The Synthesis of Acetic Acid from Ethane, Ethene, or Ethanol on Mo-V-Nb Oxides
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Introduction
Acetic acid is produced by methanol carbonylation using Rh and Ir carbonyl organometallic complexes in the presence of iodide co-catalysts. The toxicity and corrosive nature of the required reagents and catalysts can be circumvented with alternate processes using inorganic solids [1, 2] or by alternate routes involving selective oxidation of ethane on inorganic oxides. Selective oxidation of ethane to acetic acid was first reported by Thorsteinson et. al. [3] on oxide catalysts containing Mo, V, and another element (Nb, Sb, Ti, Ta, Sn, As, W, Fe). Here, we report the discovery of supported or unsupported multi-component metal oxides (Mo-V-Nb oxides) exhibiting unprecedented acetic acid selectivity and productivities in a single-stage process for oxidation of ethane, ethene or ethanol.

Materials and Methods
\( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \) was prepared by a slurry method [3]. At ambient temperature, a solution of \( \text{C}_2\text{H}_4\text{NNbO}_4 \) (Aldrich, 99.99%) was added slowly to a solution containing oxalic acid (Fluka, 99%), \( \text{NH}_3\text{VO}_3 \) (Sigma-Aldrich, 99%) and (NH\(_4\))\(_2\)MoO\(_4\cdot4\)H\(_2\)O (Aldrich, 99.98%) while stirring. Water was evaporated under dynamic vacuum at 363 K. The powders formed were dried at 393 K overnight and then treated in flowing dry air (Praxair, extra dry, 1.67 cm\(^3\) s\(^{-1}\)) at 673 K for 4 h. For the 24 \% wt \( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \)/TiO\(_2\) sample, TiO\(_2\) (Degussa, P25, BET: 50 m\(^2\)/g, anatase/rutile = 3:1) was added to the solution before adding the \( \text{C}_2\text{H}_4\text{NNbO}_4 \) solution. Oxidation of ethane, ethene or ethanol to acetic acid was carried out at a total pressure of 1.6 MPa and the reactants were consisted of ethane (533 kPa) or ethene (32 kPa) or ethanol (32 kPa, Praxair mixture, 10 % \( \text{N}_2 \), certified), \( \text{H}_2\)O (320 kPa, deionized), and He (balance, Praxair, 99.999%). The products were analyzed by on-line gas chromatography. Kinetic studies were carried out in a high pressure gradientless batch reactor located in a heated insulation box (~433 K). Reactants and products were recirculated at 20 cm\(^3\) (STP)/s\(^{-1}\) using a graphite gear micropump to maintain differentiable reaction conditions.

Results and Discussion
The behavior of \( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \) catalyst for ethane oxidation agreed well with previous reports [3]. The low surface areas of bulk \( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \) samples (7.8 m\(^2\)/g) led us to examine synthetic protocols involving the precipitation of these active components in the presence of high surface area supports. Precipitation in the presence of TiO\(_2\) led to a ten-fold increase in ethene and acetic acid synthesis rates (per active component or V-atoms in catalyst) without significant changes in selectivity compared with unsupported bulk oxide catalysts. The promoting effect of titania appears to reflect predominantly a higher exposed surface area of the active component without significant changes in its surface reactivity. Similar effects, however, were not achieved with \( \text{ZrO}_2 \) or \( \text{Al}_2\text{O}_3 \), which did not appear to provide nucleation sites for the formation of more dispersed active Mo-V-Nb oxide structures.

The significant ethene selectivities observed during ethane oxidation suggest that the secondary oxidation reaction of ethene to acetaldehyde and ultimately to acetic acid limits acetyl acid synthesis rates. The introduction of trace amounts of Pd (0.0025-0.01 %wt.) led to the almost complete depletion of ethene and to a significant increase in acetic acid synthesis rates as a result of its conversion to acetaldehyde, which can be further oxidized to acetic acid on active Mo-V-Nb structures. Acetic acid selectivity above 80 % was attained at ethane conversions of 2 – 12 %, which was limited by the depletion of \( \text{O}_2 \).

We have also found that \( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \) catalyzes ethene oxidation to acetic acid with selectivity ~ 70 %. The precipitation of active structures in the presence of TiO\(_2\) to form 24 \% Mo\(_{0.31}\)\( \text{V}_{24}\text{Nb}_{0.08} \text{O}_x \)/TiO\(_2\) gave materials with acetic acid synthesis rates (per active component) about 10 times larger than bulk materials with similar acetic acid selectivity. Moreover, the presence of trace amounts of Pd (as low as 0.0025 % wt) increased acetic acid synthesis rates by a factor of 10 with a concurrent increase in acetic acid selectivity (40-70 % to 80-90 %). These results indicate that the rate of acetic acid formation from ethene in the presence of trace amount of Pd is accelerated more efficiently than sequential or parallel combustion reactions leading to undesired CO or \( \text{CO}_2 \).

The oxidative dehydrogenation of ethanol to acetic acid is typically more facile than corresponding reactions of ethane or ethene and ethanol is becoming a fuel additive and feedstock because of its availability from renewable biomass resources. Supported Pd catalysts have received intensive studies for converting ethanol to acetic acid, but selectivities are low at practical conversions [4]. Recently, a novel catalyst consisting of Au nanoclusters on TiO\(_2\) was reported to convert aqueous ethanol to acetic acid at ~423 K and \( \text{O}_2 \) pressures of 0.6 MPa [5], with yields as high as 90 %. TiO\(_2\)-supported multi-component metal oxide catalyst gave very high acetic acid selectivities (>90 %) at complete ethanol conversions, with unprecedented acetic acid productivities of 1.1 g-acetic acid/g-cat-h. An unsupported sample, \( \text{Mo}_{0.31}\text{V}_{24}\text{Nb}_{0.08} \text{O}_x \), gave much lower productivities.

In conclusion, supported multi-component metal oxides, optionally promoted with PdO, have led to unprecedented productivities and selectivities for the conversion of a flexible set of C\(_2\) reactants (ethane, ethene, ethanol) to acetic acid at near ambient temperatures.

Significance
Selective oxidation of C\(_2\) reactants (ethane, ethene, ethanol) to acetic acid has been achieved with unprecedented rates on metal oxides containing Mo, V, and Nb precipitated on TiO\(_2\) to maximize active surface area and promoted with Pd oxide clusters that catalyze ethene oxidation to acetaldehyde intermediates.

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References