

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

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Introduction

Isolated vanadate sites supported on silica are known to be active for the selective oxidation of methanol to formaldehyde [1-4]. Theoretical studies of the elementary processes involved in the oxidation of methanol to formaldehyde over isolated vanadate species supported on silica [5,6] have shown that the adsorption of methanol occurs by addition across V-O-Si bonds leading to the formation of V-OCH₃/SiOH pairs. These studies suggest that the intramolecular transfer of a hydrogen atom from the V-OCH₃ groups to the V=O bond on the same vanadate species is the rate-limiting step in the formation of formaldehyde. While the apparent activation energies calculated in these studies are in reasonable agreement with those determined experimentally, the reported turnover frequencies are three to four orders of magnitude smaller than those observed. In addition, these studies have not addressed the issue of how the reduced vanadate site is reoxidized once formaldehyde is formed, nor have they shown whether or not the rate at which this process occurs is kinetically significant. The present study was undertaken to address these issues, and to develop a complete microkinetic analysis of the reaction kinetics from first principles.

Theoretical Methods

Isolated vanadate species supported on silica were modeled by replacing a HO-Si(O-) group in silsesquioxane, Si₈O₁₂H₈, by an O=V(O-)₃ group. DFT was used to compute the optimized structures and vibrational frequencies of all species. The B3LYP functional and 6-31G* basis set was used in Gaussian 03 for geometry optimizations. All atoms were allowed to relax in calculating optimized geometries. After optimization, a more accurate estimate of the energy was calculated using the LACV3P**++ basis set in Jaguar 6.5. The electronic structure of vanadium was described using the LANL2DZ basis set, which treats the inner core of electrons separately from the valence electrons. The growing string method (GSM) was used to calculate activation barriers and identify an initial estimate for transition state geometries. The initial estimate of the transition state geometry was then refined using the transition state search (TSS) in Gaussian 03. The broken symmetry approach was also used to calculate the energy of a transition state for reactions involving multiple spin states, where the transition state was found to have a biradicaloid electronic structure.

Values of the Gibbs free energy were calculated for the standard state of 1 atm and 650 K, the reaction temperature under which the selective oxidation of methanol to formaldehyde was studied experimentally. The partition functions for translation, rotation, and vibration, were calculated explicitly for each species and then used to evaluate the Gibbs free energy of that species. Accurate calculation of each component of the partition function is essential for obtaining an accurate description of the entropy of reaction and the entropy of activation.

Results and Discussion

The model of an isolated vanadate site used in this study reproduces nearly perfectly the experimentally determined geometry and vibrational spectrum of isolated vanadate species supported on silica. The addition of methanol across a V-O-Si bond leads to the formation of a V-OCH₃/Si-OH pair. An initial structure is formed with a ΔE of adsorption of -10.8 kcal/mol. This structure then rearranges to form a more stable structure, which has a heat of adsorption of -15.5 kcal/mol. Once formed a hydrogen atom from the V-OCH₃ groups transfers a hydrogen atom to the V=O bond of the same vanadate group. This results in weakly adsorbed CH₂O and a V-OH group. CH₂O desorbs and the V-OH and SiOH groups recombine to form a VO₃ species, in which V is in the +3 state. Reoxidation of the reduced vanadate occurs by the adsorption of O₂ to form a vanadium peroxide species. The latter species reacts with a second molecule of methanol to produce additional formaldehyde and water, and restores V to the +5 state. A plot of the free energy changes associated with all elementary steps shows that reoxidation is rapid compared to the rate-limiting step, which produces the first molecule of formaldehyde. The apparent first-order rate coefficient for formaldehyde formation is given by the product of the equilibrium constant for the adsorption of methanol and the rate coefficient for the rate-limiting step. Table 1 shows that the energy and equilibrium constant for methanol adsorption, ΔE_{ad} and K_{ad} , and the apparent rate coefficient and apparent activation energy for formaldehyde formation, k_{app} and E_{app} , are in very good agreement with experimental values.

Table 1. Comparison between theoretical and experimental measurements

Parameter	Theory	Experiment
ΔE_{ad}	-15.5 kcal/mol	-14.8 kcal/mol
K_{ad}	1.41 atm ⁻¹	1.64 atm ⁻¹
E_{RLS}	39.8 kcal/mol	--
k_{RLS}	0.14 s ⁻¹	--
E_{app}	24.3 kcal/mol	23 kcal/mol
k_{app}	0.20 s ⁻¹ atm ⁻¹	0.42 s ⁻¹ atm ⁻¹

Significance

This study has shown that the elementary processes involved in the oxidation of methanol to formaldehyde on isolated vanadate species can be fully described from first principles. Such an analysis leads to results that are in very good agreement with a number of experimental observations. The processes involved in the reoxidation of reduced vanadate species are identified for the first time and are shown not to be kinetically limiting.

References

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