

Methanol Oxidation Over Supported Vanadium Oxide Catalysts: New Fundamental Insights About Oxidation Reactions Over Metal Oxide Catalysts from Transient and Steady State Kinetics

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1. INTRODUCTION

Metal oxide catalysts are extensively employed in the chemical, petroleum and pollution control industries as oxidation catalysts (e.g., oxidation of methanol to formaldehyde, oxidation of o-xylene to phthalic anhydride, ammoxidation of propylene/propane to acrylonitrile, selective oxidation of H₂S to elemental sulfur (SuperClaus) or SO₂/SO₃, selective catalytic reduction (SCR) of NO_x with NH₃, catalytic combustion of VOCs, etc.). A special class of metal oxide catalysts consists of supported metal oxide catalysts, where an active phase (e.g., vanadium oxide) is deposited on a high surface area oxide support (e.g., alumina, titania, zirconia, niobia, ceria, etc.). Supported metal oxide catalysts provide several advantages over bulk mixed metal oxide catalysts for fundamental studies since (1) the number of surface active sites can be controlled because the active metal oxide is 100% dispersed on the oxide support below monolayer coverage, (2) the oxide support ligands can be varied in order to monitor the influence of the bridging V-O-Support bond and (3) the surface active sites can be directly monitored with *in situ* spectroscopies (e.g., Raman, IR, DRS, etc.) during oxidation reactions. In the present study, the advantages provided by the supported metal oxide catalysts are combined with transient and steady state kinetic studies in order to obtain additional fundamental insights into oxidation reactions over metal oxide catalysts.

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2. EXPERIMENTAL

The supported vanadia catalysts were synthesized via the incipient-wetness impregnation method. A vanadium isopropoxide (Alfa, 95-99% purity) methanol solution was used to impregnate the different oxide supports: Al_2O_3 (Harshaw, 225 m^2/g), TiO_2 (Degussa P-25, 55 m^2/g), ZrO_2 (Degussa, 39 m^2/g), Nb_2O_5 (Niobium Products Company, 55 m^2/g) and CeO_2 (Engelhard, 36 m^2/g). Complete details of the preparation procedure can be found in the literature [1]. Information about the various characterization experiments can also be found in the literature: Raman spectroscopy [2], Infrared (IR) Spectroscopy [3], UV-VIS Diffuse Reflectance Spectroscopy (DRS) [4] and Temperature Programmed Reaction Spectroscopy (TPRS) [5]. The transient TPRS experiments were performed by initially outgassing 100 mg of the catalyst in 5% O_2/He for 1 hour at 300 C and subsequently cooling the sample to 100 C. The sample was flushed with helium for an additional hour and methanol was adsorbed at the same temperature with helium as the carrier gas. The adsorption temperature of 100 C was selected because it minimized the amount of physisorbed methanol on the catalysts. The sample was flushed with flowing helium for an additional hour to remove any residual physisorbed methanol. The TPRS experiment was then initiated with a heating rate of 10 C/min in a helium flow rate of 100 cc/min, and product analysis was performed with an on-line mass spectrometer (Hiden Analytical Ltd.) (see reference 5 for additional experimental details). The methanol oxidation studies were performed in a fixed bed reactor at 230 C. The reaction temperatures were only varied to determine the activation energy (additional details about the reactor system can be found in reference 1).

3. RESULTS

3.1 Molecular structures of the calcined surface vanadia species

The molecular structures of the two-dimensional surface vanadia species, after calcination and under *in situ* conditions, have been determined with the aid of Raman, IR, DRS, solid state ^{51}V NMR, EXAFS/XANES and oxygen isotope exchange experiments [6-11]. These molecular characterization experiments have revealed that the surface vanadia species possess the following characteristics: (1) the calcined surface vanadia species are present in the V(+5) oxidation state, (2) the surface vanadia species possess only one terminal V=O bond (they are mono-oxo), (3) the surface vanadia species are predominantly present as VO_4 species (there is a possibility that a minor amount of surface VO_5 or VO_6 species may also be present at monolayer coverages), (4) both isolated and polymerized surface VO_4 species are present, (5) the ratio of polymerized to isolated surface vanadia species increases with surface coverage and (6) the molecular structures of the surface vanadia species on the different oxide supports (alumina, titania zirconia, niobia and ceria) are essentially identical (even the ratio of the polymerized to the isolated surface vanadia species is the same at comparable surface coverages). The only structural differences among these supported vanadia catalysts are the very minor differences in the terminal V=O bond lengths (corresponding to less than 0.01 Angstrom [12]) and the different oxide support ligands (Al, Ti, Zr, Nb and Ce). The monolayer surface coverages of the vanadia overlayers, experimentally determined by Raman spectroscopy, and the Raman vibrations of the terminal V=O bonds at monolayer coverages are presented in Table 1.

Table 1
Monolayer surface coverages and vibrations of the terminal V=O bonds, at monolayer coverage, for the supported vanadia catalysts

Catalyst	Monolayer Coverage (V atoms/nm ²)	V=O (cm ⁻¹)
25% V ₂ O ₅ /Al ₂ O ₃	7.3	1026
7% V ₂ O ₅ /Nb ₂ O ₅	8.4	1033
6% V ₂ O ₅ /TiO ₂	7.9	1030
4% V ₂ O ₅ /ZrO ₂	6.8	1030
3% V ₂ O ₅ /CeO ₂	5.7	1028

3.2 Molecular structures of the surface vanadia species and adsorbed intermediates during methanol oxidation

During methanol oxidation, the surface vanadia species becomes partially reduced by the reaction environment. *In situ* Raman studies during methanol oxidation revealed that the surface V(+5) species retained its molecular structure, but that there was about a 40-60% reduction of the Raman signal for the surface V(+5) species [13]. The actual extent of reduction was probably less than 40-60% since the catalysts became slightly darker upon reduction and decreased the amount of scattered laser light to the detector. However, the extent of reduction, within experimental error, was independent of (1) the surface coverage of the surface vanadia species, (2) the specific oxide support, and (3) the reaction temperature (230-350 C). This suggests that the fraction of participating surface vanadia sites, or active surface sites, is relatively constant for all the supported vanadia catalysts under the chosen experimental conditions. *In situ* DRS studies revealed that the reduced surface vanadia species was predominantly present as surface V(+4) species [14]. *In situ* IR spectroscopy studies also revealed the presence of surface methoxy, CH₃O, and surface formate, HCOO, species on the catalyst surface during methanol oxidation over a 5% V₂O₅/TiO₂ catalyst [15]. The 5% V₂O₅/TiO₂ catalyst corresponds to approximately monolayer surface coverage of the surface vanadia overlayer on the titania support, see Table 1, and minimizes the adsorption of methanol and its reaction products on exposed surface titania sites that are present below monolayer coverage or crystalline V₂O₅ particles that are present above monolayer coverage.

3.3 Steady state kinetics of methanol oxidation over the supported vanadia catalysts

The turnover frequencies (TOF), defined as the number of methanol molecules converted to formaldehyde per surface vanadia site per second, are presented for the different supported vanadia catalysts, at monolayer coverages, in Table 2. There is a dramatic variation in the TOFs with the specific oxide support and the variation spans approximately three orders of magnitude at monolayer coverages (the same surface density of surface vanadia species). The TOFs were also relatively independent of surface vanadia coverage [1], which indicates that the reaction rate is first order with respect to the surface vanadia

Table 2
Turnover frequencies (TOFs) and activation energies for methanol oxidation over supported vanadia catalysts at monolayer coverages of surface vanadia species

<u>Catalyst</u>	<u>TOF (cm⁻¹)</u>	<u>Activation Energy (Kcal/mol)</u>
25% V ₂ O ₅ /Al ₂ O ₃	6.8 x 10 ⁻²	20
7% V ₂ O ₅ /Nb ₂ O ₅	4.0 x 10 ⁻¹	17
6% V ₂ O ₅ /TiO ₂	1.1 x 10 ⁺⁰	22
4% V ₂ O ₅ /ZrO ₂	1.7 x 10 ⁺⁰	18
3% V ₂ O ₅ /CeO ₂	1.0 x 10 ⁺¹	20

sites. This suggests that methanol oxidation over the supported vanadia catalysts is a unimolecular reaction requiring only one surface vanadia site (the active site). The formaldehyde selectivities were 90-99% for the titania, zirconia, niobia and ceria supported vanadia catalysts. For the alumina supported vanadia catalyst, however, the formaldehyde selectivity was only about 50% and dimethyl ether was the major unselective product. The high dimethyl ether formation for the V₂O₅/Al₂O₃ catalyst reflects the presence of surface acid sites for this catalyst. The activation energies for methanol oxidation over the supported vanadia catalysts at monolayer coverage are approximately constant at 19.5 Kcal/mol, with a standard deviation of 2.5 Kcal/mol (see Table 2). Thus, the dramatic variation in the TOFs for methanol oxidation over the different supported vanadia catalysts is primarily related to differences in the preexponential factors of the kinetic expression.

3.4 Transient kinetics of methanol oxidation over the supported vanadia catalysts

The major products formed during the TPRS experiments were H₂CO (selectivity varied from about 25-55%), CO (accounting for almost all the remaining carbon containing products), and H₂O with minor amounts of CH₃OH (trace amounts), CO₂ (typically 2-4%), and CH₃OCH₃ (trace amounts only observed for the alumina supported vanadia catalyst). The much lower formaldehyde selectivity during the TPRS experiments relative to the steady state methanol oxidation experiments is a consequence of the absence of significant amounts of gas phase methanol and moisture, which efficiently retard the readsorption and oxidation of formaldehyde via competitive adsorption [16-18]. Formaldehyde is the major product of the decomposition of the surface methoxy intermediate [19] and CO is the major product from the decomposition of the surface formate intermediate [20]. The small amounts of CO₂ are due to the further oxidation of the CO product in the catalyst bed. The trace amounts of CH₃OH could originate from either some residual physisorbed methanol or from the hydrogenation of the surface methoxy intermediate [19]. The amounts of methanol adsorbed per surface vanadia species on the different supported vanadia catalysts, at approximately monolayer surface vanadia coverage and 100 C, could also be determined from integration of the calibrated product mass spectrometer signals and are presented in Table 3. Thus,

Table 3

Number of methanol molecules adsorbed per surface vanadia species at monolayer surface coverages (adsorption temperature of 100 C)

<u>Catalyst</u>	<u>Number of adsorbed methanol molecules/surface V atom</u>
25% V ₂ O ₅ /Al ₂ O ₃	0.44
5% V ₂ O ₅ /Nb ₂ O ₅	0.65
3% V ₂ O ₅ /ZrO ₂	0.57
5% V ₂ O ₅ /TiO ₂	0.37
3% V ₂ O ₅ /CeO ₂	0.50

the saturated amount of methanol molecules adsorbed on the different supported vanadia catalysts at 100 C is very similar, 0.51 with a standard deviation of 0.14, and corresponds to approximately one adsorbed methanol molecule per two surface vanadia species.

The TPRS experiments also provided additional insights into the kinetics of methanol oxidation over the supported vanadia catalysts. The TPRS experiments only provide kinetics about the surface reaction steps since the adsorption events precede the initiation of the transient temperature ramp. The TPRS peak temperatures for the production of H₂CO and CO from the different vanadia catalysts are presented in Table 4.

Table 4

Peak temperatures for the production of H₂CO and CO from CH₃OH oxidation during the TPRS studies over the supported vanadia catalysts

<u>Catalyst</u>	<u>H₂CO(°C)</u>	<u>CO(°C)</u>
25% V ₂ O ₅ /Al ₂ O ₃	210	275
5% V ₂ O ₅ /Nb ₂ O ₅	190	285
3% V ₂ O ₅ /ZrO ₂	200	--
5% V ₂ O ₅ /TiO ₂	220	270
3% V ₂ O ₅ /CeO ₂	200	265

Recall that the formation of H₂CO and CO result from the decomposition of the surface methoxy, CH₃O, and the surface formate, HCOO, intermediates, respectively. The surface formate is produced by readsorption of formaldehyde product on the surface vanadia sites [20]. The TPRS spectra reveal that the decomposition of the surface methoxy intermediates

($T_p = 190\text{-}220\text{ C}$), as well as the surface formate intermediates ($T_p = 265\text{-}285\text{ C}$), possess essentially the same kinetics on all the supported vanadia catalyst. The desorption of H_2O exhibited a very broad peak with a maximum at about 300 C for the supported vanadia catalysts. The slight variations among the different TPRS runs are related to the use of several parallel reactor systems to expedite the experiments, and are not due to different decomposition kinetics. Identical peak temperatures were obtained when two different catalysts were studied in the same reactor system. Thus, the TPRS experiments demonstrate that the dramatically different TOFs measured during the steady state methanol oxidation to formaldehyde over the supported vanadia catalyst are not related to kinetic differences in the rate determining surface reaction step, the decomposition of the surface methoxy species [19,20].

4. DISCUSSION

4.1 Molecular structure-reactivity relationships during methanol oxidation to formaldehyde over supported vanadia catalysts

The methanol adsorption experiments, at the beginning of the TPRS experiments, revealed that a maximum of one methanol molecule adsorbs per two surface vanadia sites (at monolayer surface vanadia coverage and an adsorption temperature of 100 C). The maximum number of adsorbed methanol molecules at monolayer surface vanadia coverage can be doubled by lowering the adsorption temperature to room temperature, but the increase would be strictly due to the presence of physically adsorbed or weakly interacting methanol molecules rather than to dissociatively adsorbed methanol molecules in the form of surface methoxy species (the reactive surface intermediate) [16,19]. It may be possible that the number of adsorbed methoxy species per surface vanadia sites increases to unity at low surface vanadia coverages where lateral interactions are minimized, but such quantitative data are currently not available because of complications due to competitive adsorption on the exposed oxide support sites. For silica supported vanadia catalysts, where the surface vanadia species are isolated [6,7,21] and competitive adsorption on the oxide support is not a problem at modest surface vanadia coverages [2], the maximum number of surface methoxy per surface vanadia species is close to unity [22]. A careful examination of the methanol oxidation kinetic data reveals that the TOFs were always slightly higher at low surface vanadia coverages, which would be consistent with a higher number of adsorbed methoxy species per surface vanadia site. Thus, the maximum number of adsorbed methoxy per surface vanadia species may not be constant at all surface vanadia coverages and may vary from approximately unity at low surface vanadia coverages to approximately 0.5 at high surface vanadia coverages.

It is also important to establish if methanol is directly coordinated to one or two surface vanadia sites, mono-dentate vs. bidentate, or if two surface vanadia sites are required because of lateral interactions among the surface methoxy species at monolayer surface vanadia coverage. Comparative IR studies of adsorbed methoxy on vanadia catalysts with known molecular structural reference compounds reveal that the adsorbed methoxy species is only coordinated to one surface vanadia species [20]. This coordination is consistent with the almost constant methanol oxidation TOF as a function of surface vanadia coverage and the insensitivity of the methanol oxidation TOF to the presence of secondary surface metal

oxide additives in the surface vanadia overlayer [23]. Furthermore, the essentially identical kinetics for the oxidative dehydrogenation of the surface methoxy species to formaldehyde over the different supported vanadia catalysts during the TPRS experiments (see Table 4) suggests that this rate determining step exclusively occurs on the surface vanadia site without the direct involvement of the oxide support cations or oxygen anions.

The molecular characterization studies demonstrated that the oxidized surface vanadia species in the different supported vanadia catalysts possess essentially the same molecular structures: predominantly consisting of isolated and polymerized surface VO_4 species with the same ratio of polymerized to isolated species at comparable surface vanadia coverages. The surface vanadia species even became reduced to comparable extents during methanol oxidation for all the supported vanadia catalysts. The terminal $\text{V}=\text{O}$ bond lengths for the different supported vanadia catalysts were also essentially identical, see Table 1, and the minor variations in the $\text{V}=\text{O}$ bonds did not correlate with the methanol oxidation TOFs, (see Tables 1 and 2). Thus, there are no significant molecular structural differences among the surface vanadia species on the different oxide supports to account for the dramatic variation in the TOFs during methanol oxidation over the supported vanadia catalysts.

The only significant difference among the surface vanadia species on the different oxide supports was the oxide support ligands (e.g., Al, Ti, Zr, Nb and Ce). The electronegativity of the oxide support cation affects the electron density on the bridging V-O-Support oxygen: a lower cation electronegativity will result in a slightly higher electron density (more basic oxygen) and a higher cation electronegativity will result in a slightly lower electron density (less basic oxygen). Comparison of the Sanderson electronegativities of the oxide support cations [24] ($\text{Ce} < \text{Zr} < \text{Ti} \sim \text{Nb} < \text{Al}$) with the methanol oxidation TOFs ($\text{Ce} > \text{Zr} > \text{Ti} > \text{Nb} > \text{Al}$; see Table 2), reveals an inverse correlation: the lower the oxide support cation electronegativity the higher the methanol oxidation TOF. Therefore, the more basic the bridging V-O-Support oxygen the higher the methanol oxidation TOF. It is necessary to examine the mechanism and kinetics of the methanol oxidation reaction to better understand the relationship between the basic characteristics of the bridging V-O-Support oxygen and the methanol oxidation TOFs over the supported vanadia catalysts.

4.2 Reaction mechanism and kinetics of methanol oxidation to formaldehyde

The kinetics of methanol oxidation over metal oxide catalysts were elegantly derived by Holstein and Machiels [16]. The kinetic analysis demonstrated that the dissociative adsorption of water must be included to obtain an accurate kinetic model. The reaction mechanism can be represented by three kinetic steps: equilibrated dissociative adsorption of methanol to a surface methoxy and surface hydroxyl (represented by K_1), equilibrated dissociative adsorption of water to two surface hydroxyls (represented by K_2), and the irreversible hydrogen abstraction of the surface methoxy intermediate to the formaldehyde product and a surface hydroxyl (the rate determining step, represented by k_3). For the case of a fully oxidized surface, the following kinetic expression was derived:

$$r(\text{TOF}) = k_3 * \frac{K_1}{(K_2)^{1/2}} * \frac{P_{\text{CH}_3\text{OH}}}{(P_{\text{H}_2\text{O}})} \quad (1)$$

In the above kinetic expression, the Arrhenius rate constant, k_3 , is modified by the two adsorption equilibrium constants of methanol and water during the steady state kinetic studies. During the transient TPRS experiments, however, only the Arrhenius rate constant, k_3 , is measured since there is no vapor phase methanol or water to be equilibrated. The similar TPRS results for the oxidation of the surface methoxy intermediate to formaldehyde over the different supported vanadia catalysts reveal that all the catalysts possess the same k_3 . Consequently, the dramatic differences in the steady state TOFs during methanol oxidation over the different supported vanadia catalysts must be associated with the methanol and water equilibrium adsorption constants. Both methanol and water can be viewed as weak acids that will donate a proton to a basic surface site, but methanol is more strongly adsorbed than water on oxide surfaces, $K_1 > (K_2)^{1/2}$ [16]. Furthermore, the methanol oxidation TOFs were measured at methanol conversions below 20%, differential reaction conditions, where the partial pressures of methanol were much higher than the partial pressures of water [23]. Thus, the more active catalysts have a higher steady state surface concentration of adsorbed methoxy species, or a higher ratio of surface methoxy to surface hydroxyls, on the catalyst surface during methanol oxidation due to presence of more basic bridging V-O-Support oxygens (Ce > Zr > Ti ~ Nb > Al).

The above molecular structure-reactivity relationships provide new insights into the oxidation of methanol to formaldehyde over oxide catalysts. Many investigators have proposed that methanol adsorption occurs at the mono- or di-oxo M=O sites [25,26]. The molecular characterization studies demonstrated that di-oxo functionalities are not present in the supported vanadia catalysts (a similar scenario is also found for supported molybdena catalysts [27]). Furthermore, the mono-oxo functionalities are essentially identical in all the catalysts and, consequently, their characteristics do not correlate with the dramatic variation in TOFs. The current studies demonstrate that the methanol oxidation TOFs correlate with the basicity of the bridging V-O-Support bonds (similar results were also obtained for the analogous supported molybdena catalysts [27]). These new fundamental insights suggest that methanol adsorption does not occur at a M=O functionality, but that the dissociative adsorption step preferentially occurs at the bridging M-O-Support bond to form surface M-OCH₃ and Support-OH functionalities. The dissociative adsorption of methanol is facilitated in the presence of more basic bridging M-O-Support oxygens.

It has also been proposed that methanol adsorption and its oxidation to formaldehyde occurs at coordinatively unsaturated sites, possessing four-fold coordination, rather than coordinatively saturated sites, possessing six-fold coordination [19]. Unfortunately, the surface vanadia species predominantly possess four-fold coordination which prevents this issue from being addressed with the current data. However, supported molybdena catalysts possess both four-fold and six-fold coordination and their TOFs for methanol oxidation have been measured [27]. It was found that, contrary to above hypothesis, the coordinatively saturated surface molybdena species is approximately four times more active than the coordinatively unsaturated molybdena species for titania supported molybdena catalysts. Thus, methanol oxidation proceeds on both coordinatively saturated and coordinatively unsaturated sites at relatively comparable reaction rates (TOFs).

The kinetic expression derived by Holstein and Machiels, equation 1, also qualitatively accounts for the rather constant activation energies among the different supported vanadia catalysts during methanol oxidation. The measured activation energy is an apparent activation energy that is a function of the true activation for the abstraction of

the hydrogen from the surface methoxy intermediate, the heat of adsorption of methanol and the heat of adsorption of water (see equation 1). However, the heats of methanol and water adsorption partially compensate each other because the methanol equilibrium adsorption term appears in the numerator and the water equilibrium adsorption term appears in the denominator. As a result, the apparent activation energies and the true activation energy are very similar for most catalysts during methanol oxidation (see Table 2). A consequence of this conclusion is that the variation in the TOFs primarily resides in the preexponential term of the kinetic expression of equation 1.

Several recent theories have appeared in the literature to explain the dramatic variation in the methanol oxidation TOF over the different supported vanadia catalysts. From *ab initio* quantum mechanical calculations Weber has proposed that surface methoxy decomposition occurs at the bridging M-O-support bond, the surface methoxy methyl hydrogen initially being extracted as a hydride by the support cation, and that the entropy of the activated complex is affected by the density of accessible electronic states associated with the support cation [28]. However, the TPRS experiments demonstrate that the decomposition of the surface methoxy to product formaldehyde and a surface hydroxyl occurs with the same kinetics for highly active catalysts as well as modestly active catalysts (see Table 4). Thus, this model does not account for the experimental observations and should be modified to examine the dissociative adsorption of methanol rather than the decomposition of the surface methoxy species. Steigman assigned the electronic transitions of the vanadia species in a silica matrix and concluded that the bridging V-O-Support bond would be the most active for oxidation reactions [29]. He proposed that the electron density on the bridging oxygen would be enhanced by replacing silica with less electronegative cations like titania that would further enhance the reactivity of the bridging V-O-Support bond. Thus, Steigman's model qualitatively accounts for the observed trends and needs to be examined more carefully on a quantitative basis.

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