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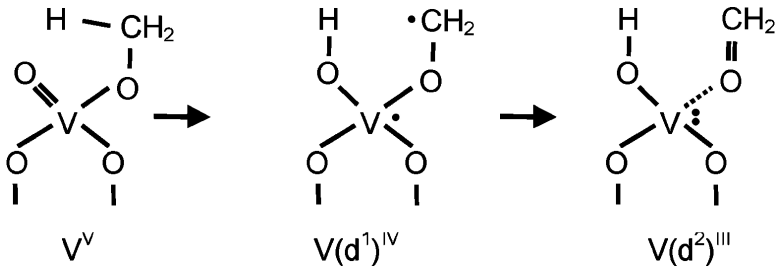

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Oxidation of Methanol to Formaldehyde on Supported Vanadium Oxide Catalysts Compared to Gas Phase Molecules

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Abstract: The oxidation of methanol to formaldehyde on silica supported vanadium oxide is studied by density functional theory. For isolated vanadium oxide species silsesquioxane-type models are adopted. The first step is dissociative adsorption of methanol yielding $CH_3O(O{=})V(O{-})_2$ surface complexes. This makes the $O{=}V(OCH_3)_3$ molecule a suited model system. The rate-limiting oxidation step involves hydrogen transfer from the methoxy group to the vanadyl oxygen atom. The transition state is biradicaloid and needs to be treated by the broken-symmetry approach. The activation energies for $O{=}V(OCH_3)_3$ and the silsesquioxane surface model are 147 and 154 kJ/mol. In addition, the $(O{=}V(OCH_3)_3)_2$ dimer (a model for polymeric vanadium oxide species) and the $O{=}V(OCH_3)_3^{\bullet+}$ radical cation are studied. For the latter the barrier is only 80 kJ/mol, indicating a strong effect of the charge on the energy profile of the reaction and questioning the significance of gas-phase cluster studies for understanding the activity of supported oxide catalysts.

1. Introduction

Supported transition metal oxides are important catalysts, and much effort is being spent to analyze their complex structure and to understand their activity and selectivity. Real catalysts are very complex systems,[1] and the size, structure, and distribution of the active transition metal oxide species are difficult to determine. Therefore, model catalysts such as vanadia clusters on crystalline Al_2O_3 and SiO_2 films[2−4] are prepared in UHV and characterized by surface science techniques. It is also claimed that transition metal oxide clusters in the gas phase are suitable models for catalytically active oxide species on supports.[5,6] However, gas phase experiments are almost exclusively made on ionized clusters[5−7] which can be stored in ion traps and investigated by mass spectroscopic techniques. It is an open question how relevant the reactivities of charged species are for the neutral particles present on the surface of real supported catalysts.

In this contribution we study the oxidation of methanol to formaldehyde for vanadium oxide supported on silica by density functional theory and compare it with analogue reactions of gas phase species. The advantage of the theoretical approach is that comparison between neutral and charged systems can be easily made, while the reactivity of neutral gas phase clusters is not easily accessible by experimental techniques. The reaction chosen can be seen as a prototype reaction for the oxidative dehydrogenation of organic molecules. It follows a Mars−van Krevelen mechanism,[8] which assumes two independent steps. In the first step H_2 is formally abstracted from the reactant, forming water with a surface oxygen atom and reducing the transition metal center.

$$CH_3OH + [V^V] = O_{surface} \rightarrow CH_2O + H_2O + [V^{III}]_{surface} \tag{1}$$

The nature of the hydrogen accepting oxygen atom is still a subject of discussion.[9,10] In the second step, which we do not study here, the active site is reoxidized by molecular oxygen.

$$[V^{III}]_{surface} + {}^1/_2O_2 \rightarrow [V]^V = O_{surface} \tag{2}$$

Different types of vanadium oxide species may be present on the silica support ranging from monomeric (isolated) to polymeric.[1,11] This study deals with isolated vanadium oxide sites only. Since methanol is highly polar and also protic, dissociative adsorption yielding a surface methoxy group **1** (see Scheme 1) is a very likely first reaction step. This assumption is supported by vibrational spectroscopy.[12,13]

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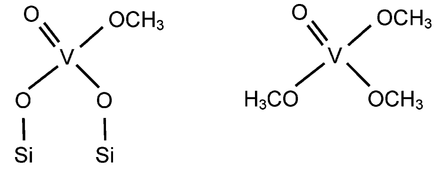
Scheme 1



1 **2**

The surface methoxy group **1** resembles the $O{=}V(OCH_3)_3$ molecule **2**. One of its three methoxy groups is the analogue of the surface methoxy group, the other two replace the V−O−Si anchors of vanadium oxide species on the silica surface. The intramolecular oxidation of the methoxy group to formaldehyde in $O{=}V(OCH_3)_3$ is therefore a gas-phase model for the corresponding surface reaction. For the $O{=}V(OCH_3)_3^{\bullet+}$ radical cation, formation of formaldehyde has indeed been observed by mass spectroscopy.[7] Using computational techniques, we can study this reaction for both the radical cation and the neutral molecule. We will see that the reactivity of the neutral $O{=}V(OCH_3)_3$ molecule is very close to that of the surface species, while the radical cation is much more reactive.

Comparison will be also made with the dimer of the $O{=}V(OCH_3)_3$ molecule, in which two of the methoxy groups bridge the two vanadium atoms (Figure 1). Such dimers are present in the solid phase of $O{=}V(OCH_3)_3$.[14,15] Each vanadium atom has also two singly coordinating methoxy ligands, so that the same type of reaction as that for the monomer seems possible. The dimer might also be a model for aggregated vanadium oxide species on the surface of a supported catalyst.

Figure 1 shows the different systems for which formaldehyde formation is studied. The $O{=}V(OCH_3)_3$ molecule, its radical cation, and its dimer in the gas phase will be compared with methanol chemisorbed on an isolated vanadium oxide site. To make calculations for isolated vanadium oxide sites on a silica support feasible, we need a surface model. For the silica surface, polyhedral oligomeric silsesquioxanes (POSS) are convenient finite size models.[16] The cubic POSS, $H_8Si_8O_{12}$ mimics the electronic structure of silica well. Due to the fused $(Si{-}O)_4$ rings it has a stable structure, but it is also sufficiently flexible to realistically simulate structure relaxations at reaction sites. For example, the $HO{-}Si_8O_{12}H_7$ model (OH group at one corner) proved to be a very good model for surface silanol groups.[17−20] To model isolated vanadia species on silica, we replace one Si−H moiety of $Si_8O_{12}H_8$ by a V=O group. The $O{=}VSi_7O_{12}R_7$ molecule with R = cyclohexyl instead of R=H at the silicon atoms has been prepared and characterized by Feher et al.[21] It is catalytically active for the polymerization of alkenes.[22]

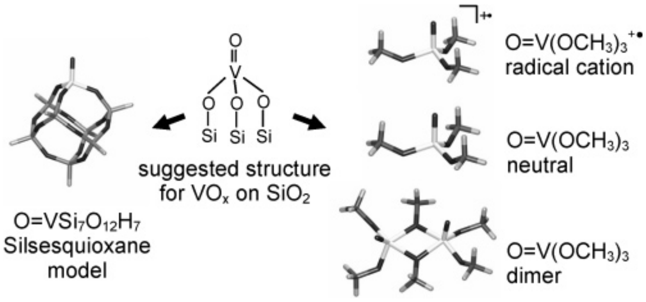


Figure 1. Overview over different model systems.

The oxidative dehydrogenation of methanol was previously studied[23] using a different cluster model of vanadia on silica support, $O{=}V[OSi(OH)_3]_3$. In their model all Si atom positions are fixed so that the structure relaxations are very limited. Moreover, the closed shell calculations made are of limited accuracy for the transition structures as we will show below.

2. Computational Details

DFT calculations were performed with the TURBOMOLE 5.6[24,25] software and employed the TZVP basis of Ahlrichs et al.[26] for all atoms. For the determination of minimum structures, initially the functional BP86[27,28] was used in conjunction with the resolution of identity (RI) method;[29,30] this was followed by reoptimization with the B3LYP[31,32] hybrid functional. This procedure has the advantage that the BP86 calculations are fast due to the RI method. All stationary points on the energy hypersurface were characterized by calculations of vibrational frequencies based on analytical second derivatives of the energy with respect to the nuclear coordinates.[33,34]

For comparison with experimental vibrational spectra a uniform scaling factor was applied to frequencies for surface methoxy species to account for anharmonicities and systematic errors in the calculated force constants. A factor of 0.968 87 was derived for methanol by a least-squares fit of the calculated frequencies to experimental values,[35,36] omitting the torsional mode of the O−H. The V=O stretching frequency was scaled separately with a factor of 0.9433, derived from the calculated and the experimental frequency.[13]

The initial search for the transition structure was made for the $O{=}V(OCH_3)_3$ molecule by the quadratic synchronous transit method (QST)[37,38] as implemented in the GAUSSIAN98 software.[39] The relaxed structures of the $O{=}V(OCH_3)_3$ reactant and the $HOV(OCH_2)(OCH_3)_2$ product (singlet closed shell state) were used as a starting point. The stationary point thus found was characterized by calculation of second derivatives to be a saddle-point of first order. The structure of the stationary point was then refined by trust radius image minimization using an analytical Hessian (statpt module of TURBOMOLE 5.6).[40] The stationary points of the other systems were determined by transferring the local structure of the known transition state to the appropriate model, calculating second derivatives and using trust radius image minimization.

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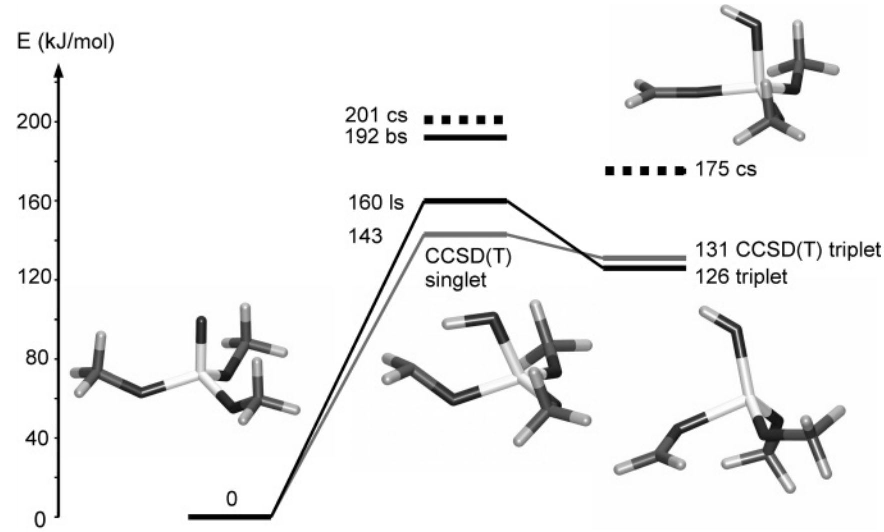


Figure 2. Formaldehyde formation from $O{=}V(OCH_3)_3$. cs: closed shell. bs: broken symmetry. ls: low spin.

For the transition structures, unrestricted Kohn−Sham (UKS) calculations were made within the broken-symmetry approach[41] as an approximation for multireference treatment. In addition a high spin (hs, triplet) calculation is made, and the projected low spin (ls) energy is calculated with the formula:[42]

$$E(\mathrm{ls}) = E(\mathrm{t}) + 2*(E(\mathrm{bs}) - E(\mathrm{t}))/(2 - \langle S^2\rangle) \qquad (1)$$

E(ls) denotes the projected low spin energy, E(bs), the energy of the "broken-symmetry" calculation, and E(t), the energy of the triplet calculation. In addition to single-point broken-symmetry calculations at the closed shell singlet transition structure, the structures of the stationary points were recalculated for the broken-symmetry solution.

The $O{=}V(OCH_3)_3$ molecule itself was treated within the point group C_{3v}. All further calculations on structures derived from this compound did not use any symmetry constrains. The structure of the silsesquioxane model $Si_8O_{12}H_8$ was optimized within the point group O_h. The model for the $O{=}V(O{-})_3$ surface site was obtained by replacing one Si−H moiety of $Si_8O_{12}H_8$ by V═O yielding a C_{3v} structure. All calculations for the following reaction steps were performed without any symmetry constrains.

Coupled cluster calculations with single and double substitutions and pertubative treatment of triple substitutions, CCSD(T),[43,44] were performed for the $O{=}V(OCH_3)_3$ molecule, the transition state and the primary product $HOV(OCH_2)(OCH_3)_2$. These calculations were done as single-point energy calculations at the closed shell B3LYP structures. The same basis set as that for the DFT calculations (TZVP) was used, and only valence electrons were correlated (V: 3d and 4s). The calculations were performed with the MOLPRO2002.3 software.[43,44]

3. Results

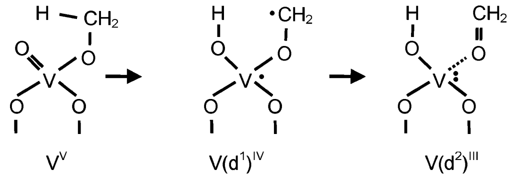
$O{=}V(OCH_3)_3$ Molecule: DFT. For the $O{=}V(OCH_3)_3$ molecule different conformations are possible as the methoxy groups can be oriented E or Z with respect to the V═O bond and can rotate around the C−O bond. The most stable conformation is the one shown in Figure 2, and some structural parameters are given in Table 1. For all subsequent calculations this conformation was used.

Table 1. Bond Distances (pm) and Angles (degree) for Formaldehyde Formation from $OV(OCH_3)_3$ and $OV(OCH_3)_3^{+\bullet}$[a]

	$OV(OCH_3)_3$			$OV(OCH_3)_3^{+\bullet}$		
	reactant singlet	TS bs	product triplet	reactant duplet	TS duplet	product duplet
$r(V{=}O)$	158.6	172.2	183.4	156.7	163.7	177.8
$r(V{-}O_r)$	177.4	179.7	204.0	188.3	191.3	200.2
$r(V{-}O)$	177.4	177.0	181.4	175.4	171.6	171.8
$r(V{-}O)$	177.4	177.0	185.4	175.4	171.2	172.2
$r(C_r{-}O_r)$	141.3	135.7	122.9	138.5	132.2	122.4
$r(C_r{-}H_r)$	109.5	150.5		109.0	131.7	
$r(O_{vanadyl}{-}H_r)$		115.7	96.1		145.4	96.8
$\angle(O{=}V{-}O_r)$	108.3	85.6	102.4	108.5	89.6	96.7
$\angle(O{=}V{-}O)$	108.3	111.1	118.3	110.9	114.7	108.8
$\angle(V{-}O_r{-}C_r)$	135.3	123.1	127.7	135.3	115.9	146.2
$\angle(O_r{-}C_r{-}H_r)$	111.3	89.2		113.7	97.1	

[a] The subscript r denotes atoms that take part in the reaction.

Scheme 2



Formaldehyde formation is achieved by hydrogen transfer from a CH_3 group to the vanadyl oxygen atom, and the primary product is an $HOV(OCH_3)_2$ molecule with an additional formaldehyde ligand at the vanadium atom, $HOV(OCH_2)(OCH_3)_2$. The oxidation state of vanadium has changed from V^V (d^0) to V^{III} (d^2) (see Scheme 2), and the ground state is expected to be triplet with the two unpaired d electrons at the vanadium atom.

The energy of the triplet product is 126 kJ/mol above the reactant. The changes in the structure with respect to the reactant are quite large. The formaldehyde is only weakly bonded to the vanadium atom with a V−O distance of 204.0 pm. The C═O distance (122.9 pm) is only slightly larger than that in the unperturbed aldehyde (120.1 pm). The two singly occupied molecular orbitals are mainly d orbitals at the vanadium atom.

When the $HOV(OCH_2)(OCH_3)_2$ complex is calculated as a closed shell singlet, the reaction energy increases by 49 kJ/mol to 175 kJ/mol. The structures of the closed shell and triplet

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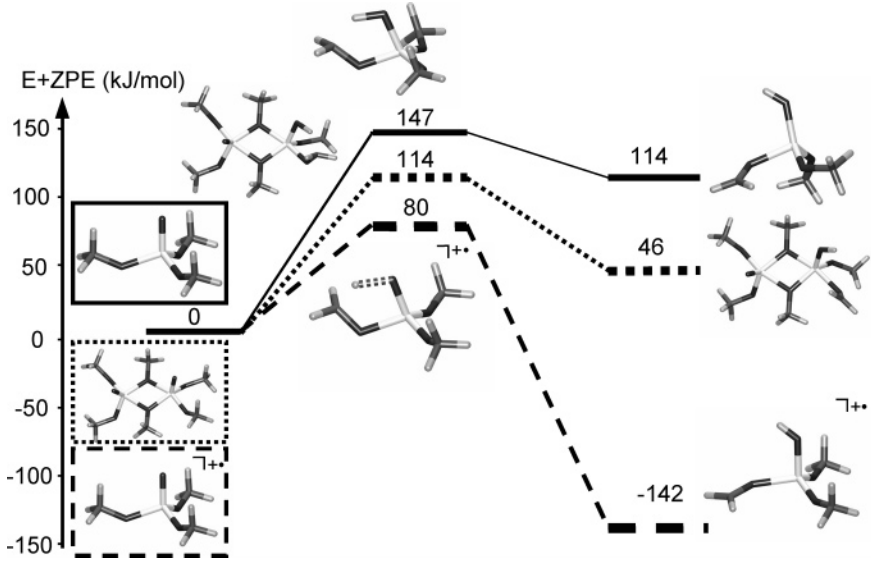

Figure 3. Comparison of formaldehyde formation for different O═V(OCH$_3$)$_3$ species.

products are also different. The V─O distance (179.6 pm) is in the same range as the V─O distances of the methoxy groups. The C═O bond length in the aldehyde is elongated to 126.5 pm. This structure is induced by a strong electronic interaction between the formaldehyde and the vanadium atom. The HOMO of the singlet product is a combination of the occupied d orbital of vanadium and the π^* orbital of the aldehyde.

The transition structure (TS) of the reaction has a strained five-membered ring with V−O−H−C−O as the key element. The hydrogen atom being transferred has increased its distance to the carbon from 109.5 to 150.5 pm and is only 115.7 pm away from the vanadyl oxygen atom (see Table 1). The TS has a biradicaloid electronic structure which can be either a triplet or a singlet open shell state. Unrestricted Kohn−Sham calculations at the structure of the singlet closed shell TS yield an energy barrier of 189 kJ/mol for the broken-symmetry method, while the triplet calculation yielded an energy of 255 kJ/mol above the reactant state. After projection with eq 1 and $\langle S^2 \rangle = 0.50$, an energy barrier of 168 kJ/mol is obtained for the low spin state. This is significantly (33 kJ/mol) lower than the closed shell barrier. An optimization on the broken-symmetry PES changes the structure only marginally, and the projected low spin energy ($\langle S^2 \rangle = 0.39$) is lowered to 160 kJ/mol above the energy of the reactant. Finally, adding the zero-point vibrational energy, an energy barrier of 147 kJ/mol is reached as the best DFT estimate.

O═V(OCH$_3$)$_3$ Molecule: CCSD(T). For the stationary points on the DFT reaction coordinate (TS, closed shell structure; product, triplet structure) we check the accuracy of the B3LYP calculations by CCSD(T) single-point calculations. The coupled cluster energy barrier, 143 kJ/mol, is 58 kJ/mol lower than the closed shell B3LYP barrier. This confirms that closed shell B3LYP calculations are not applicable. The coupled cluster barrier is even lower than the low spin result of 160 kJ/mol which indicates that B3LYP still overestimates the energy barrier even if the broken-symmetry approach is used. The value of the T1 diagnostics[45] of the coupled cluster calculation for the TS (0.0728) indicates that the Hartree−Fock (HF) wave function is not a good reference and confirms the open shell nature of the TS. More accurate results can only be obtained by a multireference method like MRCI (multireference configuration interaction).

The energy of the primary product in the triplet state was calculated by unrestricted CCSD(T) using a restricted open-shell HF reference wave function. The reaction energy for the formation of formaldehyde is 131 kJ/mol, which is in good agreement with the B3LYP value of 126 kJ/mol.

O═V(OCH$_3$)$_3$$^{+\bullet}$ Radical Cation. The ground state of the cation is a doublet, and its symmetry is reduced to C_s as the three methoxy groups are no longer equivalent. The singly occupied natural orbital consists mainly of a nonbonding p orbital at one of the methoxy groups. Accordingly, for one methoxy group the V─O bond is much longer (188.3 pm) than that for the other two (175.4 pm, see Table 1). The energy barrier for transferring hydrogen from this methoxy group to the vanadyl site is 88 kJ/mol only. The system remains in the doublet state and the primary product is similar to that of the neutral molecule (see Figure 3), but there is only one d electron at vanadium which is in the +IV oxidation state. Since V$^{\mathrm{IV}}$ is more stable than V$^{\mathrm{III}}$ the reaction changes from endothermic (neutral molecules) to exothermic (−146 kJ/mol).

O═V(OCH$_3$)$_3$ Dimer. In the gas phase, dimerization of the O═V(OCH$_3$)$_3$ molecule is slightly endothermic (21.0 kJ/mol including ZPE, 13.3 kJ/mol without ZPE), but nonetheless the dimer is a local minimum on the PES. The O═V(OCH$_3$)$_3$ dimer can undergo the same type of redox reaction as the monomer, as each vanadium atom is connected to a vanadyl oxygen atom and two singly bonded methoxy groups. To find the transition structure for the dimer, a structure similar to the TS of the monomer was constructed for a terminal methoxy group. For this structure the Hessian was calculated using a closed shell approach and the structure was optimized to the stationary point. The closed shell energy barrier is 158 kJ/mol, more than 40 kJ/mol lower than the closed shell energy barrier of the monomer. After reoptimization within the broken-symmetry approach the projected low spin energy barrier becomes 130 kJ/mol. The electronic ground state of the product is a triplet. The vanadium atom at the reaction site is reduced to the

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Table 2. Bond Distances (pm) and Angles (degree) for Formaldehyde Formation from $(OV(OCH_3)_3)_2$[a]

	reactant	TS	product
	singlet	bs	triplet
r(V═O)	158.5	172.5	185.6
r(V─O$_r$)	179.7	184.0	214.0
r(V─O)	179.1	176.1	182.8
r(V─O) bridging	196.9	193.1	195.2
r(C$_r$─O$_r$)	141.0	135.0	122.1
r(C$_r$─H$_r$)	109.5	142.4	
r(O$_{vanadyl}$─H$_r$)		120.0	96.3
∠(O═V─O$_r$)	99.8	84.1	89.7
∠(V─Or─C$_r$)	131.3	120.6	127.7
∠(O$_r$─C$_r$─H$_r$)	110.9	91.4	

[a] The subscript r denotes atoms that take part in the reaction.

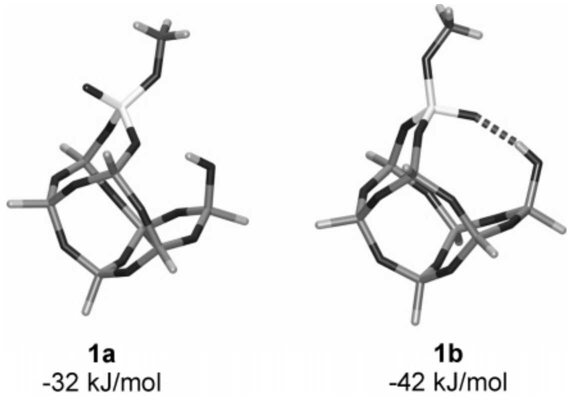

Figure 4. Adsorption energy for different structures of chemisorbed methanol.

oxidation state +III, and the product is a mixed valence state with V^{III} (d^2) and V^V (d^0). The reaction energy for the formaldehyde formation from the dimer is 46 kJ/mol. Thus the reaction is less endothermic for the dimer molecule than for the monomer. The structural parameters of interest are given in Table 2.

Silsesquioxane Surface Model. For this model the first reaction step is the dissociative adsorption of methanol, leading to formation of a silanol group and a methoxy ligand at the vanadium site. Two different arrangements for the methoxy group seem plausible, one in which the methoxy group is still close to the silanol group (**1a**, see Figure 4) and another one in which the positions of the methoxy group and the vanadyl bond are swapped so that the vanadyl group points toward the silanol (**1b**).

The calculated adsorption energies are −32 kJ/mol for **1a** and −42 kJ/mol for **1b**. The arrangement in **1b** is energetically clearly favored, but some rearrangement of the surface species has to occur in order to reach this structure. We expect that the barrier of the rearrangment is still significantly lower than the barrier of the redox step, and structure **1b** is used as the initial structure for further steps of the reaction path (see Figure 5).

To form formaldehyde, a hydrogen atom of the surface methoxy group can be transferred either to the vanadyl-oxygen atom or to the 2-fold coordinated V─O─Si interface oxygen atom. The reaction energies (products in triplet state) with respect to **1b** are 89 and 158 kJ/mol, respectively. Because of this large difference the energy barrier is calculated for H transfer to the vanadyl O only.

The search for the transition structure was first made for the closed shell state. The energy barrier is 202 kJ/mol, which is very close to the result for the $O{=}V(OCH_3)_3$ molecule (201 kJ/mol). At this structure, the broken-symmetry solution yields an energy barrier of 191 kJ/mol, and after projection 170 kJ/mol (eq 1, $\langle S^2 \rangle = 0.496$). A structure optimization on the broken-symmetry PES leads to marginal changes of the structure. The $\langle S^2 \rangle$ value is lowered (0.387) similar to the that of the $O{=}V(OCH_3)_3$ molecule. The best B3LYP result for the energy barrier of the silsesquioxane model is 170 kJ/mol.

The final steps are the desorption of the product and the regeneration of the catalyst. Direct removal of formaldehyde from **2** is energetically very unfavorable with an energy of 175 kJ/mol above **1b**. In the resulting structure vanadium (III) has only three ligands and thus is coordinatively unsaturated. However, the primary product can rearrange into a structure with a coordination of the silanol oxygen atom to vanadium, yielding 5-fold coordinated vanadium. This leads to the forma-

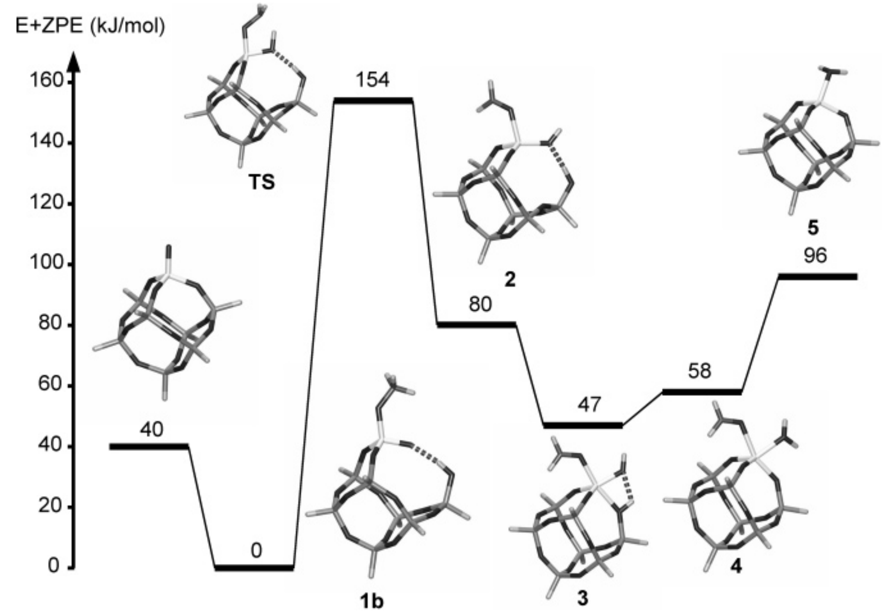

Figure 5. Reaction pathway for methanol oxidation with the silsequioxane model.

Table 3. Relative Energies of the Formaldehyde Formation in kJ/mol (Zero of Energy: Species **1b**)

structure[a]	$O{=}VSi_7O_{12}H_7$ + methanol	**1b**	**TS**	**2**	**3**	**4**	**5**
energy	41.7	0.0	170.0	89.1	53.2	64.0	107.5
energy + ZPE	39.8	0.0	153.9	80.1	47.4	58.1	95.5

[a] See Figure 5.

Table 4. Bond Distances (pm) and Angles (degree) for Methanol Oxidation on Silsesquioxane Model

system	bare	**1b**	**TS**	**2**	**3**	**4**	**5**
spin state[a]	s	s	bs	tr	tr	tr	tr
r(V═O)	157.7	159.4	172.8	184.9	186.1	209.6	211.8
r(V—O)	177.4	177.3	177.1	183.9	187.1	185.3	182.3
r(V—O)	177.4	177.3	177.1	183.9	217.8	190.5	185.6
r(V—O) methoxy		174.9	178.1	204.4	213.0	227.1	
r(Si—O) silanol		163.9	163.5	163.4	168.8	163.0	164.8
r(O—H) silanol			97.4	98.1	97.4		
r(OH···O═V)		189.0	186.7	179.7	199.2	96.9	96.9
r(C—H) methoxy		109.3	148.8				
r(C—O)	143.3	142.0	135.7	122.4	121.7	121.4	120.1
$r(O_{vanadyl}$—H)			117.1	96.3	96.3	96.3	96.8
∠(O═V—O)	110.6	109.3	111.2	120.4	124.9	124.5	129.8
∠(O═V—O) methoxy		107.9	85.6	104.1	91.2	77.7	
∠(V—O—Si)	147.2	146.2	151.9	147.3	150.3	144.2	133.3
∠(V—O—C)		135.5	123.6	127.5	123.9	120.9	
∠(Si—O—H) silanol		118.9	119.8	119.9	119.8		
∠(V—O—H)			105.1	126.4	121.9	129.8 108.9	111.4 108.6

[a] s, singlet (closed shell); tr, triplet; bs, broken symmetry.

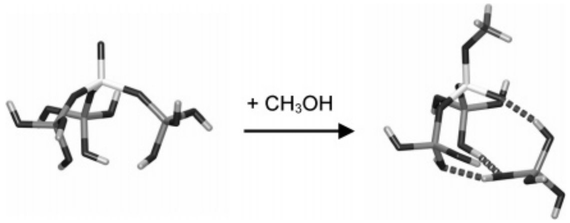

Figure 6. Cluster model of ref 23. Adsorption of methanol leads to the formation of hydrogen bonds between terminating OH groups.

tion of a bridging Si—O(H)—V hydroxyl group and closes the cubelike structure of the silsesquioxane compound (**3**). The additional coordination stabilizes **3** by 36 kJ/mol compared to **2**. The bridging "Brønsted" proton can combine with the neighboring OH group at the vanadium site to yield a water molecule (**4**). This step is slightly endothermic (11 kJ/mol) with respect to **3**. Finally the formaldehyde can desorb, leaving the vanadium atom in a tetrahedral coordination due to the water formation (**5**). This way, the desorption of the aldehyde is endothermic by only 18 kJ/mol with respect to the primary product **2**. Energies for the reaction with and without ZPE are given in Table 3, and structural parameters for the different reaction steps, in Table 4.

4. Discussion

Comparison with Previous Calculations. The oxidation of methanol has been studied before using a $O{=}V[OSi(OH)_3]_3$ model (Figure 6).[23] For silica supported vanadium oxide an adsorption energy of −88 kJ/mol is reported. Using the same model of the surface site we get an adsorption energy of about −90 kJ/mol, while our silsesquioxane model yields −42 kJ/mol. This difference is caused by the structure constraints imposed on the $O{=}V[OSi(OH)_3]_3$ model and by the termination of dangling bonds with OH groups. Upon adsorption of methanol an isolated $Si(OH)_4$ unit is created in the Khaliullin model, which can form additional hydrogen bonds with the OH groups of the adjacent Si sites. This is a consequence of the increased flexibility of the cluster after adsorption. This artificial hydrogen bonding creates an increase of the adsorption energy. We conclude that the adsorption energy of −40 kJ/mol calculated for our model is more realistic.

Table 5. Reaction Energies, ΔE, Energy Barriers, $\Delta E^\ddagger$, and Apparent Barriers, $\Delta E_a^\ddagger$, in kJ/mol (Zero-Point Energy Corrected Values Have Subscript 0)

	$O{=}V(OCH_3)_3$	$O{=}V(OCH_3)_3^+$	$(O{=}V(OCH_3)_3)_2$	$VO_{2.5}/SiO_2$
primary product, ΔE	126.3 (131.1)[a]	−145.7	56.7	89.1
primary product, ΔE_0	114.3	−141.7	45.6	80.1
barrier, $\Delta E^\ddagger$	159.8 (143.3)[a]	87.6	129.8	170.0
barrier, $\Delta E_0^\ddagger$	147.4	80.1	114.4	153.9
apparent barrier, $\Delta E_{app}^\ddagger$				128.3
apparent barrier, $\Delta E_{app,0}^\ddagger$				114.2
T (K)		298		503
calcd, $\Delta H_T^\ddagger$		77.2		116.7
obsd, $\Delta H_T^\ddagger$		52 ± 11[b]		82 ± 10[c]

[a] CCSD(T). [b] Reference 7. [c] Reference 49.

When considering the intrinsic energy barrier, the closed shell result for our model (202 kJ/mol) is very similar to the result given by Khaliullin et al.[23] (199 kJ/mol) and also the transition structures are almost identical. However, the closed shell description is not adequate, and the broken-symmetry approach reduces the barrier by 30 kJ/mol. Since the difference for the adsorption energy and the intrinsic barrier have opposite signs, the apparent barriers 128 kJ/mol (this work) and 111 kJ/mol (ref 23) differ by 17 kJ/mol only.

Accuracy of the Broken-Symmetry Approach. The limited size of the $O{=}V(OCH_3)_3$ molecule makes calculations by wave function based methods such as coupled cluster theory feasible, and this permits an assessment of the accuracy of DFT calculations within the broken-symmetry approach. For the reaction energy the difference between coupled cluster and B3LYP is within 5 kJ/mol only (Table 5), while the B3LYP barrier is too high by 16 kJ/mol if the broken-symmetry approach is used (the error is much larger for a closed shell calculation). Note that these errors are well within the general accuracy limits of B3LYP for reaction energies and energy barriers.[46]

Comparison of Surface Models with Gas-Phase Models. The transition structures (Tables 1 and 4) and the energy barriers for the oxidation step (Table 5) are very similar for the silsesquioxane surface model and for the $O{=}V(OCH_3)_3$ gas phase model. In both cases the reaction starts from a closed shell singlet state, passes through a biradicaloid transition structure (open shell singlet state), and yields a triplet product. Spin-crossing is not expected to be a problem because in the biradicaloid transition region singlet and triplet potential energy surfaces are largely parallel with a small energy splitting.

This shows that the $O{=}V(OCH_3)_3$ molecule is indeed a suited model for studying the rate-limiting step, while the remaining steps of the reaction, i.e., chemisorption of methanol and desorption of formaldehyde, require a surface model.

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(46) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.

Table 6. Vibrational Frequencies of Surface Methoxy Species, Free Methanol, and the Surface Site before Adsorption

mode	noninteracting system expt[a]	noninteracting system calcd	chemisorbed methanol expt[a]	chemisorbed methanol **1a**	chemisorbed methanol **1b**
C—H stretch out-of-phase	2999	3017	2976 (sh)	3004	3002
	2970	2938		2998	2999
C—H stretch in-phase	2844	2895	2932	2924	2925
H—C—H deformation out-of-phase	1478	1459	1448	1442	1443
	1465	1445		1438	1440
H—C—H deformation in-phase	1454	1441	1436	1427	1429
C—O stretch	1033	1004	1068	1067	1061
V═O stretch	1035	1035	1027	1021	1001

[a] See refs 12, 13.

The reaction of the O═V(OCH$_3$)$_3$ dimer leads to a mixed-valence product with vanadium atoms in two different oxidation states, V^{+V} and V^{+III}. The energy profile is again similar to that of the monomer, but the reaction energy and the energy barrier are smaller. This difference is most probably due to the higher coordination number of the vanadium atoms in the dimer. The additional coordination by electronegative oxygen atoms can lessen the energy loss upon conversion of the vanadyl (V═O) bond into a V—O single bond. These results indicate that also on supports aggregated vanadium oxide species with square pyramidal coordination might be more reactive in oxidation reactions than monomeric sites.

Comparison of Neutral Gas-Phase Models with Radical Cations. The mechanism of the oxidation of methoxy groups is similar for neutral O═V(OCH$_3$)$_3$ molecules and for O═V(OCH$_3$)$_3^{\bullet+}$ radical cations, but the energy barrier is reduced by almost 70 kJ/mol and the thermicity changes from endothermic to exothermic. The reasons are the weaker vanadium−methoxy bond in the educt and the more stable product. In the radical cation product vanadium is in the V(d^1)^{IV} oxidation state, while in the neutral product it is in the V(d^2)^{III} oxidation state. The dramatic reactivity difference between the neutral molecule and its radical cation clearly demonstrates that results obtained for charged molecules or clusters in the gas phase may be very different from the results for neutral clusters in the gas phase or on surfaces. Similar conclusions have been reached for vanadyl bond dissociation energies of vanadium oxide cluster cations and cluster anions compared to neutral clusters.[47]

The energy barrier calculated for the radical cation can be compared with results of a photoionization experiment.[7] The observed appearance energies for CH$_2$O loss from O═V(OCH$_3$)$_3^{\bullet+}$ suggest a barrier of 52 ± 10 kJ/mol.[7] This shows that the barriers predicted by B3LYP (80 kJ/mol at 0 K and 77 kJ/mol at 298 K) are too high in comparison to the experiment. This is consistent with the conclusion reached from the coupled cluster calculations for the neutral molecule.

Comparison with Experimental Results for VO$_x$/SiO$_2$ Catalysts. First, we compare our results for the silsesquioxane model with the vibrational spectra of chemisorbed methanol.[12,13] The calculated and experimental vibrational frequencies are shown in Table 6. The calculated results for the surface methoxy group are in good agreement with the experiment and reproduce qualitatively the observed shifts on adsorption. This supports the adsorption structures, but it is not possible to distinguish between the two different arrangements of the surface methoxy groups (**1a**, **1b**).

Table 7. Adsorption Constant (atm^{-1}), Oxidation Rate Constant (s^{-1}), and Apparent Rate Constant (atm^{-1} s^{-1}), Their Pre-Exponential Factors and the Corresponding Energies (kJ/mol)

step	adsorption	adsorption	oxidation	apparent	apparent
ΔE_0	−56.3[a]	−39.8	153.9	114.1	79.5 ± 10[b]
pre-exponential	3.80 (−07)	3.80 (−07)	2.66 (+12)	1.01 (+06)	1.01 (+06)
constant	0.27	5.16 (−03)	2.75 (−04)	1.42 (−06)	5.62 (−03)

[a] Calcd from observed coverage at 100 °C (ref 12) with B3LYP pre-exponential for this temperature (2.72 × 10^{-7} atm^{-1}). [b] Calcd from observed activation enthalpy (82 ± 10 kJ/mol, ref 49) with B3LYP temperature dependence.

When comparison is made with experimental kinetic data[48] one has to take into account that the rate-determining oxidation step is preceded by an adsorption equilibrium. In the low pressure (Henry) region, the adsorbed amount (site occupation) depends linearly on the methanol pressure and the reaction rate can be formulated in terms of the apparent barrier:

$$\Delta E^{\ddagger}_{0,\mathrm{app}} = \Delta E_0^{\ \ddagger} + \Delta E_{0,\mathrm{ads}}$$

where $\Delta E_0^{\ddagger}$ and $\Delta E_{0,\mathrm{ads}}$ are the intrinsic energy barrier and the energy of adsorption, respectively, at 0 K, i.e., including zero-point vibrational energy contributions.

The apparent rate is then

$$k_{\mathrm{app}} = \frac{k_{\mathrm{B}}T}{h} \cdot \frac{q^{\ddagger}}{q_{\mathrm{methanol}} \cdot q_{\mathrm{solid}}} \cdot e \cdot e^{-\Delta E^{\ddagger}_{0,\mathrm{app}}/RT} \qquad (3)$$

In this equation q is the partition function of the activated complex (‡), the reactant in the gas phase (methanol) and the solid catalyst (solid), respectively. For the solids (q_{solid} and $q^{\ddagger}$), only the vibrational contributions are considered, while, for methanol in the gas phase, also the rotational and translational degrees of freedom are included. The additional e term accounts for the volume work on adsorption of methanol, $pV = RT$ (ideal gas).

The equilibrium constant for the adsorption step is

$$K = \frac{q_{\mathrm{ads}}}{q_{\mathrm{methanol}} \cdot q_{\mathrm{solid}}} \cdot e \cdot e^{-\Delta E_{0,\mathrm{ads}}/RT} \qquad (3)$$

Unfortunately, for silica supported vanadium oxide, no independent measurement of the heat of adsorption of methanol is available and only apparent barriers and overall rates can be compared. With the adsorption energy from Table 3 we obtain $\Delta E^{\ddagger}_{0,\mathrm{app}} = 114$ kJ/mol and for the apparent activation enthalpy at the reaction temperature (503 K) $\Delta H^{\ddagger}_{503} = 117$ kJ/mol. The latter value is larger than the experimental value[49] of $\Delta H^{\ddagger}_{503} = 82 \pm 10$ kJ/mol (see Table 7), which is not unexpected because we know already from the CCSD(T) calculation of O═V(OCH$_3$)$_3$ and from gas-phase experiments on the O═V(OCH$_3$)$_3^{\bullet+}$ radical cation that our broken-symmetry B3LYP barrier is still overestimated.

Correspondingly eq 3 yields $k_{\mathrm{app}} = 1.42 \times 10^{-6}$ atm^{-1} s^{-1} at 503 K, far lower than the experimental value of 0.027−0.070 atm^{-1} s^{-1} (ref 48, TOF from Table 3 divided by methanol partial pressure).

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(47) Sauer, J.; Döbler, J. *Dalton Trans.* **2004**, *19*, 3116.

(48) Burcham, L. J.; Badlani, M.; Wachs, I. E. *J. Catal.* **2001**, *203*, 104.

(49) Deo, G.; Wachs, I. E. *J. Catal.* **1994**, *146*, 323.

We expect that our calculated pre-exponentials are more accurate than the barriers. On the other hand, the rate constants (and TOF) derived from experiment refer to the total vanadium content of the catalyst, and the active fraction is unknown. Therefore, we combine the observed apparent barrier[49] ($\Delta E_{0,\mathrm{app}} = 79.5 \pm 10$ kJ/mol, Table 7) with the calculated pre-exponential and obtain an apparent rate constant of 0.0056 $\mathrm{atm}^{-1}\ \mathrm{s}^{-1}$ with an uncertainty range between 0.061 and 0.00051 $\mathrm{atm}^{-1}\ \mathrm{s}^{-1}$. The observed rates are at the upper edge of this range, so indeed the calculated pre-exponential factor is reasonable.

Burcham et al.[12] have made an attempt to quantify the amount of adsorbed methanol by measuring the intensity of the IR bands in the 2830−2850 cm^{-1} range where $V-OCH_3$ species absorb. For V_2O_5/SiO_2 catalysts there is no methanol adsorbed on Lewis sites which would also absorb in this range. For 373 K and 10 Torr (= 0.013 16 atm) equilibrium pressure, a surface coverage of 0.27 per V atom of the catalyst is reported. This implies an adsorption constant of 20.52 atm^{-1}. Using our calculated pre-exponential for 373 K we obtain an adsorption energy $\Delta E_{0,\mathrm{ads}} = -56.3$ kJ/mol. The adsorption energy we calculate (B3LYP) is lower, −39.8 kJ/mol. However, B3LYP adsorption energies may be too low because dispersion contributions are not properly accounted for and a value around −55 kJ/mol is not unlikely. We can use the estimate of −56.3 kJ/mol (0 K) for the energy of adsorption and calculate the coverage at reaction conditions,[49] $T = 503$ K and $p_{\mathrm{methanol}} = 0.06$ atm (6% methanol in the feed gas). We obtain a surface coverage of 0.012 which is 1 order of magnitude lower than the coverage reported in ref 48.

With the above estimate of $\Delta H_{503,\mathrm{ads}} = -50$ kJ/mol for the heat of adsorption ($\Delta E_{0,\mathrm{ads}} = -56.3$ kJ/mol) and the experimental apparent barrier[49] of the 82 ± 10 kJ/mol we obtain 137 ± 10 kJ/mol for the intrinsic barrier. The best theoretical estimate, $\Delta H^{\ddagger}_{503} = 140$ kJ/mol, falls into this range. The latter we get from the broken-symmetry B3LYP calculations (153.9) and the CCSD(T) decrement (16.5 kJ/mol) yielding $\Delta E_0^{\ddagger} = 137.4$ kJ/mol.

General. The results of the present B3LYP calculations are consistent with the available experimental information for vanadium oxide supported on silica.[48,49] The mechanism discussed here with an adsorption equilibrium preceding the rate-limiting step is also proposed for methanol oxidation on vanadium oxide supported on ceria.[50] The intrinsic barrier of 147 kJ/mol (estimated from temperature programmed desorption of formaldehyde)[50] is similar to the result obtained here for the silica support. This is expected because the adsorption complex **1** is similar on Vanadia/Ceria, and even for the $O{=}V(OCH_3)_3$ molecule the same barrier is calculated. However, the heat of adsorption is significantly larger, −80 kJ/mol, and this makes the apparent barrier as low as 67 kJ/mol. These are strong hints that the support effect on the activity of vanadia catalysts in methanol oxidation is in the initial adsorption of methanol, not in the rate-determining step.

The present results also contradict suggestions that the terminal vanadyl groups are not involved in methanol oxidation.[1] The arguments used in ref 1 are the following: (1) The TOF varies drastically with the support, while the V=O frequencies show little variation. (2) During methanol oxidation $V{=}^{18}O$ bonds are gradually transformed into $V{=}^{16}O$ bonds, but with an exchange rate much slower than the effective reaction rate. These observations may be interpreted differently. Argument (1) is not compelling because the V=O frequency is an educt property and, if at all, is only expected to be a reactivity predictor if we had an early transition state. In our particular case it is much simpler. If the differences between different supports are due to the adsorption step (as we have reason to believe), the V=O bond is not expected to indicate these differences because adsorption is onto the V−O−metal bond. (2) According to our mechanism the labeled vanadyl oxygen atom ends up in the water produced. Restoring the vanadyl bond by reoxidation of the catalyst is decoupled from the oxidation of the substrate (Mars−van Krevelen mechanism) and may be much slower.

5. Conclusions

The oxidation of methanol on silica supported vanadium oxide involves two steps. The first step is dissociative adsorption of methanol on a V−O−Si interface bond between the vanadium oxide species and the support. This way a V−methoxy group and a silanol group are formed. The rate-limiting step is the transfer of a methyl H atom to the vanadyl oxygen atom concurrent with the splitting of the $V-O_{\mathrm{methoxy}}$ bond (Scheme 2) which leaves two electrons in d states at the vanadium site. The transition state has a biradicaloid electronic structure, and DFT calculations require the broken-symmetry approach. For this step, the transition structures and the energy barriers are very similar for the silsesquioxane surface model and the gas-phase $O{=}V(OCH_3)_3$ molecule. This indicates that the $O{=}V(OCH_3)_3$ molecule is a suited gas-phase model for the rate-limiting step and also implies that the barrier for the oxidation will not vary with the support if the same active site is present. Rather, the activity differences observed between different supports may be due to different heats of adsorption.

For the $O{=}V(OCH_3)_3^{\bullet+}$ radical cation the reaction mechanism is the same as that for the neutral molecule, but the energy profile changes substantially. The thermicity changes from endothermic for the neutral molecule to exothermic for the radical cation, and the energy barrier is lowered by as much as 70 kJ/mol. Apart from a systematic overestimation of the energy barriers, the present results are consistent with the experimental information available for vanadium oxide supported on silica[49] and for the $O{=}V(OCH_3)_3^{\bullet+}$ radical cation in the gas phase.[7] They question the significance of gas-phase reactivity studies on vanadium oxide cluster (radical) ions[5] for understanding supported vanadium oxide catalysts.

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Note Added in Proof. A recent study (Feng, T.; Vohs, J. M. *J. Phys. Chem. B.* **2005**, *109*, 2120−2127) of the oxidative dehydrogenation of ethanol on V_2O_5/SiO_2 infers an intrinsic barrier of 132 kJ/mol from the TPD peak of CH_3CHO at 475 K, assuming a pre-exponential of $10^{13}\ \mathrm{s}^{-1}$. This result supports our best theoretical estimate for the intrinsic barrier $\Delta E^{\neq}_0 = 137 \pm 10$ kJ/mol (Section "Comparison with Experimental Results") and the assumed pre-exponential is close to the one calculated in this work ($2.66 \times 10^{12}\ \mathrm{s}^{-1}$, Table 7).

Supporting Information Available: The complete author list of refs 4 and 39 can be found in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

JA051720E

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(50) Feng, T.; Vohs, J. M. *J. Catal.* **2004**, *221*, 619.