

Supplementary Material for the Paper Titled: “A Theoretical Investigation of the Selective Oxidation of Methanol to Formaldehyde on Isolated Vanadate Species Supported on Silica”

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Note: The reaction numbers, table numbers, and references mentioned in this document refer to the respective items specified in the main document.

Determination of Rate Constants

The rate constants in Table IV were determined by using transition state theory for all reaction steps (reactant i going to product j), except for reaction (5',6), where collision theory was used, and reaction (1,2'), which was assume to be at equilibrium. After determining ΔE for each reaction step, Eq. A1 was used to determine k_{ij} :

$$k_{i,j} = \frac{k_B T}{h} \frac{q_{i,j}^\ddagger}{q_i} \exp\left(\frac{-\Delta E_{i,j}^\ddagger}{RT}\right) \quad (\text{A1})$$

In Eq. A1, $q_{i,j}^\ddagger$ is the partition function for the transition state, q_i represents the partition function for all reactants involved in a given reaction, and $\Delta E_{i,j}^\ddagger$ is the activation energy. Using Eq. A1, the rate constants for reactions (2',3), (3,4), (4,5), (6,7), (7,8), (8,9), and (9,1) were determined. In reaction (3,4), during which weakly formed formaldehyde desorbs from the vanadate site, the activation energy was zero since no molecular rearrangement was needed prior to desorption.

In the reaction (5',6), molecular oxygen is adsorbed onto a reduced vanadate site to form a peroxide species. The rate constant for this step was determined by using collision theory and modeling the reaction step as an ideal gas impinging on a surface. The flux density was determined by using Eq. A2:

$$\Gamma = \frac{1}{4} \langle v \rangle n \quad (\text{A2})$$

In Eq. A2, $\langle v \rangle$ is the average velocity and n is the number density of O_2 . These values can be determined by using Eq. A3 and A4, respectively.

$$\langle v \rangle = \left[\frac{8RT}{\pi M_w} \right]^{1/2} \quad (\text{A3})$$

$$n = \frac{PN_{AV}}{RT} \quad (\text{A4})$$

At an oxygen partial pressure of 0.075 atm and 650 K, $\langle v \rangle = 6.56 \times 10^4 \text{ cm s}^{-1}$ and $n_{\text{O}_2} = 8.46 \times 10^7 \text{ molecules cm}^{-3}$, giving a flux density of $\Gamma = 1.39 \times 10^{22} \text{ molecules cm}^{-2} \text{ s}^{-1}$. For an experimental surface coverage of 0.4 V nm^{-2} , the collision frequency, Z , is $3.48 \times 10^8 \text{ molecules site}^{-1} \text{ s}^{-1}$. Dividing Z by P_{O_2} yields the rate constant for (5',6), $k_{5',6} = 4.63 \times 10^9 \text{ atm}^{-1} \text{ s}^{-1}$.

Calculation of Surface Species Concentrations

The surface species concentrations were determined by writing out the rate expression for each reaction. Of particular interest, are the surface concentrations of species, **5'**, **6**, and **7**, which were determined by using Eqs. A5-A7, where $R_{\text{CH}_2\text{O}}$ is 0.0175 s^{-1} , the experimental reaction rate at 650 K and $P_{\text{MeOH}} = 0.05 \text{ atm}$.

$$\theta_{5'} = \frac{R_{\text{CH}_2\text{O}}}{k_{5',6} P_{\text{O}_2}} \quad (\text{A5})$$

$$\theta_6 = \frac{R_{\text{CH}_2\text{O}}}{k_{6,7}} \quad (\text{A6})$$

$$\theta_7 = \frac{R_{\text{CH}_2\text{O}}}{k_{7,8}} \quad (\text{A7})$$

Using the rate constants in Table IV, $\theta_{5'} = 5.04 \times 10^{-11}$, $\theta_6 = 1.47 \times 10^{-10}$, and $\theta_7 = 2.86 \times 10^{-5}$. Since all of these surface species concentrations are quite small, this indicates that the reoxidation mechanism is rapid, which is consistent with experimental observations.

The surface concentration of species **1** and **2'** can also be calculated in a similar manner. The coverage of **2'** can be determined from the Langmuir adsorption equation, Eq. A8, consistent with the assumption that reaction (1,2') is a reversible, equilibrium step.

$$\theta_{2'} = \frac{K_{1,2'} P_{MeOH}}{1 + K_{1,2'} P_{MeOH}} \quad (A8)$$

Using the computed value for $K_{1,2'}$, 4.23 atm^{-1} , $\theta_{2'} = 0.17$, which agrees well with the experimental value of 0.15.³ This indicates that $\theta_1 = 1 - \theta_{2'}$, or 0.83, since species **1** and **2'** are the most abundant surface species and all the other species exist in very small concentrations.