

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

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Received: March 4, 2004

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–CH₃OH acetalization reactions lead to hemiacetal or methoxy-methanol intermediates that convert to dimethoxymethane in reactions with CH₃OH 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 CH₃OH 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,^{1,2} 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–CH₃OH mixtures with liquid or solid acids. Direct CH₃OH oxidation with significant DMM yields has been recently reported on ReO_x-based catalysts⁶ and on polyoxometalate Keggin clusters.⁷

CH₃OH oxidation to MF on MoO_x and VO_x catalysts involves rate-determining C–H activation steps to form HCHO and subsequent HCHO reactions with intermediates derived from CH₃OH or HCHO.^{1,8,9} These intermediates also form CO_x 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 CO_x 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–CH₃OH 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 ZrO_{2-x}(OH)_{2x}, Sn(OH)₄, TiO₂ (Degussa, P25), Al₂O₃ (Alcoa, HiQ31), 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

[†] Part of the special issue "Michel Boudart Festschrift".

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(Airgas, zero grade, 0.7 cm³/g-s) at 673 K for 2 h. ZrO_{2-x}(OH)_{2x}, Sn(OH)₄, 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 NH₄OH (14.8 N, Fisher Scientific), followed by filtration of precipitated powders, and treatment in ambient air at 393 K overnight. SnO₂ was prepared by hydrolysis of tin (IV) chloride pentahydrate (98%, Alfa Aesar) at a pH of ~7 using NH₄OH (14.8 N, Fisher Scientific), followed by treatment of the resulting solids in dry air (Airgas, zero grade, 0.7 cm³/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 cm³/g-s) at 773 K for 8 h. Al₂O₃ 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/nm², based on the Ru content and BET surface area for each sample. Surface areas were measured using N₂ at its normal boiling point (Autosorb-1; Quantachrome) and BET analysis methods. The dispersion of Ru crystallites was measured using H₂ chemisorption at 313 K after reduction of RuO₂ domains in H₂ 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 RuO₂ clusters present during oxidation catalysis.

Reduction rates of supported RuO₂ domains in H₂ 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% H₂/Ar (1.33 cm³ s⁻¹) (Matheson UHP). The H₂ content in the effluent was measured by thermal conductivity after H₂O 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 H₂ (99.995%, Aldrich). Reduction rates were measured from H₂ 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% O₂/He (O₂, Praxair, 99.999%; He, Airgas, 99.999%; 0.67 cm³/s) flow at 573 K for 1 h before catalytic measurements. Reactants were 4 kPa CH₃OH (Merck, 99.99%), 9 kPa O₂, 1 kPa N₂ (Praxair, Certified O₂/N₂ mixture) and 86 kPa balance He (Airgas, 99.999%). The kinetic effects of CH₃OH (4–40 kPa) and O₂ (4.5–28 kPa) pressures on CH₃OH reaction rates and selectivities were also examined. Similar procedures were used for CH₃OH and C₂H₅OH (99.5% Aldrich) reactants. CH₃OD (CDN Isotopes, 99.6 at. % D) and CD₃OD (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 CH₃OH appearing as a given product. Rates are reported as the molar CH₃OH conversion rates per total Ru or surface Ru atom. Blank experiments using empty reactors did not lead to detectable CH₃OH conversions at any of the conditions of our study.

Anaerobic CH₃OH 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 CH₃OH oxidation on RuO₂ domains. Samples (0.1–0.3 g) were diluted with quartz powder (~0.5 g) and treated in 20% O₂/He (O₂, Praxair, 99.999%; He, Airgas, 99.999%; 0.67 cm³/s) flow at 573 K for 1 h. Steady-state CH₃OH oxidation reactions were carried out in 4 kPa CH₃OH (1 cm³(STP) s⁻¹ Merck, 99.99%), 9 kPa O₂, 1 kPa N₂ (Praxair, Certified O₂/N₂ mixture) with He as balance (Airgas, 99.999%) before this reactant mixture was flushed with pure He (1 cm³ s⁻¹) for 300 s. Then, a mixture CH₃OH (4 kPa) diluted with He was passed over the samples until CH₃OH conversion was no longer detected. Finally, O₂ was introduced into this CH₃OH/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 CH₃OH oxidation rates (normalized by either total or surface-exposed Ru atoms) and selectivities at 393 K on RuO₂ domains supported on SiO₂, Al₂O₃, ZrO₂, TiO₂, SnO₂, and MgO with similar Ru fractional dispersion (0.174–0.215) and crystallite diameters (6.0–7.6 nm; from Ru dispersion assuming hemispherical crystallites). Raman spectra for these samples showed that RuO₂ 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 RuO₂ structures, as also inferred from measured chemisorption uptakes on reduced forms of these samples.

HCHO, MF, DMM, and CO₂ were detected as products; neither CO nor dimethyl ether products were detected. Rates and selectivities are compared at similar CH₃OH conversions (~20%) in Table 1, because relative contributions of primary and secondary reactions depend on residence time and CH₃OH conversion, as discussed later. CH₃OH turnover rates were higher on RuO₂ supported on SnO₂, ZrO₂, and TiO₂ than on Al₂O₃ or SiO₂, while RuO₂ supported on MgO led to nearly undetectable CH₃OH conversions. Turnover rates changed by less than 5% during catalytic experiments (~15 h). Bulk RuO₂ (Aldrich, 99.9%) with relatively low surface area gave very low CH₃OH conversion rates (Table 1). Pure supports did not give detectable CH₃OH conversion rates in the absence of RuO₂, even at 473 K, a temperature much higher than required for significant conversions on RuO₂-containing samples.

As discussed below, CH₃OH oxidation requires rate-determining C–H activation in CH₃OH-derived methoxide intermediates to form HCHO through redox cycles using lattice oxygen atoms within RuO_x domains. HCHO then reacts in subsequent reactions with CH₃OH to form hemiacetal or methoxymethanol intermediates (CH₃OCH₂OH),⁵ which can undergo condensation reactions with CH₃OH 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 RuO₂ domains or active supports.

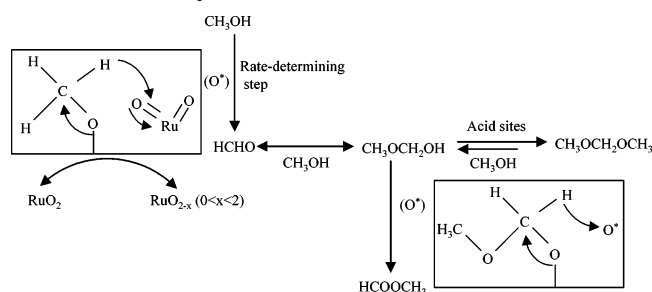
The irreversible nature of the oxidative conversion of CH₃OH to HCHO requires one oxidative CH₃OH dehydrogenation (ODH) event for each HCHO, DMM, and MF molecule formed.

TABLE 1: Methanol Oxidation Rates and Selectivities on Supported RuO₂ Catalysts at Similar Methanol Conversion (~20%),^a and on Previously Reported Catalysts

catalyst (Ru wt %)	Ru surface density (Ru/nm ²)	temperature/ CH ₃ OH pressure (K/kPa)	CH ₃ OH conversion rate (mol/g-atom M _{total} -h)	turnover rate (mol/g-atom Ru _{surf} -h)	calculated ODH turnover rate ^b (mol/g-atom Ru _{surf} -h)	initial reduction rate (mol H ₂ / g-atom Ru-h)	selectivity (%)			
							HCHO	MF	DMM	CO _x
RuO ₂ /SiO ₂ (4.3%)	1.1	393/4	8.3	41.5	19.4	5.3	12.4	31.0	56.1	0.6
RuO ₂ /Al ₂ O ₃ (4.4%)	1.3	393/4	14.9	71.0	32.5	7.5	11.6	30.1	57.4	1.0
RuO ₂ /ZrO ₂ (4.1%)	2.1	393/4	17.6	88.9	53.2	11.6	6.6	70.7	5.6	16.8
RuO ₂ /TiO ₂ (2.2%)	3.1	393/4	14.5	84.7	52.1	10.8	25.2	69.9	4.1	0.9
RuO ₂ /SnO ₂ (4.1%)	2.5	393/4	30.6	142.3	79.1	22.3	20.0	60.7	15.5	3.8
RuO ₂ /SnO ₂ (4.1%)	2.5	333/4	2.0	9.3	5.0		10.2	83.1	6.7	0
RuO ₂ /SnO ₂ ^c (4.1%)	2.5	333/80	4.3	19.9	8.7		1.6	57.3	40.8	0
RuO _x /Al ₂ O ₃ ^c (4.4%)	1.3	333/80	2.0	9.5	4.1		9.4	23.4	66.8	0.4
RuO ₂ /MgO (4.3%)	2.3	393/4	0.3	1.7	1.4	0.4				
bulk RuO ₂		393/4	2.3	26.7 ^h	16.6 ^h		34.9	53.5	2.2	9.4
V ₂ O ₅ -TiO ₂ ^{(2)d}		443/9	3.4				7	80	3	5
Mo-Sn-O ^{(3)e}		433/6	1.0				5	90	0	2
Mo-Sn-O ^{(4)f}		453/18	1.8				27.2	47.0	0	1.5
MoO ₃ /SiO ₂ ^{(5)g}		533/7	1.1					95.9	-	3.0

^a Ru dispersion: 0.174–0.215, 9 kPa O₂, 1 kPa N₂. ^b Rate for primary CH₃OH oxidative dehydrogenation to HCHO. ^c 80 kPa CH₃OH, 18 kPa O₂, 2 kPa N₂. ^d ~9 kPa CH₃OH, ~10 kPa O₂, balance N₂, V/Ti (atomic ratio) = 0.0375. ^e ~6 kPa CH₃OH, ~4 kPa O₂, balance N₂, Mo/Sn (atomic ratio) = 3/7. ^f 18 kPa CH₃OH, 7 kPa O₂, balance He, Mo/Sn (atomic ratio) = 3/7. ^g 7 kPa CH₃OH, 19 kPa O₂, balance He, 0.18 wt % Mo. ^h Estimated by assuming the number of surface Ru atoms to be 10¹⁹/m² for the bulk RuO₂.

SCHEME 1: Proposed Primary and Secondary CH₃OH Reaction Pathways



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 RuO₂ was supported on SnO₂ than on ZrO₂ and TiO₂ and 2.5–4 times greater than when supported on Al₂O₃ and SiO₂ (Table 1). ODH rates are much lower and near our detection limits (~0.1 mol/g-atom-Ru-h) on RuO₂/MgO.

SnO₂ 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% CH₃OH conversion (Table 1). Higher CH₃OH 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 CH₃OH pressure effects are similar to those observed on RuO₂/Al₂O₃ (Table 1); they reflect secondary DMM synthesis pathways influenced by thermodynamic constraints that become less severe as CH₃OH pressure increases.

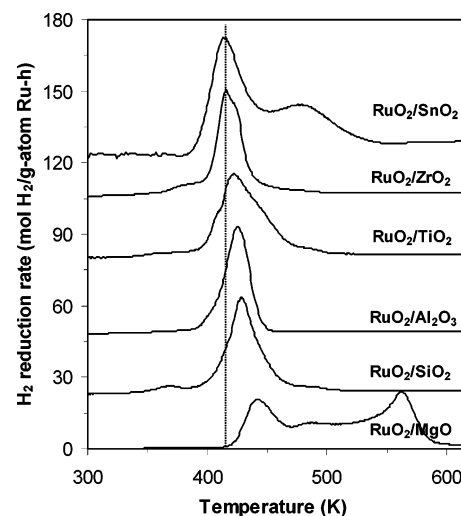


Figure 1. Temperature-programmed reduction profiles for RuO₂ domains supported on SnO₂, ZrO₂, TiO₂, SiO₂, Al₂O₃, and MgO with similar Ru dispersion of 0.174–0.215 (Ru surface densities: 1.1–3.1 Ru/nm²).

The observed effects of support on ODH turnover rates (Table 1) reflect changes in the reactivity of RuO_x surfaces caused by concurrent effects of supports on RuO_x reducibility and thus on its ability to undergo reduction in kinetically relevant steps required for oxidation turnovers. Figure 1 shows incipient reduction rates for RuO₂ domains using H₂ as a stoichiometric reductant as the sample temperature increased from 298 to 793 K. Incipient reduction rates obtained by a kinetic analysis of the low-temperature part of the first reduction peak in Figure 1 are shown for each sample in Table 1. Reduction peak temperatures increased by ~30 K (416 to 447 K) as the support changed from SnO₂ to ZrO₂, TiO₂, Al₂O₃, SiO₂, and MgO. RuO₂/SnO₂ shows two additional reduction peaks at 486 K and

at >620 K (not shown), which reflect SnO₂ reduction at temperatures above those of catalytic relevance. RuO₂ domains on MgO gave two reduction features at higher temperatures, suggestive of refractory RuO₂ domains strongly interacting with MgO. H₂ consumption stoichiometries were 1.9–2.2 H₂/Ru for all samples, indicating that all Ru⁴⁺ cations in RuO₂ (as detected by Raman spectroscopy) reduce completely to Ru⁰ during these H₂ treatments.

Initial reduction rates were extracted by kinetic analysis of the incipient reduction region of the reduction profiles^{15,16} in Figure 1. These incipient reduction processes are most relevant to those occurring in nearly stoichiometric RuO₂ during the redox cycles required for methanol oxidation turnovers, evidence for which is presented below from the observed kinetic effects of CH₃OH and O₂ on catalytic oxidation rates. RuO₂ domains supported on reducible oxides (SnO₂, ZrO₂, and TiO₂) undergo more facile reduction than those supported on more insulating and refractory oxides (Al₂O₃, SiO₂, and MgO) (Table 1). If hydrogen abstraction from methoxide intermediates by lattice O-atoms is the kinetically relevant step during HCHO synthesis on RuO_x, the rates of catalytic CH₃OH oxidation and of incipient stoichiometric reduction in H₂ should increase in parallel, as indeed was found (Figure 2). These reduction rates and the corresponding CH₃OH oxidation rates (Table 1) are much higher than for previously reported catalysts based on MoO_x and VO_x domains.^{2–5,15,16,18}

Supports also influence CH₃OH reaction selectivities on RuO_x-based catalysts. Support effects on selectivities are reported at ~20% CH₃OH conversion, but the trends observed are similar at other conversion levels. Acid functions on Al₂O₃ and SiO₂ surfaces favor DMM synthesis (57.4 and 56.1% selectivity), but MF also forms (30.1 and 31.0%). Supports, such as SnO₂, ZrO₂, and TiO₂, 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., CH₃OCH₂OH) required for DMM or MF syntheses.

The role of supports in catalyzing HCHO–CH₃OH reactions or in some manner directing reaction intermediates toward a given product was confirmed by physically mixing supported RuO₂ catalysts with additional amounts of various pure supports. Al₂O₃ addition to RuO₂/TiO₂ (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, Al₂O₃ supports, even in pure form, directed HCHO–CH₃OH reactions toward DMM, decreasing the availability of HCHO (or its intermediate reaction products) for MF synthesis on the RuO₂/TiO₂ component of this composite catalyst. Conversely, DMM selectivities on RuO₂/Al₂O₃ decreased from 57.4 to 32.6% when pure TiO₂ (3:1 mass ratio) was added, while the MF selectivity markedly increased from 30.1 to 60.4%; thus, TiO₂ surfaces either converted HCHO–CH₃OH mixtures to MF or scavenged reactive gas-phase intermediates (e.g., CH₃OCH₂OH; Scheme 1) that would have otherwise formed DMM on Al₂O₃ acid sites and directed them instead toward MF synthesis on RuO_x domains. Oxidative dehydrogenation rates were not influenced by mixing pure supports, consistent with the required involvement of RuO_x domains in the initial HCHO synthesis step. CH₃OH consumption rates changed only to the extent required to satisfy the different CH₃OH stoichiometric requirements for DMM and MF synthesis in secondary CH₃OH–HCHO reactions (Scheme 1).

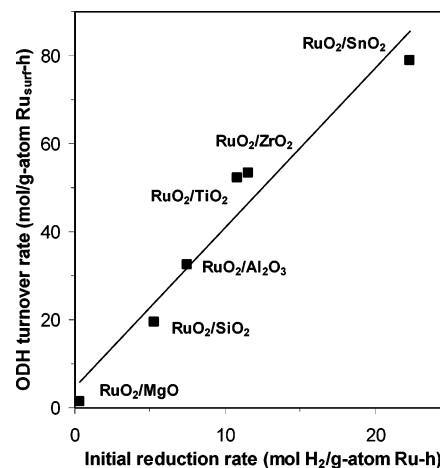
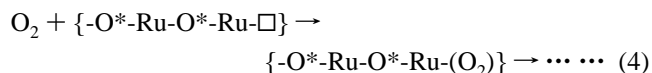
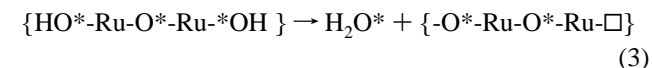
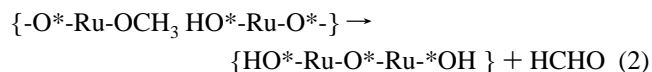
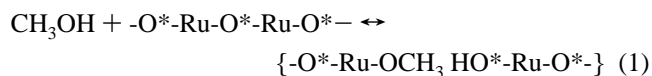


Figure 2. Dependence of rates of oxidative dehydrogenation (per g-atom surface Ru) of CH₃OH to HCHO at 393 K on initial reduction rates in H₂ (per g-atom Ru) at 403 K for RuO₂ domains supported on SnO₂, ZrO₂, TiO₂, SiO₂, Al₂O₃, and MgO with similar Ru dispersion of 0.174–0.215 (Ru surface densities: 1.1–3.1 Ru/nm²).

A plausible sequence of elementary steps for methanol oxidation on RuO_x domains is shown as steps 1–4 below; it is consistent with the results presented above and with HCHO synthesis pathways previously proposed.^{1,5,7,8}



In this sequence, the $\{\text{-O}^*\text{-Ru-O}^*\text{-Ru-O}^*\text{-}\}$ is meant to depict in general RuO_x structures with reactive lattice oxygen atoms (O^{*}). These postulated elementary steps include dissociative CH₃OH chemisorption to form methoxide (CH₃O⁻) intermediates (Step 1), followed by hydrogen abstraction from CH₃O⁻ using lattice oxygen atoms (O^{*}) in RuO_x to form HCHO (Step 2). H₂O desorption via recombination of OH groups forms an oxygen vacancy (□) (Step 3), and O₂ dissociative chemisorption (Step 4) ultimately restores the missing lattice oxygen in a series of steps that complete a Mars-van Krevelen redox cycle.^{1,19} These steps are consistent with the kinetic dependence of reaction rates on CH₃OH and O₂ partial pressures, as we discuss next.

Figure 3 shows CH₃OH oxidative dehydrogenation rates and product selectivities as a function of CH₃OH partial pressure (0–40 kPa) at 393 K and 9 kPa O₂ on RuO₂/TiO₂ (3.1 Ru/nm²). At similar conversions (~10%), ODH rates first increased almost linearly with increasing CH₃OH 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 CH₃OH-derived reactive intermediates (e.g., CH₃O⁻) as CH₃OH 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 CH₃OH partial pressures; HCHO selectivities concurrently decreased from 42.5 to 10.3%. CO_x selectivities were very

TABLE 2: Methanol Oxidation Rates and Selectivities on Physical Mixtures of RuO₂/TiO₂ + Al₂O₃, and RuO₂/Al₂O₃ + TiO₂ at a Mass Ratio of 1/3, and for Comparison on RuO₂/TiO₂ (6.2 Ru/nm²) and RuO₂/Al₂O₃ (1.3 Ru/nm²)^a

catalyst (mass ratio)	CH ₃ OH conversion rate (mol/g-atom Ru-h)	calculated ODH rate ^b (mol/g-atom Ru-h)	selectivity (% carbon)			
			HCHO	MF	DMM	CO _x
RuO ₂ /TiO ₂ + Al ₂ O ₃ (1/3)	12.6	6.1	11.6	45.2	41.9	1.4
RuO ₂ /Al ₂ O ₃ + TiO ₂ (1/3)	13.8	6.5	6.2	60.4	32.6	0.8
RuO ₂ /TiO ₂	10.9	6.6	24.9	65.2	8.9	1.0
RuO ₂ /Al ₂ O ₃	14.9	6.8	11.6	30.1	57.4	1.0

^a 393 K, 4% CH₃OH, 9% O₂, 1% N₂, ~20% CH₃OH conversion. ^b Rate for primary CH₃OH oxidative dehydrogenation to HCHO.

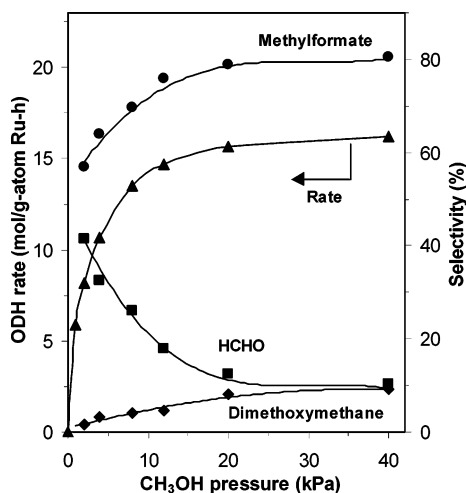


Figure 3. Effect of methanol partial pressure on rates of oxidative dehydrogenation (per g-atom Ru) of CH₃OH to HCHO and selectivities at 393 K on RuO₂/TiO₂ (3.1 Ru/nm², 9 kPa O₂, 1 kPa N₂, balance He, CH₃OH conversion: ~10%).

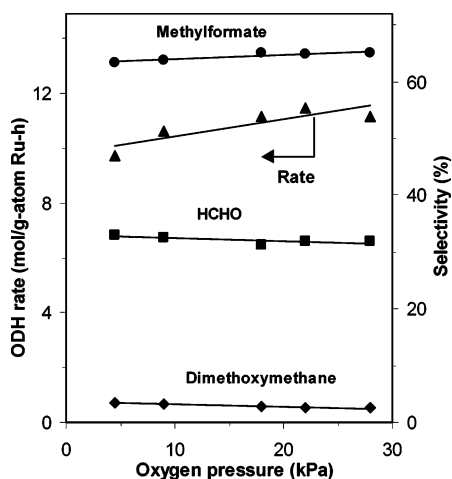


Figure 4. Effect of oxygen partial pressure on rates of oxidative dehydrogenation (per g-atom Ru) of CH₃OH to HCHO and selectivities at 393 K on RuO₂/TiO₂ (3.1 Ru/nm², 4 kPa CH₃OH, balance He, CH₃OH conversion: ~10%).

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 CH₃OH-derived intermediates (Scheme 1), the rate of which depends on pressure more sensitively than initial HCHO synthesis rates.

Figure 4 shows the effects of O₂ partial pressure on oxidative CH₃OH dehydrogenation rates and product selectivities on RuO₂/TiO₂ (3.1 Ru/nm²) (393 K, 4 kPa CH₃OH). Reaction rates and selectivities were essentially unaffected by O₂ partial pressures (4.5–28 kPa). Such kinetic insensitivity to O₂ concentrations is typical of catalytic oxidation reactions pro-

TABLE 3: Kinetic Isotopic Effects for Methanol Oxidation on RuO₂/TiO₂ at 393 K^a

	CH ₃ OH conversion rate (mol/g-atom Ru-h)	calculated ODH rate ^b (mol/g-atom Ru-h)	MF synthesis rate (mol/g-atom Ru-h)
CH ₃ OH	16.3	10.5	11.4
CH ₃ OD	15.8	10.3	10.9
CD ₃ OD	6.5	4.4	3.7
$k_{\text{CH}_3\text{OH}}/k_{\text{CH}_3\text{OD}}$	1.03	1.02 (1.11) ^c	1.05
$k_{\text{CH}_3\text{OH}}/k_{\text{CD}_3\text{OD}}$	2.51	2.38 (3.33) ^c	3.07

^a 3.1 Ru/nm², 4% methanol, 9% O₂, ~10% methanol conversion.

^b Rate for primary methanol oxidative dehydrogenation to formaldehyde.

^c Data in parentheses were obtained on Fe₂(MoO₄)₃ at 473 K from ref 20.

ceeding via Mars-van Krevelen mechanism¹⁹ using lattice oxygen atoms on nearly stoichiometric surfaces, a finding confirmed by anaerobic transient CH₃OH reaction data reported below. Measurements at 20 kPa CH₃OH and varying O₂ concentrations led to essentially identical trends and conclusions.

Methanol molecules deuterated at all positions (CD₃OD) or only at the hydroxyl group (CH₃OD) were used to probe the kinetic relevance of elementary steps involving methoxide formation and H-abstraction from methoxide during CH₃OH oxidation on RuO_x domains. Kinetically relevant methanol dissociation steps would lead to normal kinetic isotope effects (KIE) for both CH₃OD and CD₃OD reactants. In contrast, the kinetic relevance of H-abstraction from CH₃O⁻ to form HCHO would lead to normal KIE for CD₃OD and weak thermodynamic isotope effects for CH₃OD.

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 O₂ on RuO₂/TiO₂ at 393 K. At these conditions, oxidation rates are linear in methanol concentration and independent of O₂ pressure (Figures 3 and 4). CD₃OD 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 CH₃OD was used instead of CH₃OH 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 CH₃OH dehydrogenation on RuO_x domains.

These CD₃OD and CH₃OD kinetic isotope effects resemble those measured for HCHO synthesis on Fe₂(MoO₄)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. CD₃OD KIE values on RuO_x domains are smaller than on Fe₂(MoO₄)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

catalysts; C–D and C–H bonds are consequently less disrupted within the activated complex along the reaction coordinate on RuO_x than on $\text{Fe}_2(\text{MoO}_4)_3$ 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 RuO_x 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 $\text{Fe}_2(\text{MoO}_4)_3$.

The involvement of lattice oxygen atoms in CH_3OH oxidation was confirmed by transient CH_3OH reactions without O_2 co-reactants on $\text{RuO}_2/\text{TiO}_2$ 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 $\text{CH}_3\text{OH}-\text{O}_2$ mixtures were carried out for 1.5 h, and then introducing a CH_3OH -containing stream without O_2 co-reactants. Figure 5a,b show that removal of O_2 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 CH_3OH 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 O_2 into the CH_3OH stream led to the rapid and complete recovery of the initial catalytic CH_3OH 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 RuO_2 clusters after reduction in H_2 (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 RuO_2 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 RuO_2 domains dispersed on TiO_2 before methanol oxidation catalysis was suppressed; similar oxygen removal stoichiometries ($\text{O}/\text{Ru} = 1.1-1.3$) were observed for RuO_x domains supported on ZrO_2 and Al_2O_3 . These values indicate that RuO_2 species prevalent during steady-state catalysis become unreactive as lattice oxygen is removed and the system undergoes a two-electron reduction of Ru^{4+} centers ($\text{Ru}^{4+} \rightarrow \text{Ru}^{2+}$) during anaerobic CH_3OH reactions; they also show that reduction to Ru^0 does not occur during either aerobic or anaerobic oxidation of CH_3OH at conditions required for these reactions and that RuO species are unreactive in methanol activation at these

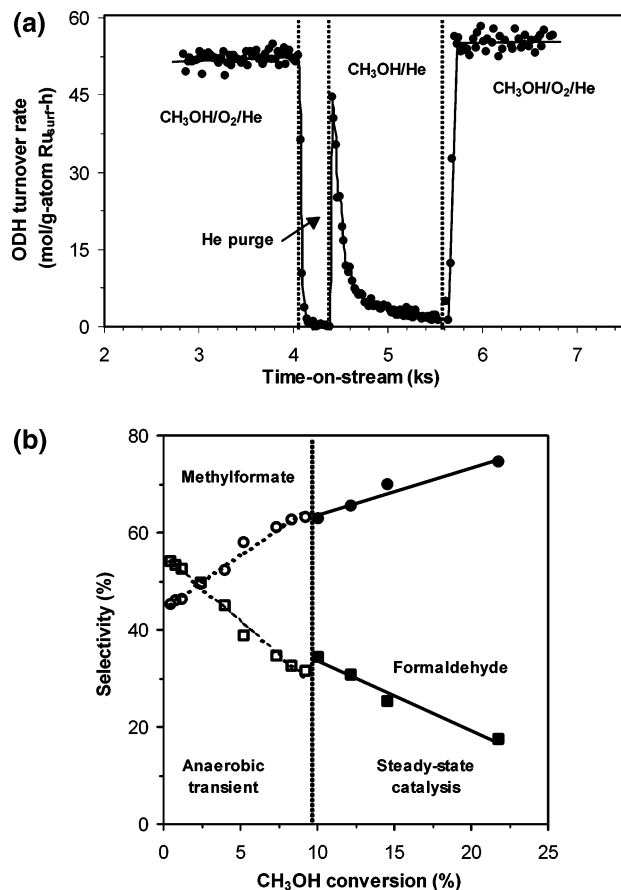


Figure 5. Oxidative dehydrogenation turnover rates (a) and HCHO and MF selectivities (b) during steady-state catalysis and during transient anaerobic oxidation of CH_3OH on $\text{RuO}_2/\text{TiO}_2$. Conversion was varied by changing space velocity during steady-state catalysis and by allowing lattice oxygen depletion during anaerobic transients (3.1 Ru/nm^2 , 4 kPa CH_3OH , 9 kPa O_2 or no O_2 , balance He).

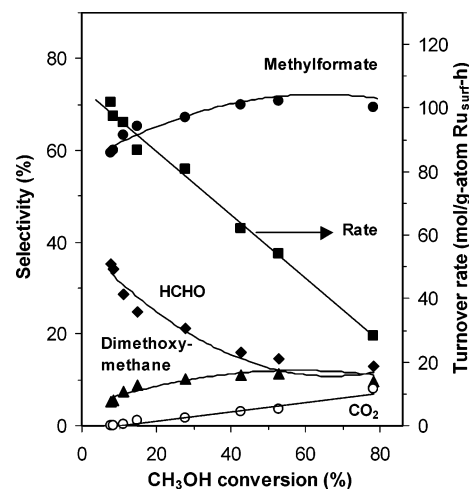


Figure 6. CH_3OH conversion turnover rates and selectivities as a function of CH_3OH conversion changed by varying residence time (18–610 g-atom Ru-s/mol CH_3OH) at 393 K on $\text{RuO}_2/\text{TiO}_2$ (6.2 Ru/nm^2 , fractional Ru dispersion: 0.125, 4 kPa CH_3OH , 9 kPa O_2 , 1 kPa N_2 , balance He).

reaction conditions. These conclusions are consistent with the weak kinetic consequences of O_2 concentration on catalytic CH_3OH oxidation rates (Figure 4).

Figure 6 shows the effects of CH_3OH conversion, changed by varying residence time, on CH_3OH conversion turnover rates and product selectivities at 393 K on $\text{RuO}_2/\text{TiO}_2$ (6.2 Ru/nm^2).

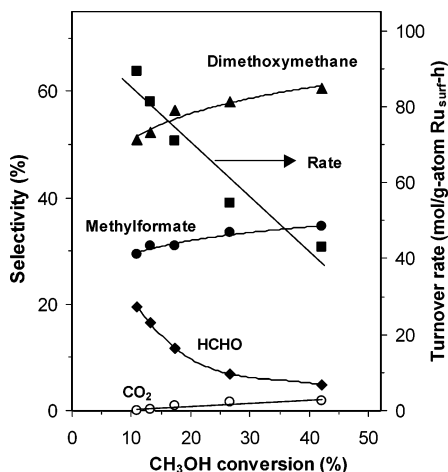


Figure 7. CH_3OH conversion turnover rates and selectivities as a function of CH_3OH conversion changed by varying residence time (35–290 g-atom Ru-s/mol CH_3OH) at 393 K on $\text{RuO}_2/\text{Al}_2\text{O}_3$ (1.3 Ru/nm^2 , fractional Ru dispersion: 0.209, 4 kPa CH_3OH , 9 kPa O_2 , 1 kPa N_2 , balance He).

Turnover rates decreased with increasing residence time (and CH_3OH 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_3OH 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_3OH , but also via readsorption 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_3OH reactants. No CO was detected at any reaction conditions, as expected from the high CO oxidation rates reported on RuO_x surfaces.¹¹ Similar residence time effects on CH_3OH conversion turnover rates and selectivities were observed on $\text{RuO}_2/\text{Al}_2\text{O}_3$ (1.3 Ru/nm^2), on which DMM instead of MF is preferentially formed (Figure 7). This indicates that CH_3OH oxidative conversion proceeds via similar reaction pathways (Scheme 1) on RuO_x domains dispersed on both supports.

These residence time and support effects suggest that CH_3OH initially forms HCHO, which then reacts to form DMM and MF via methoxymethanol ($\text{CH}_3\text{OCH}_2\text{OH}$) intermediates or hemiacetal adsorbed species.⁷ HCHO acetalization with nucleophilic methoxides (CH_3O^-) can lead to $\text{CH}_3\text{OCH}_2\text{OH}$ intermediates,^{5,21–23} which condense with CH_3OH on acid sites to form DMM in equilibrium-constrained reactions, or dehydrogenate on redox sites to form MF (and H_2O) in thermodynamically favored reactions catalyzed by either RuO_x domains or active supports. These reactions occur, at least in part, on support surfaces containing acid or dehydrogenation sites, leading to the observed effects of supports on selectivity. Molecular simulations have suggested that $\text{CH}_3\text{OCH}_2\text{OH}$ dehydrogenation forms MF much faster than HCHO dimerization (Tischenko reaction) or CH_3OH reactions with adsorbed formate (HCOO^-) on V_2O_5 .²² $\text{CH}_3\text{OCH}_2\text{OH}$ was not detected during our study of CH_3OH reactions on RuO_x , apparently because of its unfavorable equilibrium and high reactivity.

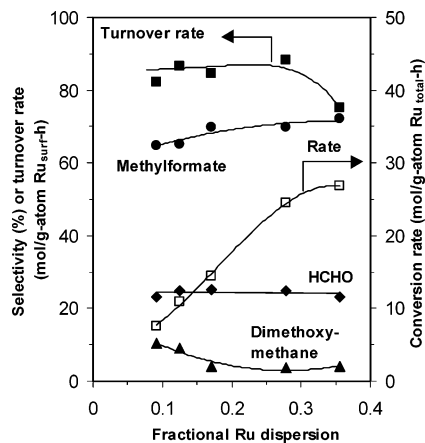


Figure 8. CH_3OH oxidation rates and selectivities as a function of fractional Ru dispersion at 393 K on $\text{RuO}_2/\text{TiO}_2$ at conversions of ~15–20% (0.8–13.1 Ru/nm^2 , 4 kPa CH_3OH , 9 kPa O_2 , 1 kPa N_2 , balance He).

CH_3OH 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_3OH 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_x surfaces, which are required to form the required HCHO intermediates.

These RuO_x catalysts are compared with previously reported CH_3OH oxidation catalysts in Table 1. $\text{V}_2\text{O}_5\text{-TiO}_2$ prepared by coprecipitation and $\text{MoO}_3/\text{SiO}_2$ prepared via impregnation method catalyze MF synthesis with high selectivity (~80 and 95.9%, at ~75 and 5% conversion, respectively);^{2,5} reaction rates are much lower than on RuO_x catalysts, even at the higher temperatures of these previous studies. $\text{RuO}_2/\text{TiO}_2$ (4.1 wt %), gave reaction rates of 4.8 mol/g-atom $\text{Ru}_{\text{total}}\text{-h}$ at 78.2% CH_3OH conversion and 393 K (Figure 6), which exceed those reported on $\text{V}_2\text{O}_5\text{-TiO}_2$ (~3.4 mol/g-atom $\text{V}_{\text{total}}\text{-h}$ at ~80% CH_3OH 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_3OH) at 453 K in another study.⁴

$\text{RuO}_2/\text{SiO}_2$ (1.1 Ru/nm^2) and $\text{RuO}_2/\text{SnO}_2$ (2.5 Ru/nm^2) also convert ethanol- O_2 reactant mixtures with high rates and selectivity to form acetaldehyde, diethoxyethane (acetal), and ethyl acetate at 393 K (Table 4). Neither diethyl ether nor CO_x 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 $\text{C}_2\text{H}_5\text{OH}$ pressure increased from 2 to 40 kPa, products shifted from acetaldehyde (97.3 to 17.6%), formed in primary oxidative dehydrogenation steps, to diethoxyethane (0 to 81%), which forms via condensation reactions favored kinetically and thermodynamically at higher $\text{C}_2\text{H}_5\text{OH}$ pressures (Table 4). Residence time effects on selectivities showed that reaction

TABLE 4: Ethanol Oxidation Rates and Selectivities on RuO₂/SiO₂ (1.1 Ru/nm²) and RuO₂/SnO₂ (2.5 Ru/nm²) at 393 K^a

catalyst	C ₂ H ₅ OH pressure (kPa)	ethanol conversion turnover rate (mol/g-atom Ru _{surf} -h)	ODH turnover rate ^b (mol/g-atom Ru _{total} -h)	selectivity (%)			
				acetaldehyde	ethyl acetate	acetal	CO _x
RuO ₂ /SiO ₂	4	30.6	30.1	97.1	0	2.9	0
RuO ₂ /SnO ₂	2	51.6	50.9	97.3	2.7	0	0
RuO ₂ /SnO ₂	4	76.3	73.2	93.4	2.0	4.6	0
RuO ₂ /SnO ₂	10	108.6	83.5	64.8	2.2	33.0	0
RuO ₂ /SnO ₂	20	157.4	86.1	30.8	1.2	68.0	0
RuO ₂ /SnO ₂	40	188.9	85.9	17.6	1.4	81.0	0

^a 9 kPa O₂, 1 kPa N₂, ~10–15% C₂H₅OH conversion. ^b Rate for primary oxidative dehydrogenation of C₂H₅OH to acetaldehyde.

pathways involve initial acetaldehyde formation in oxidative dehydrogenation steps and subsequent acetalization reactions of acetaldehyde and ethanol to form diethoxyethane.

To our knowledge, these supported RuO_x 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 ~373 K.^{12–14} Idriss and co-workers²⁴ adsorbed methanol on RuO₂ and only ~0.6% of the adsorbed methanol formed methylformate in stoichiometric reactions of methanol preadsorbed at ambient temperature. In this study, the reduction of RuO₂ to Ru metal at 573 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 RuO_x-based materials in selective oxidation reactions of CH₃OH and C₂H₅OH.

In marked contrast, the supported RuO₂ domains reported here gave unprecedented CH₃OH conversion rates and allow CH₃OH oxidation reactions to proceed at significant rates near ambient temperatures with >99% combined selectivities to useful formaldehyde, methylformate, and dimethoxymethane 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 diethoxyethane (acetal) and acetaldehyde 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 measure-

ments 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 dimethoxymethane 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 acetaldehyde and diethoxyethane at 300–400 K.

Acknowledgment. The authors dedicate this manuscript to Professor Michel Boudart on the occasion of his 80th birthday and acknowledge with thanks his pioneering contributions to the science and applications of catalysis, as well as his mentorship of several generations of students, colleagues, and friends. This work was supported by BP as part of the Methane Conversion Cooperative Research Program at the University of California at Berkeley. This work was also supported in part by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. The authors acknowledge the assistance of Ms. Patricia Cheung with the anaerobic transient experiments, as well as helpful technical discussions with Dr. Theo Fleisch of BP during the early stages of this study.

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