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Selective Oxidation of Methanol and Ethanol on Supported Ruthenium Oxide Clusters at Low Temperatures†

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RuO₂ domains supported on SnO₂, ZrO₂, TiO₂, Al₂O₃, and SiO₂ catalyze the oxidative conversion of methanol to formaldehyde, methylformate, and dimethoxymethane with unprecedented rates and high combined selectivity (>99%) and yield at low temperatures (300–400 K). Supports influence turnover rates and the ability of RuO₂ domains to undergo redox cycles required for oxidation turnovers. Oxidative dehydrogenation turnover rates and rates of stoichiometric reduction of RuO₂ in H₂ increased in parallel when RuO₂ domains were dispersed on more reducible supports. These support effects, the kinetic effects of CH₃OH and O₂ on reaction rates, and the observed kinetic isotope effects with CH₃OD and CD₃OD reactants are consistent with a sequence of elementary steps involving kinetically relevant H-abstraction from adsorbed methoxide species using lattice oxygen atoms and with methoxide formation in quasi-equilibrated CH₃OH dissociation on nearly stoichiometric RuO₂ surfaces. Anaerobic transient experiments confirmed that CH₃OH oxidation to HCHO requires lattice oxygen atoms and that selectivities are not influenced by the presence of O₂. Residence time effects on selectivity indicate that secondary HCHO→CH₂OH acetalization reactions lead to hemiacetal or methoxymethanol intermediates that convert to dimethoxymethane in reactions with CH₂OH on support acid sites or dehydrogenate to form methylformate on RuO₂ and support redox sites. These conclusions are consistent with the tendency of Al₂O₃ and SiO₂ supports to favor dimethoxymethane formation, while SnO₂, ZrO₂, and TiO₂ preferentially form methylformate. These support effects on secondary reactions were confirmed by measured CH₂OH oxidation rates and selectivities on physical mixtures of supported RuO₂ catalysts and pure supports. Ethanol also reacts on supported RuO₂ domains to form predominately acetaldehyde and diethoxyethane at 300–400 K. The bifunctional nature of these reaction pathways and the remarkable ability of RuO₂-based catalysts to oxidize CH₃OH to HCHO at unprecedented low temperatures introduce significant opportunities for new routes to complex oxygenates, including some containing C–C bonds, using methanol or ethanol as intermediates derived from natural gas or biomass.

1. Introduction

Methanol oxidation reactions lead to formaldehyde (HCHO), dimethoxymethane (CH₃OCH₂OCH₃, DMM), and methylformate (HCOOCH₃, MF) products. Oxidative routes to HCHO are practiced on silver-based and iron-molybdate catalysts.¹ Methylformate, a precursor to formamides, carboxylic acids, and their ethers,¹² is produced via (nonoxidative) CH₃OH dehydrogenation on CuO or carbonylation using liquid bases.²,³ The direct oxidative conversion of methanol to methylformate occurs only at modest reaction rates.²–⁵ DMM is produced in a two-step process involving methanol oxidation to HCHO followed by acetalization of HCHO→CH₂OH mixtures with liquid or solid acids. Direct CH₂OH oxidation with significant DMM yields has been recently reported on ReO₂-based catalysts⁶ and on polynoxometalate Keggin clusters.⁷ CH₂OH oxidation to MF on MoO₂ and VO₂ catalysts involves rate-determining C–H activation steps to form HCHO and subsequent HCHO reactions with intermediates derived from CH₂OH or HCHO.¹,⁸,⁹ These intermediates also form CO₂ at conditions required for HCHO synthesis. Acid-catalyzed acetalization is favored by thermodynamics at low temperatures;¹⁰ current DMM synthesis routes form dimethyl ether and CO₂ as undesired byproducts. Higher MF and DMM selectivities will require that HCHO intermediates be formed at lower temperatures than on existing catalysts.

RuO₂ domains catalyze CO oxidation (at ambient temperatures),¹¹ as well as the oxidation of C₅+ alcohols to aldehydes and ketones (at ~373 K).¹²–¹⁴ Here, we report unprecedented methanol and ethanol oxidation rates and selectivities on RuO₂ domains at very low temperatures (300–400 K) and a specific role of supports in directing HCHO→CH₂OH reactions toward MF or DMM products with high selectivity. We probe the redox character of the catalytic sequence, the nature of the kinetically relevant steps, and the relation between reduction dynamics and catalytic reactivity of RuO₂ domains. These findings suggest selective routes to a broad range of complex oxygen-containing products via oxidative reactions of methanol and ethanol.

2. Experimental Section

Supported RuO₂ catalysts were prepared by incipient wetness impregnation of ZrO₂–(OH)₂, Sn(OH)₄, TiO₂ (Degussa, P25), Al₂O₃ (Alcoa, Hq31), SiO₂ (Cab-O-Sil), and MgO with aqueous solutions of Ru(NO)(NO₃)₃·xH₂O (Aldrich, 56 wt % Ru) at 298 K for 5 h. Impregnated supports were dried in ambient air at 398 K overnight and then in flowing dry air.
(Airgas, zero grade, 0.7 cm$^3$g-s) at 673 K for 2 h. ZrO$_2$-x(OH)$_{2x}$, Sn(OH)$_3$, and MgO were prepared as in previous reports.$^{15}$ ZrO$_2$-x(OH)$_{2x}$ was prepared by hydrolysis of aqueous zirconyl chloride solutions (>98%, Aldrich) at a pH of ~10 using NH$_4$OH (14.8 N, Fisher Scientific), followed by filtration of precipitated powders, and treatment in ambient air at 393 K overnight. SnO$_2$ was prepared by hydrolysis of tin (IV) chloride pentahydrate (98%, Alfa Aesar) at a pH of ~7 using NH$_4$OH (14.8 N, Fisher Scientific), followed by treatment of the resulting solids in dry air (Airgas, zero grade, 0.7 cm$^3$g-s) at 773 K for 3 h. MgO was prepared by contacting MgO (>98%, Aldrich) with deionized water at 355–365 K for 4 h, and then treating samples in flowing dry air (Airgas, zero grade, 0.7 cm$^3$g-s) at 773 K for 8 h. Al$_2$O$_3$ was treated in flowing dry air at 823 K for 5 h before use.

The nominal Ru surface density for each sample is reported as Ru/nm$^2$, based on the Ru content and BET surface area for each sample. Surface areas were measured using N$_2$ at its normal boiling point (Autosorb-1; Quantachrome) and BET analysis methods. The dispersion of Ru crystallites was measured using H$_2$ chemisorption at 313 K after reduction of RuO$_2$ domains in H$_2$ at 573 K for 1 h (Autosorb-1; Quantachrome). Repeated reduction–oxidation cycles did not influence measured dispersions, indicating that the resulting metal crystallites represent a reasonable relative measure of the dispersion of RuO$_2$ clusters present during oxidation catalysis.

Reduction rates of supported RuO$_2$ domains in H$_2$ were measured using a Quantachrome analyzer (Quantachrome Corp.) modified with electronic flow controllers. Samples (2 mg Ru) were placed in a quartz cell (4 mm I.D.) containing a quartz well in contact with samples and heated linearly from 298 to 793 K at 0.167 K s$^{-1}$ in flowing 20% H$_2$/Ar (1.33 cm$^3$ s$^{-1}$) (Matheson UHP). The H$_2$ content in the effluent was measured by thermal conductivity after H$_2$O formed during reduction was removed from the effluent using a 13X sieve trap at ambient temperature. The thermal conductivity detector was calibrated by reducing CuO powder in H$_2$ (99.995%. Aldrich). Reduction rates were measured from H$_2$ consumption rates using previously reported protocols.$^{15,16}$

Methanol reactions were carried out in a packed-bed quartz microreactor. Catalyst powders (0.1–0.3 g) were diluted with quartz powder (~0.5 g) to prevent temperature gradients and treated in 20% O$_2$/He (O$_2$, Praxair, 99.999%; He, Airgas, 99.999%; 0.67 cm$^3$/s) flow at 573 K for 1 h before catalytic measurements. Reactants were 4 kPa CH$_3$OH (Merck, 99.999%), 9 kPa O$_2$, 1 kPa N$_2$ (Praxair, Certified O$_2$/N$_2$ mixture) and 86 kPa balance He (Airgas, 99.999%). The kinetic effects of CH$_3$OH (4–40 kPa) and O$_2$ (4.5–28 kPa) pressures on CH$_3$OH reaction rates and selectivities were also examined. Similar procedures were used for CH$_3$OH and C$_2$H$_5$OH (99.5% Aldrich) reactants. CH$_3$OD (CDN Isotopes, 99.6 at. % D) and CD$_3$OD (Cambridge Isotopes, 99.8 at. % D) were used as reactants to measure kinetic isotope effects.

Reactants and products were analyzed by on-line gas chromatography (Hewlett-Packard 6890GC) using a methyl-silicone capillary column (HP-1; 50 m × 0.25 mm, 0.25 μm film thickness) and a Porapak Q packed column (80–100 mesh, 1.82 m × 3.18 mm) connected to flame ionization and thermal conductivity detectors, respectively. Selectivities are reported on a carbon basis as the percentage of the converted CH$_3$OH appearing as a given product. Rates are reported as the molar CH$_3$OH conversion rates per total Ru or surface Ru atom. Blank experiments using empty reactors did not lead to detectable CH$_3$OH conversions at any of the conditions of our study.

Anaerobic CH$_3$OH reactions were carried out in transient mode using a packed-bed quartz microreactor to determine the role of lattice oxygen atoms and the involvement of redox pathways in CH$_3$OH oxidation on RuO$_2$ domains. Samples (0.1–0.3 g) were diluted with quartz powder (~0.5 g) and treated in 20% O$_2$/He (O$_2$, Praxair, 99.999%; He, Airgas, 99.999%; 0.67 cm$^3$/s) flow at 573 K for 1 h. Steady-state CH$_3$OH oxidation reactions were carried out in 4 kPa CH$_3$OH (1 cm$^3$(STP) s$^{-1}$ Merck, 99.999%), 9 kPa O$_2$, 1 kPa N$_2$ (Praxair, Certified O$_2$/N$_2$ mixture) with He as balance (Airgas, 99.999%) before this reactant mixture was flushed with pure He (1 cm$^3$ s$^{-1}$) for 300 s. Then, a mixture CH$_3$OH (4 kPa) diluted with He was passed over the samples until CH$_3$OH conversion was no longer detected. Finally, O$_2$ was introduced into this CH$_3$OH/He mixture to confirm the recovery of initial catalytic oxidation turnover rates after these anaerobic transients. Reactants and products were analyzed every 8 s using on-line mass spectroscopy (Hewlett-Packard 5972, mass selective detector) during these experiments.

### 3. Results and Discussion

Table 1 shows CH$_3$OH oxidation rates (normalized by either total or surface-exposed Ru atoms) and selectivities at 393 K on RuO$_2$ domains supported on SiO$_2$, Al$_2$O$_3$, ZrO$_2$, TiO$_2$, SnO$_2$, and MgO with similar Ru fractional dispersion (0.174–0.215) and crystal lattice diameters (6.0–7.6 nm; from Ru dispersion assuming hemispherical crystallites). Raman spectra for these samples showed that RuO$_2$ species were well-dispersed on support surfaces, as evidenced by weak Raman features at 533, 637, and 712 cm$^{-1}$ (data not shown), corresponding to E$_g$, A$_{1g}$, and B$_{2g}$ modes, respectively.$^{17}$ The weak nature of these features is consistent with small RuO$_2$ structures, as also inferred from measured chemisorption uptakes on reduced forms of these samples.

CH$_3$OH oxidation requires rate-determining C–H activation in CH$_3$OH-derived methoxide intermediates to form HCHO through redox cycles using lattice oxygen atoms within RuO$_2$ domains. HCHO then reacts in subsequent reactions with CH$_3$OH to form hemiacetal or methoxymethanol intermediates (CH$_3$OCH$_3$OH),$^3$ which can undergo condensation reactions with CH$_3$OH to form DMM or sequential hydrogen abstraction to form MF (Scheme 1). Reactions listed along the horizontal direction in Scheme 1 require acid sites, while those depicted along the vertical direction involve some reactive form of lattice oxygen (O*) on either RuO$_2$ domains or active supports.

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The irreversible nature of the oxidative conversion of CH$_3$OH to HCHO requires one oxidative CH$_3$OH dehydrogenation (ODH) event for each HCHO, DMM, and MF molecule formed.
Thus, ODH rates are reported as the combined molar formation rates of these products; ODH rates rigorously reflect the intrinsic oxidation reactivity of active domains, without contributions from methanol molecules consumed because of various secondary reactions. ODH turnover rates (per exposed Ru) are 1.5 times greater when RuO$_2$ was supported on SnO$_2$ than on ZrO$_2$ and TiO$_2$ and 2.5–4 times greater than when supported on Al$_2$O$_3$ and SiO$_2$ (Table 1). ODH rates are much lower and near our detection limits ($0.1 \text{ mol/g-atom-Ru-h}$) on RuO$_2$/MgO.

SnO$_2$ supports led to RuO$_x$ domains with the highest reactivity, to significant reaction rates even near ambient temperatures (333 K), and to combined selectivities to MF, HCHO, and DMM above 99% (and 83% MF selectivity) at 10% CH$_3$OH conversion (Table 1). Higher CH$_3$OH pressures (80 vs 4 kPa) increased reaction rates (by a factor of 2) and DMM selectivities (6.7 to 40.8%) at the expense of lower MF selectivities (83.1 to 57.3%). These CH$_3$OH pressure effects are similar to those observed on RuO$_2$/Al$_2$O$_3$ (Table 1); they reflect secondary DMM synthesis pathways influenced by thermodynamic constraints that become less severe as CH$_3$OH pressure increases.

<table>
<thead>
<tr>
<th>catalyst (Ru wt %)</th>
<th>Ru surface density (Ru/nm$^2$)</th>
<th>temperature/CH$_3$OH pressure (K/kPa)</th>
<th>CH$_3$OH conversion rate (mol/g-atom Ru, h$^{-1}$)</th>
<th>turnover rate (mol/g-atom Ru, h$^{-1}$)</th>
<th>calculated ODH turnover rate (mol/g-atom Ru, h$^{-1}$)</th>
<th>initial reduction rate (mol H$_2$/g-atom Ru-h)</th>
<th>selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$/SiO$_2$ (4.3%)</td>
<td>1.1</td>
<td>393/4</td>
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<td>41.5</td>
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<td>5.3</td>
<td>12.4 31.0 56.1 0.6</td>
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<td>RuO$_2$/Al$_2$O$_3$ (4.4%)</td>
<td>1.3</td>
<td>393/4</td>
<td>14.9</td>
<td>71.0</td>
<td>32.5</td>
<td>7.5</td>
<td>11.6 30.1 57.4 1.0</td>
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<td>393/4</td>
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<td>88.9</td>
<td>53.2</td>
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<td>6.6 70.7 5.6 16.8</td>
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<td>RuO$_2$/TiO$_2$ (2.2%)</td>
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<td>393/4</td>
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<td>10.8</td>
<td>25.2 69.9 4.1 0.9</td>
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<td>393/4</td>
<td>30.6</td>
<td>142.3</td>
<td>79.1</td>
<td>22.3</td>
<td>20.0 60.7 15.5 3.8</td>
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<td>333/4</td>
<td>2.0</td>
<td>9.3</td>
<td>5.0</td>
<td>10.2</td>
<td>83.1 6.7 0</td>
</tr>
<tr>
<td>RuO$_2$/SnO$_2$ (4.1%)</td>
<td>2.5</td>
<td>333/80</td>
<td>4.3</td>
<td>19.9</td>
<td>8.7</td>
<td>1.6</td>
<td>57.3 40.8 0</td>
</tr>
<tr>
<td>RuO$_2$/Al$_2$O$_3$ (4.1%)</td>
<td>1.3</td>
<td>333/80</td>
<td>2.0</td>
<td>9.5</td>
<td>4.1</td>
<td>9.4</td>
<td>23.4 66.8 0.4</td>
</tr>
<tr>
<td>RuO$_2$/SnO$_2$ (4.1%)</td>
<td>2.3</td>
<td>393/4</td>
<td>0.3</td>
<td>1.7</td>
<td>1.4</td>
<td>0.4</td>
<td>95.9 - 3.0</td>
</tr>
</tbody>
</table>

$^a$ Ru dispersion: 0.174–0.215, 9 kPa O$_2$, 1 kPa N$_2$. $^b$ Rate for primary CH$_3$OH oxidative dehydrogenation to HCHO. $^c$ 80 kPa CH$_3$OH, 18 kPa O$_2$, 2 kPa N$_2$. $^d$ ~9 kPa CH$_3$OH, ~10 kPa O$_2$, balance N$_2$, V/Ti (atomic ratio) = 0.0375. $^e$ ~6 kPa CH$_3$OH, ~4 kPa O$_2$, balance N$_2$, Mo/Sn (atomic ratio) = 3/7. $^f$ 18 kPa CH$_3$OH, 7 kPa O$_2$, balance He, He/Mo/Sn (atomic ratio) = 3/7. $^g$ 7 kPa CH$_3$OH, 19 kPa O$_2$, balance He, 0.18 wt % Mo. $^h$ Estimated by assuming the number of surface Ru atoms to be $10^{19}$/m$^2$ for the bulk RuO$_2$.
markedly increased from 30.1 to 60.4%; thus, TiO$_2$ surfaces in the incipient reduction region of the reduction profiles in supports, even in pure form, directed HCHO-

Supports also influence CH$_3$OH reaction selectivities on RuO$_2$-based catalysts. Support effects on selectivities are reported at ~20% CH$_3$OH conversion, but the trends observed are similar at other conversion levels. Acid functions on Al$_2$O$_3$ and SiO$_2$ surfaces favor DMM synthesis (57.4 and 56.1% selectivity), but MF also forms (30.1 and 31.0%). Supports, such as SnO$_2$, ZrO$_2$, and TiO$_2$, with amphoteric surfaces or known hydrogenation-dehydrogenation functions, preferentially formed MF (60.7–70.7%; Table 1). These effects of supports on selectivity indicate that secondary reactions of primary HCHO products can occur on support surfaces or that such surfaces can intercept reaction intermediates (i.e., CH$_3$OCH$_2$OH) required for DMM or MF syntheses.

The role of supports in catalyzing HCHO–CH$_3$OH reactions or in some manner directing reaction intermediates toward a given product was confirmed by physically mixing supported RuO$_2$ catalysts with additional amounts of various pure supports. Al$_2$O$_3$ addition to RuO$_2$/TiO$_2$ (3:1 support/catalyst mass; 393 K) increased DMM selectivities from 8.9 to 41.9%, while MF selectivity decreased from 65.2 to 45.2% (Table 2). Thus, Al$_2$O$_3$ supports, even in pure form, directed HCHO–CH$_3$OH reactions toward DMM, decreasing the availability of HCHO (or its intermediate reaction products) for MF synthesis on the RuO$_2$/TiO$_2$ component of this composite catalyst. Conversely, DMM selectivities on RuO$_2$/Al$_2$O$_3$ decreased from 57.4 to 32.6% when pure TiO$_2$ (3:1 mass ratio) was added, while the MF selectivity markedly increased from 30.1 to 60.4%; thus, TiO$_2$ surfaces either converted HCHO–CH$_3$OH mixtures to MF or scavenged reactive gas-phase intermediates (e.g., CH$_3$OCH$_2$OH; Scheme 1) that would have otherwise formed DMM on Al$_2$O$_3$ acid sites and directed them instead toward MF synthesis on RuO$_2$ domains. Oxidative dehydrogenation rates were not influenced by mixing pure supports, consistent with the required involvement of RuO$_2$ domains in the initial HCHO synthesis step.

CH$_3$OH consumption rates changed only to the extent required to satisfy the different CH$_3$OH stoichiometric requirements for DMM and MF synthesis in secondary CH$_3$OH–HCHO reactions (Scheme 1).

![Figure 2. Dependence of rates of oxidative dehydrogenation (per g-atm surface Ru) of CH$_3$OH to HCHO at 393 K on initial reduction rates in H$_2$ (per g-atm Ru) at 403 K for RuO$_2$ domains supported on SnO$_2$, ZrO$_2$, TiO$_2$, SiO$_2$, Al$_2$O$_3$, and MgO with similar Ru dispersion of 0.174–0.215 (Ru surface densities: 1.1–3.1 Ru/nm$^2$)](image)

In this sequence, the \{O*-Ru-O*-Ru-O*\} is meant to depict in general RuO$_2$ structures with reactive lattice oxygen atoms (O$^\bullet$). These postulated elementary steps include dissociative CH$_3$OH chemisorption to form methoxide (CH$_3$O$-$) intermediates (Step 1), followed by hydrogen abstraction from CH$_3$O$^-$ using lattice oxygen atoms (O$^\bullet$) in RuO$_2$ to form HCHO (Step 2). H$_2$O desorption via recombination of OH groups forms an oxygen vacancy (\(\square\)) (Step 3), and O$_2$ dissociative chemisorption (Step 4) ultimately restores the missing lattice oxygen in a series of steps that complete a Mars-van Krevelen redox cycle. These steps are consistent with the kinetic dependence of reaction rates on CH$_3$OH and O$_2$ partial pressures, as we discuss next.

Figure 3 shows CH$_3$OH oxidative dehydrogenation rates and product selectivities as a function of CH$_3$OH partial pressure (0–40 kPa) at 393 K and 9 kPa O$_2$ on RuO$_2$/TiO$_2$ (3.1 Ru/nm$^2$). At similar conversions (~10%), ODH rates first increased almost linearly with increasing CH$_3$OH pressure (below 8 kPa) and then more gradually, ultimately reaching nearly constant values above 12 kPa. This behavior indicates that active surfaces become saturated with CH$_3$OH-derived reactive intermediates (e.g., CH$_3$O$^-$) as CH$_3$OH pressure increases. In parallel, MF and DMM selectivities increased (from 56.9 and 1.5%, respectively) and approached constant values (80.2 and 9.1%) with increasing CH$_3$OH partial pressures; HCHO selectivities concurrently decreased from 42.5 to 10.3%. CO$_2$ selectivities were very
low (≤1%), and they are not shown in Figure 3. These selectivity trends reflect the secondary nature of reaction pathways leading to MF and DMM synthesis, which require sequential bimolecular coupling between HCHO and CH$_3$OH-derived intermediates (Scheme 1), the rate of which depends on pressure more sensitively than initial HCHO synthesis rates.

Figure 4 shows the effects of O$_2$ partial pressure on oxidative CH$_3$OH dehydrogenation rates and product selectivities on RuO$_2$/TiO$_2$ (3.1 Ru/nm$^2$) (393 K, 4 kPa CH$_3$OH). Reaction rates and selectivities were essentially unaffected by O$_2$ partial pressures (4.5–28 kPa). Such kinetic insensitivity to O$_2$ concentrations is typical of catalytic oxidation reactions proceeding via Mars-van Krevelen mechanism$^{19}$ using lattice oxygen atoms on nearly stoichiometric surfaces, a finding confirmed by anaerobic transient CH$_3$OH reaction data reported below. Measurements at 20 kPa CH$_3$OH and varying O$_2$ concentrations led to essentially identical trends and conclusions. Methanol molecules deuterated at all positions (CD$_3$OD) or only at the hydroxyl group (CH$_3$OD) were used to probe the kinetic relevance of elementary steps involving methoxide formation and H-abstraction from methoxide during CH$_3$OH oxidation on RuO$_x$ domains. Kinetically relevant methanol dissociation steps would lead to normal kinetic isotope effects (KIE) for both CH$_3$OD and CD$_3$OD reactants. In contrast, the kinetic relevance of H-abstraction from CH$_3$O$^-$ to form HCHO would lead to normal KIE for CD$_3$OD and weak thermodynamic isotope effects for CH$_3$OD.

Table 3 shows kinetic isotope effects (defined as the ratio of ODH rates for undeuterated and deuterated methanol) measured at 4 kPa methanol and 9 kPa O$_2$ on RuO$_2$/TiO$_2$ at 393 K. At these conditions, oxidation rates are linear in methanol concentration and independent of O$_2$ pressure (Figures 3 and 4). CD$_3$OD reactants gave kinetic isotope effects greater than 2 for the rate of each reaction (methanol total conversion, oxidative dehydrogenation, and methylformate synthesis). In contrast, each of these rates was almost unchanged when CH$_3$OD was used instead of CH$_3$OH as reactants (KIE values of 1.02–1.05). Thus, deuterium substitution at the methanol hydroxyl group is kinetically inconsequential, indicating that dissociative chemisorption to form methoxide species is quasi-equilibrated during oxidative CH$_3$OH dehydrogenation on RuO$_x$ domains.

These CD$_3$OD and CH$_3$OD kinetic isotope effects resemble those measured for HCHO synthesis on Fe$_2$(MoO$_4$)$_3$ at 473 K (Table 3),$^{20}$ which led to conclusions about the kinetic relevance of methoxide C–H bond activation similar to those reached here for RuO$_x$-based catalysts. CD$_3$OD KIE values on RuO$_x$ domains are smaller than on Fe$_2$(MoO$_4$)$_3$, even though the lower temperatures used on RuO$_x$ catalysts would typically lead to larger isotope effects for identical reaction coordinate and rate-determining step. This appears to indicate that transition states retain more reactant character during H-abstraction on RuO$_x$. 

### Table 2: Methanol Oxidation Rates and Selectivities on Physical Mixtures of RuO$_2$/TiO$_2$ + Al$_2$O$_3$ and RuO$_2$/Al$_2$O$_3$ + TiO$_2$ at a Mass Ratio of I/3, and for Comparison on RuO$_2$/TiO$_2$ (6.2 Ru/nm$^2$) and RuO$_2$/Al$_2$O$_3$ (1.3 Ru/nm$^2$)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_3$OH conversion rate (mol/g-atom Ru-h)</th>
<th>calculated ODH rate$^b$ (mol/g-atom Ru-h)</th>
<th>selectivity (% carbon)</th>
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</thead>
<tbody>
<tr>
<td>RuO$_2$/TiO$_2$ + Al$_2$O$_3$ (1/3)</td>
<td>12.6</td>
<td>6.1</td>
<td>HCHO 11.6</td>
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<tr>
<td>RuO$_2$/Al$_2$O$_3$ + TiO$_2$ (1/3)</td>
<td>13.8</td>
<td>6.5</td>
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<tr>
<td>RuO$_2$/TiO$_2$</td>
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<tr>
<td>RuO$_2$/Al$_2$O$_3$</td>
<td>14.9</td>
<td>6.8</td>
<td>CO$_2$ 1.4</td>
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</tbody>
</table>

$^a$ 393 K, 4% CH$_3$OH, 9% O$_2$, 1% N$_2$, ~20% CH$_3$OH conversion. $^b$ Rate for primary CH$_3$OH oxidative dehydrogenation to HCHO.

### Table 3: Kinetic Isotopic Effects for Methanol Oxidation on RuO$_2$/TiO$_2$ at 393 K$^c$

<table>
<thead>
<tr>
<th>CH$_3$OH, CH$_3$OD, CD$_3$OD</th>
<th>CH$_3$OH conversion rate (mol/g-atom Ru-h)</th>
<th>calculated ODH rate$^b$ (mol/g-atom Ru-h)</th>
<th>MF synthesis rate (mol/g-atom Ru-h)</th>
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</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>16.3</td>
<td>10.5</td>
<td>11.4</td>
</tr>
<tr>
<td>CH$_3$OD</td>
<td>15.8</td>
<td>10.3</td>
<td>10.9</td>
</tr>
<tr>
<td>CD$_3$OD</td>
<td>6.5</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>$k_{CH3,OD}/k_{CH3,OD}$</td>
<td>1.03</td>
<td>1.02 (1.11)$^c$</td>
<td>1.05</td>
</tr>
<tr>
<td>$k_{CD3,OD}/k_{CD3,OD}$</td>
<td>2.51</td>
<td>2.38 (3.33)$^c$</td>
<td>3.07</td>
</tr>
</tbody>
</table>

$^c$ 3.1 Ru/nm$^2$, 4% methanol, 9% O$_2$, ~10% methanol conversion. $^b$ Rate for primary methanol oxidative dehydrogenation to formaldehyde. $^c$ Data in parentheses were obtained on Fe$_2$(MoO$_4$)$_3$ at 473 K from ref 20.
RuO species are reactive in methanol activation at these reaction conditions. These conclusions are consistent with the weak kinetic consequences of O2 concentration on catalytic CH3OH oxidation rates (Figure 4).

Figure 6 shows the effects of CH3OH conversion, changed by varying residence time, on CH3OH conversion turnover rates and product selectivities at 393 K on RuO2/TiO2 (6.2 Ru/nm2, fractional Ru dispersion: 0.125, 4 kPa CH3OH, 9 kPa O2 or no O2, balance He).

Figure 5. Oxidative dehydrogenation turnover rates (a) and HCHO and MF selectivities (b) during steady-state catalysis and during transient anaerobic oxidation of CH3OH on RuO2/TiO2. Conversion was varied by changing space velocity during steady-state catalysis and by allowing lattice oxygen depletion during anaerobic transients (3.1 Ru/nm2, 4 kPa CH3OH, 9 kPa O2 or no O2, balance He).

catalysts; C–D and C–H bonds are consequently less disrupted within the activated complex along the reaction coordinate on RuO2 than on Fe2(MoO4)3 catalysts. This leads, in turn, to smaller differences in reactivity between molecules containing C–H and C–D bonds. This shift toward reactant-like activated complexes becomes stronger as elementary steps become more exothermic, a process that also leads to lower activation energies, through ubiquitous Bronsted-Polanyi-type relations between kinetic and thermodynamic parameters, and to higher reaction rates. Thus, the lower KIE values measured on RuO2 catalysts are consistent with the observed ability of these materials to catalyze the overall reaction sequence, and the kinetically relevant H-abstraction step, more effectively (and at lower temperatures) than Fe2(MoO4)3.

The involvement of lattice oxygen atoms in CH3OH oxidation was confirmed by transient CH3OH reactions without O2 co-reactants on RuO2/TiO2 at 393 K. These data were obtained by removing reactants and reactive intermediates using a pure He purge for 300 s after steady-state catalytic reactions of CH3OH–O2 mixtures were carried out for 1.5 h, and then introducing a CH3OH-containing stream without O2 co-reactants. Figure 5a,b show that removal of O2 from the reactant mixture did not initially influence ODH (or MF synthesis) rates or selectivities, indicating that lattice oxygen atoms are sufficient to form all reaction products observed during steady-state oxidation catalysis. These anaerobic rates decreased with time as lattice oxygen was gradually depleted by CH3OH oxidation events. In the process, methanol conversion decreased, leading to changes in product selectivity consistent with those obtained when conversion was varied instead by changing residence time (Figure 5b). The reintroduction of O2 into the CH3OH stream led to the rapid and complete recovery of the initial catalytic CH3OH conversion rates and selectivities (Figure 5a).

The characteristic time for reoxidation during these transients was much shorter than for oxygen depletion, consistent with rapid and kinetically irrelevant reoxidation steps and with low steady-state concentrations of oxygen vacancies during catalysis, as suggested by the kinetic analysis and mechanistic proposals described. The initial decay in methanol conversion rates with time can be accurately described by a first-order dependence on the concentration of remaining lattice oxygen atoms. The time constant obtained from fitting the resulting exponential function in time led to a turnover rate estimate of 33 h–1, which resembles steady-state turnover rates measured before and after these anaerobic transients and based on the dispersion of RuO2 clusters after reduction in H2 (53 h–1). This agreement, although qualitative, is nevertheless remarkable; it confirms the accuracy of dispersion measurements and suggests that all lattice oxygen atoms in RuO2 domains exhibit similar reactivity in H-abstraction reactions.

This transient behavior is characteristic of catalytic oxidations proceeding via Mars-van Krevelen mechanisms using lattice oxygen atoms. About 1.2 oxygen atoms were removed per Ru from RuO2 domains dispersed on TiO2 before methanol oxidation catalysis was suppressed; similar oxygen removal stoichiometries (O/Ru = 1.1–1.3) were observed for RuO2 domains supported on ZrO2 and Al2O3. These values indicate that RuO2 species prevalent during steady-state catalysis become unreactive as lattice oxygen is removed and the system undergoes a two-electron reduction of Ru4+ centers (Ru4+ → Ru2+) during anaerobic CH3OH reactions; they also show that reduction to Ru0 does not occur during either aerobic or anaerobic oxidation of CH3OH at conditions required for these reactions and that RuO species are unreactive in methanol activation at these conditions.
Turnover rates decreased with increasing residence time (and CH$_3$OH conversion) as a result of reactant depletion, combined with weak kinetic inhibition effects by water co-products formed in oxidative dehydrogenation and condensation reactions. MF and DMM selectivities increased with increasing CH$_3$OH conversion, while HCHO selectivity concurrently decreased, as expected from sequential pathways involving HCHO intermediates and the formation of MF and DMM. The nonzero MF selectivities observed as conversion decreases indicate that MF can be formed to some extent directly from CH$_3$OH, but also via readsoption of desorbed HCHO initial products, which tends to be favored as the concentration of HCHO increases with increasing residence time. CO$_2$ selectivities were low (0–8%) and increased with increasing residence time, suggesting that CO$_2$ forms predominately via sequential oxidation or decomposition of HCHO, MF, and DMM products, and not via direct combustion of CH$_3$OH reactants. No CO was detected at any reaction conditions, as expected from the high CO oxidation rates reported on RuO$_2$ surfaces. Similar residence time effects on CH$_3$OH conversion turnover rates and selectivities were observed on RuO$_2$/Al$_2$O$_3$ (1.3 Ru/nm$^2$), on which DMM instead of CH$_3$OH conversion turnover rates and selectivities were much lower when RuO$_2$ domains were present, compared to RuO$_2$/Al$_2$O$_3$ (1.3 Ru/nm$^2$), on which CH$_3$OH conversion turnover rates and selectivities were reported on RuO$_2$/Al$_2$O$_3$ (1.3 Ru/nm$^2$). These RuO$_2$, catalysts compared with previously reported CH$_3$OH oxidation catalysts in Table 1. V$_2$O$_5$–TiO$_2$ prepared by coprecipitation and MoO$_3$/SiO$_2$ prepared via impregnation method catalyze MF synthesis with high selectivity (≈80 and 95.9%, at 15% and 5% conversion, respectively);$^{25}$ reaction rates are much lower than on RuO$_2$ catalysts, even at the higher temperatures of these previous studies. RuO$_2$/TiO$_2$ (4.1 wt %), gave reaction rates of 4.8 mol/g-atom Ru$_{total}$-h at 78.2% CH$_3$OH conversion and 393 K (Figure 6), which exceed those reported on V$_2$O$_5$–TiO$_2$ (≈3.4 mol/g-atom V$_{total}$-h at ≈80% CH$_3$OH conversion) at 433 K, with comparable MF and CO$_2$ selectivities of 70.4 and 7.9% (vs 80 and 5%), respectively. High MF selectivities (≈90%) have also been reported on Mo–Sn mixed oxides at 433 K at low reaction rates,$^3$ but similar compositions led to much lower MF selectivities (47% at ≈40% CH$_3$OH) at 453 K in another study.$^4$

CH$_3$OH reaction rates (per Ru-atom) increased almost linearly with increasing Ru dispersion (changed by varying Ru content from 0.6 to 8.2 wt %) on TiO$_2$, indicating that turnover rates are essentially insensitive to RuO$_2$ domain size in this dispersion range (Figure 8). The slightly lower turnover rate measured on the sample with the highest Ru dispersion reflects the lower reducibility expected for the prevalent small oxide domains,$^{15}$ which was confirmed by H$_2$ reduction rate measurements. Selectivities were influenced weakly by Ru content and dispersion. MF selectivities (at 15–20% CH$_3$OH conversion) increased slightly as dispersion increased (Figure 8), a trend that merely reflects a concomitant increase in exposed TiO$_2$ surfaces, which catalyze secondary reactions of HCHO to form MF, relative to exposed RuO$_2$ surfaces, which are required to form the required HCHO intermediates.

These RuO$_2$, catalysts are compared with previously reported CH$_3$OH oxidation catalysts in Table 1. V$_2$O$_5$–TiO$_2$ prepared by coprecipitation and MoO$_3$/SiO$_2$ prepared via impregnation method catalyze MF synthesis with high selectivity (≈80 and 95.9%, at 15% and 5% conversion, respectively);$^{25}$ reaction rates are much lower than on RuO$_2$ catalysts, even at the higher temperatures of these previous studies. RuO$_2$/TiO$_2$ (4.1 wt %), gave reaction rates of 4.8 mol/g-atom Ru$_{total}$-h at 78.2% CH$_3$OH conversion and 393 K (Figure 6), which exceed those reported on V$_2$O$_5$–TiO$_2$ (≈3.4 mol/g-atom V$_{total}$-h at ≈80% CH$_3$OH conversion) at 433 K, with comparable MF and CO$_2$ selectivities of 70.4 and 7.9% (vs 80 and 5%), respectively. High MF selectivities (≈90%) have also been reported on Mo–Sn mixed oxides at 433 K at low reaction rates,$^3$ but similar compositions led to much lower MF selectivities (47% at ≈40% CH$_3$OH) at 453 K in another study.$^4$

RuO$_2$/SiO$_2$ (1.1 Ru/nm$^2$) and RuO$_2$/SnO$_2$ (2.5 Ru/nm$^2$) also convert ethanol-O$_2$ reactant mixtures with high rates and selectivity to form acetaldehyde, diethoxymethane (acetal), and ethyl acetate at 393 K (Table 4). Neither diethyl ether nor CO$_2$ products were detected. As in methanol reactions, ethanol oxidation turnover rates were higher when RuO$_2$ domains were supported on SnO$_2$ than on SiO$_2$. Ethanol conversion rates increased with pressure and then reached a constant value; as C$_2$H$_5$OH pressure increased from 2 to 40 kPa, products shifted from acetaldehyde (97.3% to 17.6%), formed in primary oxidative dehydrogenation steps, to diethoxymethane (0 to 81%), which forms via condensation reactions favored kinetically and thermodynamically at higher C$_2$H$_5$OH pressures (Table 4).

Residence time effects on selectivities showed that reaction
pathways involve initial acetaldehyde formation in oxidative dehydrogenation steps and subsequent acetalization reactions of acetaldehyde and ethanol to form diethylether.

To our knowledge, these supported RuO2 materials have not been previously used for the activation and conversion of CH3OH, C2H5OH, or other short-chain alcohols, even though Ru oxides catalyze the oxidation of more reactive C5+ alcohols in the liquid phase to form aldehydes and ketones at ~737 K.12–14 Idriss and co-workers24 adsorbed methanol on RuO2 and only ~0.6% of the adsorbed methanol formed formylmethylene in stoichiometric reactions of methanol preadsorbed at ambient temperature. In this study, the reduction of RuO2 to Ru metal at 757 K in H2 led to higher stoichiometric MF yields (~11%), via non-oxidative reactions unrelated to those prevalent on RuO2.24 These previous studies did not detect or report evidence for the remarkable activity and selectivity shown here for RuO2-based materials in selective oxidation reactions of CH3OH and C2H5OH.

In marked contrast, the supported RuO2 domains reported here gave unprecedented CH3OH oxidation rates and allow CH3OH oxidation reactions to proceed at significant rates near ambient temperatures with >99% combined selectivities to useful formaldehyde, methyleformate, and dimethoxymethylene products. The mechanistic details and the marked effects of support on rate and selectivity reported here suggest significant opportunities for the kinetic coupling of these low-temperature oxidative CH3OH activation pathways with other catalytic functions, such as condensation, methylation, and hydration reactions of HCHO, MF, and DMM to form more complex oxygenate molecules, including those containing new C=C bonds. The unique behavior of these supported RuO2 clusters is not restricted to CH3OH activation reactions, and it appears to extend to higher alcohols,25 thus providing opportunities for also converting ethanol to diethylether (acetal) and acetaldheyde with high rates and selectivities near ambient temperatures.

### 4. Conclusions

Supported RuO2 domains on SnO2, ZrO2, TiO2, Al2O3, and SiO2 provide low-temperature paths for CH3OH activation to form HCHO and for its subsequent conversion to MF and DMM. The unprecedented ability of these materials to catalyze oxidative CH3OH near ambient temperatures leads to favorable thermodynamics and to selective kinetic paths for the formation of the products. This unique reactivity reflects the ability of small RuO2 domains to undergo fast redox cycles without significant formation of unselective Ru metal clusters. Turnover rates and selectivities depend on the nature of the support, which influences RuO2 reducibility and thus the rate of kinetically relevant hydrogen abstraction from adsorbed methoxide intermediates. The kinetic effects of CH3OH and O2 reactant concentrations and the results of transient anaerobic measurements are consistent with Mars-van Krevelen redox mechanisms requiring lattice oxygen atoms. CD3OD reactants led to normal kinetic isotope effects, while CH3OD and CH3OH oxidation rates were nearly identical, consistent with quasi-equilibrated methoxide formation and rate-determining H-abstraction from methoxide intermediates. DMM forms via acid-catalyzed secondary reactions of CH3OH with intermediates derived from CH3OH–HCHO acetalization reactions on support acid sites, while MF appears to form via H-abstraction from these intermediates on RuO2 or support redox active sites. Acid sites on Al2O3 and SiO2 favor dimethoxymethylene formation, while redox and amphoteric sites on SnO2, ZrO2, and TiO2 preferentially form methylformate. The effects of residence time and of mixing pure supports with supported RuO2 catalysts are consistent with these conclusions. These materials also catalyze the selective oxidation of ethanol to acetaldheyde and diethylether at 300–400 K.

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### References and Notes

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