Selective Catalytic Oxidation of Ethanol to Acetic Acid on Dispersed Mo-V-Nb Mixed Oxides

Xuebing Li and Enrique Iglesia[a]

Abstract: The direct oxidation of ethanol to acetic acid is catalyzed by multicomponent metal oxides (Mo-V-NbOx) prepared by precipitation in the presence of colloidal TiO₂ (Mo0.61V0.31Nb0.08Ox/TiO₂). Acetic acid synthesis rates and selectivities (~95% even at 100% ethanol conversion) were much higher than in previous reports. The presence of TiO₂ during synthesis led to more highly active surface areas without detectable changes in the reactivity or selectivity of exposed active oxide surfaces. Ethanol oxidation proceeds via acetaldehyde intermediates that are converted to acetic acid. Water increases acetic acid selectivity by inhibiting acetaldehyde synthesis more strongly than its oxidation to acetic acid, thus minimizing prevalent acetaldehyde concentrations and its intervening conversion to CO. Kinetic and isotopic effects indicate that C–H bond activation in chemisorbed ethoxide species limits acetaldehyde synthesis rates and overall rates of ethanol conversion to acetic acid. The VOx component in Mo-V-Nb is responsible for the high reactivity of these materials. Mo and Nb oxide components increase the accessibility and reducibility of VOx domains, while concurrently decreasing the number of unselective V-O-Ti linkages in VOx domains dispersed on TiO₂.

Keywords: acetaldehyde · acetic acid · ethanol · molybdenum · oxidation · sustainable chemistry · vanadium

Introduction

The conversion of alcohols to aldehydes, ketones, and carboxylic acids by using stoichiometric oxidants (e.g., CrVI[1] and MnVII species[2]) leads to toxic waste by-products. Catalytic processes using O₂ or air as stoichiometric oxidants minimize the cost and environmental impact of these chemical processes.[3] Specifically, inorganic solids, easily separated from organic reactants and products, and gas-phase processes that avoid solid–liquid separations and use packed-bed reactors, would improve process efficiency. Inorganic catalysts for the oxidation of alcohols to aldehydes, ketones, and carboxylic acids typically consist of dispersed clusters of noble metals and their oxides (e.g., Pt,[4] Pd,[5] Ru).[6]

Ethanol has emerged as a fuel and a chemical feedstock available from biomass and could provide alternative routes to producing chemicals, such as acetaldehyde and acetic acid, currently produced from ethane, ethene, or methanol. Pd-based catalysts convert ethanol–O₂ reactants to acetic acid, but with low reaction rates and modest selectivities (433 K, 70–90% acetic acid selectivity; 0.2 g-acetic acid g-catalyst⁻¹ h⁻¹).[7] Au clusters dispersed on MgAl₂O₄ convert aqueous ethanol solutions to acetic acid at ~453 K and 0.6 MPa O₂ pressure with yields of up to 90%.[8] Reducible oxides (e.g., Sn-MoOₓ)[9] also catalyze this reaction (~60% acetic acid selectivity) at 423–573 K. A catalyst with VOₓ as the active component (VOₓ/TiO₂/clay) exhibited the best catalytic results for the oxidation of ethanol to acetic acid (97% acetic acid selectivity at 92% ethanol conversion).[10] A summary of previous reports is included in Table 1.

Multicomponent inorganic oxides containing V and Mo catalyze reactions of O₂ with alkanes to form alkenes and acids,[11] they also catalyze ethanol–O₂ reactions, but with low acetic acid productivities (0.02 g-acetic acid g-catalyst⁻¹ h⁻¹) and modest selectivities (~70%).[12]

We have recently found that mixed Mo-V-Nb oxides precipitated in the presence of TiO₂ colloidal suspensions (P25, Degussa) give unprecedented acetic acid productivities and very high selectivities for the catalytic oxidation of ethane and ethene by using O₂.[13] These experiments showed that acetic acid synthesis rates are controlled by elementary...
steps involving activation of C–H bonds in ethane, followed by hydrogen abstraction to form ethene and acetaldehyde; the acetaldehyde is then readily converted to acetic acid by using O2 and H2O. The disabable reactivity of these dispersed oxides in the conversion of reactants with more facile oxidative dehydrogenation routes to acetaldehyde than ethane or ethene reactants. This process and catalysts reported here exploit the remarkable reactivity of these dispersed oxides described here as supported or unsupported TiO2 (24 wt% active components),[13] gave more comparable areal rates, and the similar selectivities in these two samples, indicate that the higher reaction rates increasing residence time (Figure 1), because of the role of temperature, caused by higher local bed temperatures on such supported sample reflects a slightly higher catalyst temperature, but are reversed as conversion) in the oxidation of these active structures on the same matrix, but are reversed as conversion) in the oxidation of these active structures.

Results and Discussion

Rates and selectivities were measured at 473–533 K by using C2H5OH (32 kPa) and O2 (107 kPa). H2O (0–640 kPa) was added because it increases acetic acid selectivity.[10] Helium (1130 kPa) was used to dilute reactants and avoid explosive mixtures. Mo0.61V0.31Nb0.08O2/TiO2, prepared by precipitation of active components in the presence of colloidal suspensions of TiO2 (24 wt% active components),[13] gave more than 90% acetic acid selectivities at complete ethanol conversion (Table 2). Acetic acid synthesis rates (>1.0 g-catalyst−1 h−1) were much higher than on unsupported surfaces consisting of Mo0.61V0.31Nb0.08O2, and uncovered TiO2 directly from the unselective physisorption of N2. We have therefore used CO2 chemisorption at 313 K to measure the fraction of the total surface area consisting of exposed TiO2.[5] These data show that about 82% of the TiO2 surface was covered by Mo0.61V0.31Nb0.08O2 during precipitation of these active structures. From these data, we estimate the surface area of active Mo0.61V0.31Nb0.08O2 components in this sample to be 28 m2 g−1, whereas the surface area of bulk Mo0.61V0.31Nb0.08O2 powders is 7.8 m2 g−1. Areal acid synthesis rates (normalized by these active surface areas) then become 16 × 10−4 and 7.7 × 10−4 mol m−2 s−1 on Mo0.61V0.31Nb0.08O2/TiO2 and Mo0.61V0.31Nb0.08O2, respectively. These comparable areal rates, and the similar selectivities in these two samples, indicate that the higher reaction rates (per mass of active component) measured on TiO2-containing catalysts reflect a higher dispersion of active structures when such structures are precipitated in the presence of colloidal TiO2. The slightly higher areal rate measured on the supported sample reflects a slightly higher catalyst temperature, caused by higher local bed temperatures on such highly active catalysts. The temperature of the Mo0.61V0.31Nb0.08O2/TiO2 bed was about 10 K higher than for the unsupported Mo0.61V0.31Nb0.08O2 sample for the same heater temperature.

Primary acetaldehyde products were detected at low ethanol conversions, but their concentration decreased with increasing residence time (Figure 1), because of the role of acetaldehyde as an intermediate in acetic acid synthesis (Scheme 1), evidenced by the high acetic acid selectivity (95% at 100% acetaldehyde conversion) in the oxidation of acetaldehyde at 473 K. Esterification of acetic acid with ethanol led to small amounts of ethyl acetate; these equilibriumn-limited reactions are favored at intermediate conversions, but are reversed as conversion increases, because ethyl

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T[K]</th>
<th>Ethanol conv[%]</th>
<th>CH3-CHO</th>
<th>CH3-COOH</th>
<th>CH3CO-OCH3</th>
<th>CO2</th>
<th>CO3</th>
<th>Synthesis rate [g g-catalyst−1 h−1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo0.61V0.31Nb0.08O2/TiO2</td>
<td>481</td>
<td>78</td>
<td>1.7</td>
<td>85</td>
<td>11</td>
<td>2.6</td>
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<tr>
<td>24% Mo0.61V0.31Nb0.08O2/TiO2</td>
<td>510</td>
<td>100</td>
<td>0.04</td>
<td>95</td>
<td>0.5</td>
<td>4</td>
<td>1.16</td>
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<tr>
<td>24% Mo0.61V0.31Nb0.08O2/TiO2</td>
<td>533</td>
<td>100</td>
<td>0.05</td>
<td>92</td>
<td>0.01</td>
<td>6</td>
<td>1.12</td>
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</tr>
<tr>
<td>Mo0.61V0.31Nb0.08O2/TiO2</td>
<td>473</td>
<td>57</td>
<td>4</td>
<td>75</td>
<td>17</td>
<td>3</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>VO2/TiO2</td>
<td>483</td>
<td>100</td>
<td>14</td>
<td>67</td>
<td>0.1</td>
<td>19</td>
<td>0.81</td>
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</tr>
<tr>
<td>Mo2O7/VO/TiO2</td>
<td>473</td>
<td>17</td>
<td>94</td>
<td>1.5</td>
<td>0.7</td>
<td>3</td>
<td>0.003</td>
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</tr>
<tr>
<td>Mo2O7/VO/TiO2</td>
<td>481</td>
<td>100</td>
<td>26</td>
<td>58</td>
<td>0.5</td>
<td>16</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>[a] Reaction conditions: partial pressure: ethanol: 32 kPa; O2: 107 kPa; H2O: 320 kPa; He: 1130 kPa and N2: 11 kPa; total pressure: 1.6 MPa.</td>
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</tr>
</tbody>
</table>
amounts of CO were about 1% (Figure 1), indicating that only trace expected from the preferential formation of CO. Acetic acid and ethyl acetate are formed via direct combustion of ethanol reaction, because primary acetaldehyde products acetate hydrolyzes to acetic acid as ethanol reactants are depleated. Traces of diethyl ether formed via ethanol dehydration on acidic sites. The selectivity towards acetate conversion, because primary acetaldehyde products react to form acetic acid in sequential reactions (Scheme 1). CO$_2$ selectivities increased with increasing conversion, as expected from the preferential formation of CO$_2$ via secondary oxidation of acetaldehyde and acetic acid (Figure 1). The CO$_2$ selectivities extrapolated to zero ethanol conversion were about 1% (Figure 1), indicating that only trace amounts of CO$_2$ formed via direct combustion of ethanol reactants.

A proposed sequence of elementary steps for ethanol oxidation is shown in Scheme 2, in which O* represents a lattice oxygen (M$_i$=O, M$_i$=O-M$_j$, where M$_i$, M$_j$=Mox$^+$, V$^-$, or Nb$^5$+), CH$_2$CHO$_2$ is an ethoxide species attached to a M$_i$ cation (C$_2$H$_5$O-M$_j$), and CH$_3$CHO$^+$ and CH$_3$CO$_2$ are adsorbed acetaldehyde and acetic acid species, respectively. *OH denotes a hydroxyl group and * represents a reduced metal center, consisting of an oxygen vacancy in the reducible mixed oxides. Typically, catalytic reactions involving lattice oxygen atoms and Mars van Krevelen redox cycles are limited by the elementary steps in the reduction part of the cycle, which includes the required C–H bond activation.

$$\text{CH}_3\text{CH}_2\text{OH} + \text{O}^* \rightarrow K_1 \text{CH}_3\text{CHO}^* + \text{*OH} \quad (1)$$

$$\text{CH}_3\text{CHO}^* + \text{O}^* \rightarrow K_2 \text{CH}_3\text{CHO} + \text{*OH} \quad (2)$$

$$\text{CH}_3\text{CHO}^* \rightarrow K_3 \text{CH}_3\text{CHO} + \text{*} \quad (3)$$

$$\text{CH}_3\text{CHO}^* + \text{O}^* \rightarrow K_4 \text{CH}_3\text{CHO}_2^* + \text{*} \quad (4)$$

$$\text{CH}_3\text{CHO}_2^* + \text{*} \rightarrow K_5 \text{CH}_3\text{COOH} + \text{*} \quad (5)$$

$$\text{*OH} + \text{*OH} \rightarrow K_6 \text{H}_2\text{O} + \text{O}^* \quad (6)$$

$$\text{O}_2 + \text{*} \rightarrow K_7 \text{O}^* \quad (7)$$

Scheme 2. Mars van Krevelen redox cycle for ethanol oxidation on Mo-V-Nb oxide catalysts.

Steps[15] in Scheme 2, step 1 involves quasi-equilibrated dissociative chemisorption of ethanol to form ethoxide species, from which lattice oxygen atoms abstract hydrogen in kinetically relevant steps to form chemisorbed acetaldehyde and *OH. These *OH groups recombine to form H$_2$O leaving behind an oxygen vacancy (step 6); lattice oxygen atoms are ultimately restored via irreversible dissociative chemisorption of O$_2$ co-reactants (step 7). Adsorbed acetaldehyde reacts with lattice oxygen atoms to form adsorbed acetate species (step 4), which then desorb as acetic acid (step 5).

Acetaldehyde is the predominant product at low ethanol conversions and, therefore, steps 4 and 5 become unimportant under such conditions. The elementary steps in Scheme 2 under the assumptions that: 1) all intermediates are at pseudosteady-state; 2) steps 1 and 6 are quasi-equilibrated, and 3) O*, *OH, * and C$_2$H$_5$O* are the most abundant adsorbed species, lead to an equation for the rate of ethanol oxidation [Eq. (8)]:

$$\text{rate} = \alpha_1 \left( \frac{P_{\text{CH}_2\text{CHO}_2^*}}{P_{\text{CH}_3\text{CHO}^*}} \right)^{1/3} + \alpha_2 \left( \frac{P_{\text{CH}_3\text{CHO}^*}}{P_{\text{CH}_3\text{CHO}}} \right)^{1/3} + \alpha_3 \left( \frac{P_{\text{CH}_3\text{COOH}}}{P_{\text{CH}_3\text{CHO}^*}} \right)^{1/3} + \alpha_4 \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{CH}_3\text{CHO}^*}} \right)^{1/3}$$

(8)

where $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$ are given by Equations (9)–(12), respectively.

$$\alpha_1 = \frac{K_1^{1/3} \cdot K_2^{1/3} \cdot K_6^{1/3}}{K_3^{1/3}}$$

(9)

$$\alpha_2 = \frac{K_2^{2/3} \cdot K_1^{1/3} \cdot K_6^{1/3}}{K_3^{2/3}}$$

(10)

$$\alpha_3 = \frac{K_1^{1/3} \cdot K_2^{1/3}}{K_5^{1/3}}$$

(11)

$$\alpha_4 = \frac{K_1^{4/3} \cdot K_5^{1/3}}{K_7^{4/3}}$$

(12)

At the high H$_2$O pressures in this study, *OH is likely to prevail as the most abundant adsorbed species, an assumption confirmed by the kinetic data reported below. As a
result the third term in the denominator becomes dominant and ethanol oxidation rates are given by Equations (13) and (14):

\[
\text{rate} = \frac{k_{\text{eff}} \cdot P_{O_2}^{1/3} \cdot P_{\text{CH}_3\text{CH}_2\text{OH}}^{2/3}}{P_{H_2O}^{4/3}}
\]  

(13)

\[
k_{\text{eff}} = k_1^{1/3} \cdot k_2^{2/3} \cdot K_1^{1/3} \cdot K_6^{4/3}
\]  

(14)

The effects of ethanol and \(O_2\) pressure on reaction rates are shown in Figure 2 as a function of residence time. Rates extrapolated to zero residence time give reaction orders in ethanol (0.62) and \(O_2\) (0.27) consistent with those predicted from Equation (13) when \(^{\bullet}\)OH is the most abundant adsorbed species (0.67 and 0.33, respectively).

The effects of \(H_2O\) partial pressure on ethanol oxidation rates at low conversions (<10%; acetaldehyde selectivity >83%) are shown in Figure 3. Reaction rates decreased as \(H_2O\) pressure increased, consistent with the functional form of the rate equation [Eq. (13)]. These data indicate that ethanol oxidation is inhibited by \(H_2O\), although these inhibition effects are somewhat weaker than predicted from Equation (13).

The kinetic relevance of \(C-H\) bond activation steps in the chemisorbed ethoxide species (step 2), evident from the \(k_2\) term in the effective rate constant [Eq. (14)], was probed by measuring the relative rates of \(C_2H_5OH\) and \(C_2D_5OD\) reactions with \(O_2\) (Figure 4). Effective rate constants were 3.3 times larger for \(C_2H_5OH\) than for \(C_2D_5OD\) oxidation at 473 K. These kinetic isotope effects contain a kinetic contribution from step 2 (\(k_2\)), as well as smaller thermodynamic contributions from quasi-equilibrated steps 1 and 6 (\(K_1\) and \(K_6\)). The relative contributions of each term are uncertain, but steps 1 and 2 would lead to normal kinetic isotope effects, as observed experimentally.

The kinetic analysis described above was carried out by extrapolating rates to zero conversion by using reaction time data or rates at low ethanol conversion, for which acetic acid and its ester are present at low concentrations. At higher ethanol conversions, acetic acid is formed by sequential steps that oxidize acetaldehyde (step 4 in Scheme 2). The assumption of quasi-equilibrium for acetaldehyde adsorption–desorption (step 3 in Scheme 2) leads to an expression for acetate selectivities (combined acetic acid and ethyl acetate) based on these elementary steps:
Ethanol oxidation on binary MoO\textsubscript{x}/C\textsubscript{0} showed high reactivity for ethanol oxidation, but MoO\textsubscript{3} rate with the data shown in Figure 5. H\textsubscript{2}O increased the ratio of H\textsubscript{2}O and CO\textsubscript{2} selectivities on MoO\textsubscript{3} (Table 2) gave similar rates and selectivities as VO\textsubscript{3} scavenging of acetaldehyde by H\textsubscript{2}O to form more stable the energy of their respective weakest C\textsubscript{0}bility of acetic acid relative to acetaldehyde, inferred from domnant product with selectivities of 90%. The higher sta- tivation of reactive acetaldehyde to CO\textsubscript{2} x, which appear to catalyze the unselective oxidation of acetaldehyde to CO\textsubscript{2}.\textsuperscript{[20]}

The catalytic conversion of ethanol to acetic acid in the gas phase was achieved with unprecedented rates and selectivitites on Mo-V-Nb oxides precipitated in the presence of colloidial TiO\textsubscript{2}. Acetic acid forms via sequential oxidation of primary acetaldehyde products, a step promoted by H\textsubscript{2}O. The rapid scavenging of acetaldehyde to form more stable acetic acid prevents its intervening combustion to CO\textsubscript{2} and leads to acetic acid yields of >90% at 510 K. Kinetic and isotopic data are consistent with a reduction–oxidation cata- lytic cycle limited by C–H bond activation.

The role of individual MoO\textsubscript{3} and VO\textsubscript{2} species on oxidation rates was examined by comparing ethanol oxidation rates and selectivities on MoO\textsubscript{3} or VO\textsubscript{2} domains dispersed on TiO\textsubscript{2} at surface densities (vanadium: 9.0 molecules nm\textsuperscript{-2}, molybdenum: 4.8 molecules nm\textsuperscript{-2}) corresponding to near monolayer coverages (vanadium: 8.0 molecules nm\textsuperscript{-2}\textsuperscript{[19]} molybdenum: 5.0 molecules nm\textsuperscript{-2}\textsuperscript{[20]}) VO\textsubscript{2} domains on TiO\textsubscript{2} showed high activity for ethanol oxidation, but MoO\textsubscript{3} domains were much less reactive and formed predominantly acetaldehyde because of their lower reactivity and the lower concomitant ethanol conversions (Table 2). VO\textsubscript{3}/TiO\textsubscript{2} catalyts gave 19 and 14% selectivities for CO\textsubscript{2} and acetaldehyde, respectively, at 100% ethanol conversion; these selectivities should increase with H\textsubscript{2}O partial pressure, consistent with the data shown in Figure 5. H\textsubscript{2}O increased the ratio of primary acetaldehyde products, a step promoted by H\textsubscript{2}O. The rapid scavenging of acetaldehyde to form more stable acetic acid prevents its intervening combustion to CO\textsubscript{2} and leads to acetic acid yields of >90% at 510 K. Kinetic and isotopic data are consistent with a reduction–oxidation catalytic cycle limited by C–H bond activation.

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Selective Catalytic Oxidation of Ethanol

He (Praxair, 99.999%, 0.49 cm³·s⁻¹) and N₂O₃ (Praxair mixture, 10% N₂ in O₂, certified, 0.09 cm³·s⁻¹) flows at 673 K for 2 h. Kinetic studies were performed at 473–533 K. High-pressure syringe pumps (Teleylene Isco Inc., model 500 D) were used to introduce H₂O (deionized) and ethanol. An on-line gas chromatograph (HP 5890, Series II), equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) were used to measure the concentration of all species in the reactor effluent. N₂, O₂, CO, CO₂, and H₂O were analyzed by a HP Plot Q capillary column (30 m × 0.32 mm) connected to a TCD detector. Ethene, ethanol, acetaldheyde, ethyl acetate, and acetic acid were analyzed by a HP Plot U capillary column (30 m × 0.32 mm) connected to a flame ionization detector.

Deuterated ethanol (C₂D₅OD, 99% D, anhydrous, Cambridge isotopes) and ethanol reactions were also carried out in a stainless-steel gradientless batch recirculating reactor at 1.6 MPa. In order to avoid the condensation of water and acetic acid, all the wetted parts were maintained at a constant temperature of 435 K. The reactor contents (volume = 206 cm³) were recirculated at 20 cm³·s⁻¹ (STP) by using a graphic gear micropump (Micropump 182-336). The protocols for analysis of reactants and products were similar to those described above.

Appendix

Derivation of rate expressions: At low ethanol conversion, acetaldheyde is the predominant product. Thus, the steps that lead to formation of acetate species will not be taken into account in deriving initial ethanol oxidation rates. The rate of this reaction (see Eq. (16)) can be obtained from the rate of any irreversible steps in Scheme 2, for example, step 2:

\[
rate = k_1 \cdot [CH_3CH_2O^*] \cdot [O^*]
\]

where \([O^*]\) is the concentration of oxygen atoms.

Therefore, the fraction of ethanol converted to acetic acid can be expressed by Equation (26):

\[
\frac{rate_{rate}}{rate} = \frac{k_1}{k_1 \cdot \frac{[CH_3CHO]^{\text{rate}}}{K_3}} \times \frac{[O^*]}{[\text{rate}]} = \frac{k_4 \cdot k_1^{1/3} \cdot k_2^{1/3} \cdot P_{\text{CH}_3\text{CHO}}^{1/3} \cdot P_{\text{CH}_3\text{CHO}}^{2/3}}{k_1^{1/3} \cdot k_1^{1/3} \cdot k_2^{1/3} \cdot P_{\text{CH}_3\text{CHO}}^{1/3} \cdot P_{\text{CH}_3\text{CHO}}^{2/3}}
\]

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