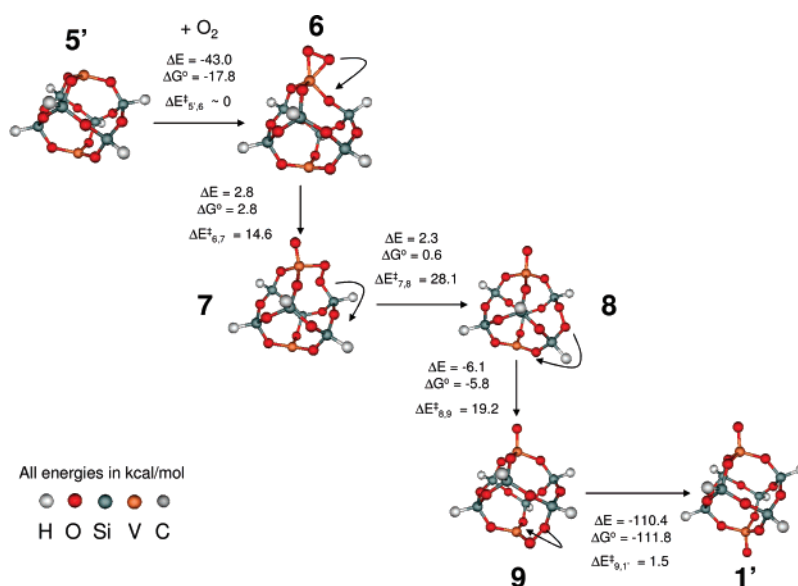


Figure 6. The reoxidation pathway involves formation of a peroxide species, **6**, which is active for methanol oxidation. The starting active site, **1'**, is regenerated. ΔE and ΔG° are shown in kcal/mol at 650 K.

proton associated with the Si–OH group first transfers to the V–OH group to form a V–O–Si bond and H_2O bound to the V atom. The last step of the reaction was then envisioned to be desorption of formaldehyde from the preceding intermediate.

The vanadium in species **5**, formed upon desorption of water, must be reoxidized in order to complete the catalytic cycle. Experimental studies suggest that this process is very rapid and, hence, kinetically irrelevant as evidenced by a zero-order dependence of the rate of formaldehyde formation on oxygen partial pressure.^{3,8,9} Consistent with this conclusion, in situ Raman spectroscopy shows that virtually all of the vanadium remains in the +5 state under reaction conditions.³ Since the oxidation of species **5** to **1** involves O_2 but only one O atom is required per V atom, it is of interest to elucidate how this process might occur.

Figure 6 shows a possible mechanism for the oxidation of **5** to **1**. In this scheme, two V^{3+} cations are shown at opposite corners of the silsesquioxane cube, species **5'**. In the first step O_2 is adsorbed to form a peroxide species **6** on one of the reduced vanadium centers. The change in energy for this step is $\Delta E = -43.0$ kcal/mol and the change in the Gibbs free energy

is $\Delta G^\circ = -17.8$ kcal/mol and, hence, is favorable at 650 K. As shown in Figure 6, an O atom of the peroxide can migrate from **6** to form **7**, which contains a V–O–O–Si bond. At 650 K, the Gibbs free energy change for this process is only 2.8 kcal/mol and the activation energy is 14.6 kcal/mol. Further migration of the peroxide group to form **8** can occur, leading to the formation of an Si–O–O–Si bond. The change in Gibbs free energy for this step is 0.6 kcal/mol and the activation energy is 28.1 kcal/mol. Subsequent migration of the peroxide group leads to species **9** and **1'** via reactions that are thermodynamically favorable and have activation barriers that are comparable or much lower to those for the preceding steps shown in Figure 6. Thus, the proposed scheme suggests that reoxidation proceeds via adsorption of O_2 to form a peroxide species followed by O atom migration via the support to reoxidize a second reduced V^{3+} cation.

Several pieces of evidence support the reoxidation scheme presented in Figure 6. First, peroxy species have been reported to form on vanadium complexes in solution³⁵ and similar complexes formed on molybdenum complexes have been shown to be active for the oxidation of alcohols.^{36,37} Peroxy species have also been suggested as active species in the oxidation of

TABLE 4: The Activation Energy ΔE_{ij}^\ddagger , Pre-Exponential Factor k_{ij}^0 , and Rate Constant k_{ij} for the Conversion of Reactant i into Product j

	reaction (i,j)	ΔE_{ij}^\ddagger (kcal/mol)	k_{ij}^0	k_{ij}
reaction pathway	(1,2') ^a			
	(2',3)	39.8	$1.92 \times 10^{12} \text{ s}^{-1}$	$7.95 \times 10^{-2} \text{ s}^{-1}$
	(3,4)	~0		$1.35 \times 10^{13} \text{ s}^{-1}$
	(4,5)	14.5	$5.49 \times 10^{13} \text{ s}^{-1}$	$7.31 \times 10^8 \text{ s}^{-1}$
reoxidation pathway	(5',6)	~0		$4.63 \times 10^9 \text{ atm}^{-1} \text{ s}^{-1}$
	(6,7)	14.6	$9.58 \times 10^{12} \text{ s}^{-1}$	$1.19 \times 10^8 \text{ s}^{-1}$
	(7,8)	28.1	$1.72 \times 10^{12} \text{ s}^{-1}$	$6.11 \times 10^2 \text{ s}^{-1}$
	(8,9)	19.2	$9.20 \times 10^{10} \text{ s}^{-1}$	$3.16 \times 10^4 \text{ s}^{-1}$
	(9,1')	1.5	$4.71 \times 10^{12} \text{ s}^{-1}$	$1.44 \times 10^{12} \text{ s}^{-1}$

^a Reaction (1,2') assumed to be at equilibrium and reversible, with an adsorption constant of $K_{1,2'} = 4.23 \text{ atm}^{-1}$ at 650 K.

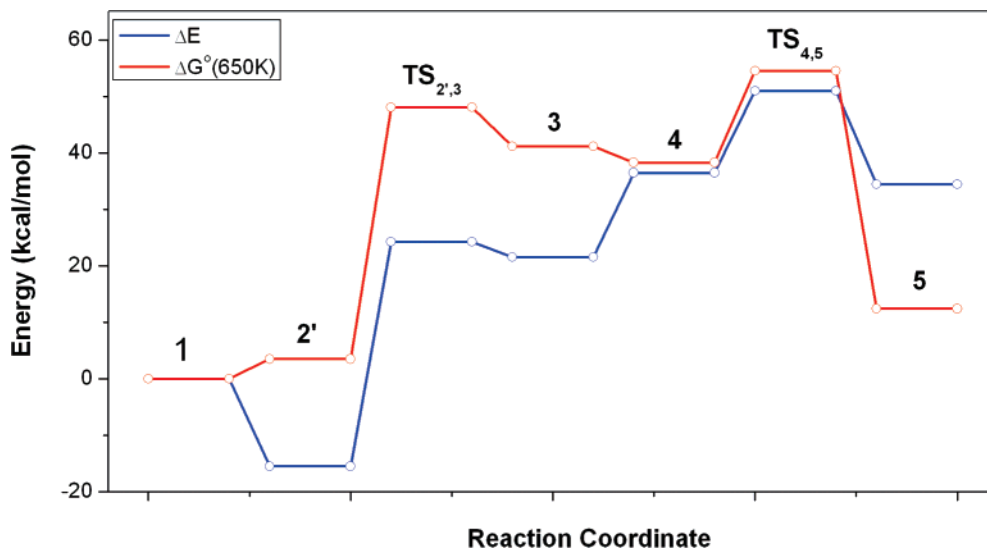


Figure 7. Energy profile of ΔE and ΔG° at 650 K for the reaction mechanism. The numbers above the plot refer to the corresponding species.

methane on FePO_4 .³⁸ Second, both experimental^{39a-e} and theoretical studies^{40a-c} have shown that Si-O-O-Si structures (peroxy linkages) are involved in the diffusion of oxygen through silica. Moreover, the activation barrier for this process and the O-O bond distance in the transition state are very similar to those for the conversion of species **7** to **8** reported here. Third, when H_2 reduced VO_x/SiO_2 or $\text{MoO}_x/\text{SiO}_2$ are reoxidized in $^{18}\text{O}_2$, one ^{18}O atom is consumed per reduced metal center;^{41,42} however, Raman spectroscopy shows that the V=O or Mo=O initially formed are primarily ^{16}O labeled. These observations suggest that ^{18}O atoms derived from $^{18}\text{O}_2$ can form V- ^{18}O -Si, V- ^{18}O - ^{16}O -Si, and Si- ^{18}O - ^{16}O -Si bonds.

The pre-exponential factors and activation barriers for each of the elementary steps presented in Figures 5 and 6 are listed in Table 4. Also shown there are the rate coefficients for each step evaluated at 650 K. The rate constants for the steps involved in the reoxidation mechanism are all large, and hence not kinetically relevant.

Figure 7 shows the changes in both the internal energy and the Gibbs free energy at 650 K for the series of steps involved in the oxidation of methanol to formaldehyde (see Figure 5). The profile in the Gibbs free energy indicates that methanol adsorption to form **2'** will be at equilibrium and that the rate-determining step will be the conversion of **2'** to **3**. A similar set of energy and free energy profiles is shown in Figure 8 for the reoxidation of reduced V^{3+} centers. This plot indicates that **6** and **7** will be at equilibrium and that the conversion of **7** to **8** is the slowest step in the reoxidation process.

Comparison with Experimental Results. On the basis of the results in Figure 7, it is concluded that the adsorption of methanol is reversible and at equilibrium and that the rate-limiting process at low methanol conversion is the process leading from **2'** to **3**. It then follows that the rate of formaldehyde formation, $R_{\text{CH}_2\text{O}}$, and the apparent rate constant, k_{app} , are given by

$$R_{\text{CH}_2\text{O}} = k_{\text{app}} P_{\text{MeOH}} \quad (2)$$

$$k_{\text{app}} = K_{1,2'} k_{2',3} = k_{\text{app}}^0 \exp\left(\frac{-\Delta E_{\text{app}}}{RT}\right) \quad (3)$$

where $K_{1,2'}$ is the equilibrium constant for the adsorption of methanol as **2'**, $k_{2',3}$ is the rate constant for the rate-limiting step, ΔE_{app} is the apparent activation energy, and P_{MeOH} is the partial pressure of methanol.

The equilibrium constant for methanol adsorption can be evaluated using eq 4:

$$K_{1,2'} = \frac{\sigma_{1,2'} q_{2'}}{q_{\text{MeOH}} q_1} \exp\left(\frac{PV}{RT}\right) \exp\left(\frac{-\Delta E_{1,2'}}{RT}\right) \quad (4)$$

In this equation, q_i is the partition function for species i and $\sigma_{1,2'}$ is the symmetry factor for the reaction of **1** to **2'**. Since any one of three V-O-Si support bonds can be broken, $\sigma_{1,2'}$ is 3. Using the value of $\Delta E_{1,2'} = -15.5 \text{ kcal/mol}$ for the adsorption of methanol by **1** to form **2'**, gives $K_{1,2'} = 4.23 \text{ atm}^{-1}$ at 650 K. This value of $K_{1,2'}$ can be compared with the one estimated from the experimental data of Wachs et al.^{7,8} for

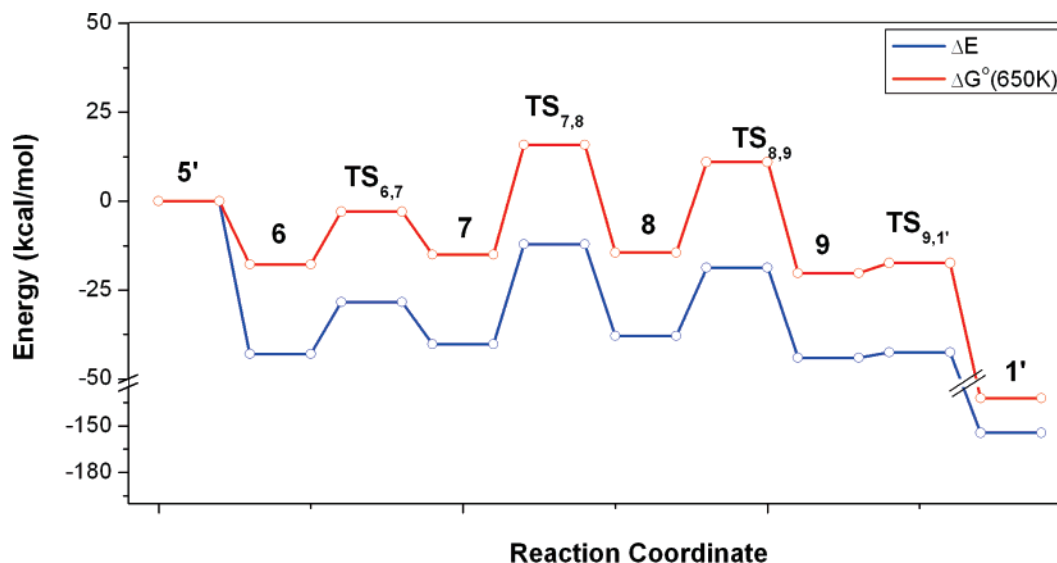


Figure 8. Energy profile of ΔE and ΔG° at 650 K for the reoxidation mechanism. The numbers above the plot refer to the corresponding species.

TABLE 5: A Comparison of Theoretical and Experimental Values of the Rate Parameters Contributing to the Apparent Rate Parameters

		theory	theory ^a	exp
adsorption step	$\Delta E_{1,2'}$ (kcal/mol)	-15.5	-9.5	-13.4, ^b -13.3 ^c
	$K_{1,2'}^0$ (atm ⁻¹)	2.60×10^{-5}		$5.12 \times 10^{-5},$ ^b 2.04×10^{-4} ^c
	$K_{1,2'}$ (atm ⁻¹)	4.23		1.64, ^{b,d} 6.04 ^c
rate-limiting step	$\Delta E_{2',3}^\ddagger$ (kcal/mol)	39.8	36.8	
	$k_{2',3}^0$ (s ⁻¹)	1.92×10^{12}		
	$k_{2',3}$ (s ⁻¹)	0.0795		
apparent kinetics	ΔE_{app} (kcal/mol)	24.3	27.3	23 ± 1 ^c
	k_{app}^0 (atm ⁻¹ s ⁻¹)	4.00×10^7	1.34×10^6	1.90×10^7 ^c
	k_{app} (atm ⁻¹ s ⁻¹)	0.27	8.86×10^{-4}	0.35 ^c

^a Reference 12. ^b Reference 7. ^c Reference 3. ^d Reference 8.

methanol adsorption at 373 and 503 K. Using these data $\Delta E_{1,2'}$ = -13.4 kcal/mol and $K_{1,2'} = 1.64 \text{ atm}^{-1}$ at 650 K. A value of $K_{1,2'}$ can also be determined from in situ infrared spectra of V-OCH₃ taken at temperatures between 423 and 673 K reported by Bronkema and Bell.³ These data yield a value of $\Delta E_{1,2'} = -13.3 \text{ kcal/mol}$ and $K_{1,2'} = 6.04 \text{ atm}^{-1}$ at 650 K. Thus, the value of $K_{1,2'}$ calculated theoretically in the present study is seen to be in reasonable agreement with the values determined experimentally.

As discussed above, the rate-limiting step in the oxidation of methanol to formaldehyde is the transfer of a hydrogen atom from an adsorbed methoxy group to a vanadyl oxygen atom, the reaction of **2'** to form **3**. The computed activation energy for this step is 39.8 kcal/mol. The rate constant was determined from the following expression, eq 5:

$$k_{2',3} = \sigma_{2',3} \kappa(T) \frac{k_B T}{h} \frac{q_{2',3}^\ddagger}{q_{2'}} \exp\left(\frac{-\Delta E_{2',3}^\ddagger}{RT}\right) \quad (5)$$

In eq 5, $q_{2',3}^\ddagger$ and $q_{2'}$ are the partition function for the transition state involved in the transformation of species **2'** to **3** and the partition function for species **2'**, respectively. The symmetry factor, $\sigma_{2',3}$, in the pre-exponential factor is equal to 3 because any one of three hydrogen atoms in the methoxy group of **2'** can transfer to the vanadyl group. The transmission coefficient, κ , for tunneling is included because the transition state involves transferring a hydrogen atom. Wigner's approximation to the barrier, which uses an Eckart potential, was applied in calculating κ .⁴³ The effect of tunneling causes a 13% increase in the

rate constant at 650 K. At 650 K, the pre-exponential term is $1.92 \times 10^{12} \text{ s}^{-1}$ and $k_{2',3} = 7.95 \times 10^{-2} \text{ s}^{-1}$.

A comparison of our computed values for $K_{1,2'}$, $k_{2',3}$, and k_{app} at 650 K with those obtained by Sauer and co-workers¹² and with the experimental values reported by Wachs and co-workers^{7,8} and by Bronkema and Bell³ are presented in Table 5. The value of $\Delta E_{1,2'}$ for the adsorption of methanol as **2'** is lower than that determined by Sauer and co-workers¹² by 6.0 kcal/mol but only 2.1 kcal/mol lower than that determined from the experimental observations of Wachs and co-workers.^{7,8} The difference in the two theoretical values of $\Delta E_{1,2'}$ is likely a consequence of the basis sets used. As noted above, the absolute value of $K_{1,2'}$ determined at 650 K is in reasonable agreement with that determined from the results of the latter researchers. The activation energy associated for the rate-limiting step determined in the present study is 3.0 kcal/mol higher than that reported by Sauer and co-workers.¹² On the other hand, the apparent activation energy calculated in the present study is 3.0 kcal/mol lower than that predicted by Sauer and co-workers¹² but only 1.3 kcal/mol higher than that reported in recent experimental work by Bronkema and Bell.³ More notably, the pre-exponential factor for the apparent first-order rate coefficient, k_{app}^0 , determined in the present study agrees closely with that found experimentally but is an order of magnitude larger than that determined from the results reported by Sauer and co-workers.¹² As shown in Table 5, the value of k_{app} evaluated at 650 K is within a factor of 2 of that measured experimentally.³ By contrast, the value of k_{app} determined from the work of Sauer

et al.¹² is 3 orders of magnitude smaller than that observed experimentally.

As noted earlier, experimental studies indicate that the rate of catalyst reoxidation is very rapid and, hence, kinetically irrelevant. To assess whether the reoxidation scheme shown in Figure 6 is consistent with this observation, calculations were made to determine the fraction of the V atoms that are present in the form of species **5'**, **6**, and **7**. The fraction of V present as **5'** was determined by dividing the rate of formaldehyde formation per V atom observed experimentally by Bronkema and Bell³ at 650 K for a methanol partial pressure of 0.05 atm and an oxygen partial pressure of 0.075 atm, $1.75 \times 10^{-2} \text{ s}^{-1}$, by the rate coefficient for the conversion of **5'** to **6** and the oxygen partial pressure. This leads to an occupancy by **5'** of $\theta_{5'} = 5.04 \times 10^{-11}$. The sum of species **6** and **7** is determined in a similar manner and is $\theta_{6+7} = 2.86 \times 10^{-5}$. It is apparent, therefore, that the fractions of vanadium present as reduced centers, **5'**, or peroxide-containing centers, **6** and **7**, is very small, consistent with the observation that the reoxidation of V centers is very rapid compared to the rate of their reduction.

The results of the present study can also be used to estimate the fraction of the vanadium sites containing methoxide groups in the form of **2'** under the reaction conditions reported by Bronkema and Bell.³ A value of $\theta_{2'}$ was determined using the following relationship:

$$\theta_{2'} = \frac{K_{1,2'} P_{\text{MeOH}}}{1 + K_{1,2'} P_{\text{MeOH}}} \quad (6)$$

Using the value of $K_{1,2'}$ given in Table 5 and a methanol partial pressure of 0.05 atm, the value of $\theta_{2'}$ is found to be 0.17. Since all other species are present in very low concentration, the value of $\theta_1 = 0.83$. The value of $\theta_{2'}$ determined theoretically is in excellent agreement with that deduced from in situ Raman observations reported by Bronkema and Bell.³ At 673 K these authors observed values of $\theta_{2'} = 0.15$. The close agreement of theory and experiment provides additional support for the calculated value of $K_{1,2'}$.

Conclusions

The present study shows that substitution of a V=O group for a Si-H group in the corner of silsesquioxane provides a very good model for isolated vanadate species supported on amorphous silica. A theoretical investigation of the mechanism and kinetics of methanol oxidation conducted using this model of the active center shows that the reaction is initiated by the reversible adsorption of methanol across one of the three V-O-Si bonds connecting the vanadate species to the support. This process produces both V-OCH₃/SiOH and V-OH/SiOCH₃ pairs, only the first of which is involved in the formation of formaldehyde. The structure of the initial V-OCH₃/SiOH pair is **2**. This species then rearranges to form the thermodynamically preferred structure **2'** via a process that involves the adsorption and desorption of a second molecule of methanol. The calculated heat of adsorption to form **2'**, -15.5 kcal/mol, and the vibrational spectrum of this species are in very good agreement with experimental evidence. The rate-limiting step for the formation of formaldehyde is the transfer of a hydrogen atom from an adsorbed methoxy group to a vanadyl oxygen atom. The activation energy for this step is 39.8 kcal/mol. Formaldehyde and water then desorb, leading to the reduction of the vanadium site. Reoxidation of the reduced vanadium center is hypothesized to occur via the adsorption of O₂ and subsequent migration of one of the O atoms associated with this structure

across the surface of the support. The calculated rate coefficient for the elementary processes involved in vanadium reoxidation are considerably larger than that for the rate-limiting step involved in the formation of formaldehyde and, consequently, the reoxidation process is found to be kinetically irrelevant, in agreement with experimental observation. The calculated values for the apparent activation energy and the pre-exponential factor for the apparent first-order rate coefficient for formaldehyde formation are 24.3 kcal/mol and $4.00 \times 10^7 \text{ atm}^{-1} \text{ s}^{-1}$, respectively. These values are in very good agreement with those determined experimentally, as is an estimate of the coverage of the catalyst surface by V-OCH₃ groups, **2'**, under reaction conditions.

Acknowledgment. This work was supported by the Methane Conversion Cooperative funded by BP.

Supporting Information Available: A zip archive containing details of rate calculations, surface species concentrations, minimum energy geometries, and transition states is included. The archive also contains subdirectories with minimum energy structures and transition state structures in XYZ format from Gaussian03. README.txt files are included within the archive to guide the reader. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Baltes, M.; Cassiers, K.; Van Der Voort, P.; Weckhuysen, B. M.; Schoonheydt, R. A.; Vansant, E. F. *J. Catal.* **2001**, *197*, 160.
- Lim, S.; Haller, G. L. *Appl. Catal.* **1999**, *188*, 277.
- Bronkema, J.; Bell, A. T. *J. Phys. Chem. C* **2007**, *111*, 420.
- Burcham, L. J.; Wachs, I. E. *Catal. Today* **1999**, *49*, 467.
- Burcham, L. J.; Deo, G.; Gao, X.; Wachs, I. E. *Top. Catal.* **2000**, *11/12*, 85.
- Feng, T.; Vohs, J. M. *J. Phys. Chem. B* **2005**, *109*, 2120.
- Burcham, L. J.; Briand, L. E.; Wachs, I. E. *Langmuir* **2001**, *17*, 6164.
- Burcham, L. J.; Badlani, M.; Wachs, I. E. *J. Catal.* **2001**, *203*, 104.
- Deo, G.; Wachs, I. E. *J. Catal.* **1994**, *146*, 323.
- Koningsberger, D.C.; Prins, R. *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*; Wiley-Interscience: New York, 1988.
- Khaliullin, R. Z.; Bell, A. T. *J. Phys. Chem. B* **2002**, *106*, 7832.
- Döbler, J.; Pritzsche, M.; Sauer, J. *J. Am. Chem. Soc.* **2005**, *127*, 10861.
- Hart, G. *Am. Mineral.* **1927**, *12*, 383.
- Chuang, I. S.; Maciel, G. E. *J. Phys. Chem. B* **1997**, *101*, 3052.
- Uchino, T.; Tokuda, Y.; Yoko, T. *Phys. Rev. B* **1998**, *58*, 5322.
- Redfern, P. C.; Zapol, P.; Sternberg, M.; Adiga, S. P.; Zygumunt, S. A.; Curtiss, L. A. *J. Phys. Chem. B* **2006**, *110*, 8363.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
- Jaguar*, Version 6.5; Schrödinger, LLC: New York, 2005.
- Scott, A. P.; Random, L. *J. Phys. Chem.* **1996**, *100*, 16502.
- Peters, B.; Heyden, A.; Bell, A. T.; Chakraborty, A. *J. Chem. Phys.* **2004**, *120*, 7877.
- Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.
- Peng, C.; Schlegel, H. B. *Isr. J. Chem.* **1993**, *33*, 449.

- (23) Noodleman, L. J. *J. Chem. Phys.* **1981**, *74*, 5737.
- (24) Caballo, R.; Castell, O.; Illas, F.; Moreira, I. de P. R.; Malrieu, J. P. *J. Phys. Chem. A* **1997**, *101*, 7860.
- (25) Ochterski, J. W. *Thermochemistry in Gaussian*; Gaussian, Inc.: Pittsburgh, PA, 2000.
- (26) McQuarrie, D. A. *Statistical Mechanics*; University Science Books, Sausalito, CA, 2000.
- (27) Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford University Press: New York, 1987.
- (28) Atkins, P.; dePaula, J. *Physical Chemistry*, 7th ed.; W.H. Freeman & Co.: New York, 2002.
- (29) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications, Inc.: New York, 1986.
- (30) van Lingen, J. N. J.; Gijzeman, O. L. J.; Weckhuysen, B. M.; van Lenthe, J. H. *J. Catal.* **2006**, *239*, 34.
- (31) Phillips, J. C. *Phys. Rev. B* **1986**, *33*, 4443.
- (32) Phillips, J. C. *Phys. Rev. B* **1987**, *35*, 6409.
- (33) Smithson, H.; Marianetti, C. A.; Morgan, D.; Van der Ven, A.; Predith, A.; Cedar, G. *Phys. Rev. B* **2002**, *66*, 144107.
- (34) Wong, G. S.; Concepcion, M. R.; Vohs, J. M. *J. Phys. Chem. B* **2002**, *106*, 6451.
- (35) Campbell, N. J.; Dengel, A. C.; Griffith, W. P. *Polyhedron* **1989**, *8*, 1379.
- (36) Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1987**, 991.
- (37) Maiti, S. W.; Abdul, Malik, K. M.; Bhattacharyya, R. *Inorg. Chem. Commun.* **2004**, *7*, 823.
- (38) Otsuka, K.; Wang, Y. *Appl. Catal. A* **2001**, *222*, 145.
- (39) Skuja, L.; Güttler, B. *Phys. Rev. Lett.* **1996**, *77*, 2093. Orellana, W.; da Silva, A. J. R.; Fazzio, A. *Phys. Rev. Lett.* **2001**, *87*, 155901. Bongiorno, A.; Pasquarello, A. *Phys. Rev. Lett.* **2002**, *88*, 125901. Hoshino, T.; Hata, M.; Neya, S.; Nishioka, Y.; Watanabe, T.; Tatsumura, K.; Ohdomari, I. *Jpn. J. Appl. Phys., Part 1* **2003**, *42*, 6535. Tatsumura, K.; Shimura, T.; Mishima, E.; Kawamura, K.; Yamasaki, D.; Yamamoto, H.; Watanabe, T.; Umeno, M.; Ohdomari, I. *Phys. Rev. B* **2005**, *72*, 045205.
- (40) Hamann, D. R. *Phys. Rev. Lett.* **1998**, *81*, 3447. Ng, K. O.; Vanderbilt, D. *Phys. Rev. B* **1999**, *59*, 10132. Hoshino, T.; Hata, M.; Nishioka, Y.; Watanabe, T.; Tatsumura, K.; Ohdamari, I. *Jpn. J. Appl. Phys., Part 1* **2003**, *42*, 3560.
- (41) Ohler, N.; Bell, A. T. *J. Phys. Chem. B* **2005**, *109*, 23419.
- (42) Bronckema, J. L.; Bell, A. T. Department of Chemical Engineering, University of California, Berkeley, CA, unpublished results.
- (43) Masel, R. I. *Chemical Kinetics & Catalysis*; Wiley-Interscience: New York, 2001.