Structures and Properties of Zirconia-Supported Ruthenium Oxide Catalysts for the Selective Oxidation of Methanol to Methyl Formate

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The effects of RuO₄ structure on the selective oxidation of methanol to methyl formate (MF) at low temperatures were examined on ZrO₂-supported RuO₄ catalysts with a range of Ru surface densities (0.2–3.8 Ru/nm²). Their structure was characterized using complementary methods (X-ray diffraction, Raman and X-ray photoelectron spectra, and reduction dynamics). The structure and reactivity of RuO₄ species change markedly with Ru surface density. RuO₄ existed preferentially as RuO₄⁻²⁶ species below 0.4 Ru/nm², probably as isolated Zr(RuO₄)₂ interacting with ZrO₂ surfaces. At higher surface densities, highly dispersed RuO₂ domains coexisted with RuO₄⁻²⁶ and ultimately formed small clusters and became the prevalent form of RuO₄ above 1.9 Ru/nm². CH₃OH oxidation rates per Ru atom and per exposed Ru atom (turnover rates) decreased with increasing Ru surface density. This behavior reflects a decrease in intrinsic reactivity as RuO₄ evolved from RuO₄⁻²⁶ to RuO₂, a conclusion confirmed by transient anaerobic reactions of CH₃OH and by an excellent correlation between reaction rates and the number of RuO₂⁻²⁶ species in RuO₄/ZrO₂ catalysts. The high intrinsic reactivity of RuO₂⁻²⁶ structures reflects their higher reducibility, which favors the reduction process required for the kinetically relevant C–H bond activation step in redox cycles using lattice oxygen atoms involved in CH₃OH oxidation catalysis. These more reactive RuO₂⁻²⁶ species and the more exposed ZrO₂ surfaces on samples with low Ru surface density led to high MF selectivities (e.g. ~96% at 0.2 Ru/nm²). These findings provide guidance for the design of more effective catalysts for the oxidation of alkanes, alkenes, and alcohols by the synthesis of denser Zr(RuO₄)₂ monolayers on ZrO₂ and other high surface area supports.

Introduction

Methyl formate (HCOOCH₃; MF) is an important chemical precursor to other chemicals, such as carboxylic acids, esters, and formamides,¹⁻⁴ and in the synthesis of ethylene glycol. MF synthesis currently involves the carboxylation of methanol with CO using strong liquid bases such as sodium methoxide or nonoxidative dehydrogenation of methanol on CuO-based catalysts.²⁻⁵ These processes involve waste byproducts, energy inefficiencies, or thermodynamic constraints. Oxidation processes are catalyzed by dispersed VOₓ and MoOₓ domains with favorable thermodynamics and modest MF selectivities, but improvements in reaction rates and selectivities are required for industrial practice.

The oxidation of methanol to MF on VOₓ and MoOₓ catalysts involves rate-determining C–H bond activation steps to form HCHO and their subsequent reactions with intermediates derived from CH₃OH or HCHO,¹⁻⁸,⁹ which also form COₓ (CO + CO₂) at the conditions required for HCHO formation. RuO₄ domains dispersed on ZrO₂, TiO₂, SnO₂, Al₂O₃, or SiO₂ catalyze CH₃OH oxidation to HCHO at unprecedented low temperatures (330–400 K). HCHO then converts to dimethoxymethane (DMM) or MF via methoxyethanol or hemiacetal intermediates (Scheme 1).¹⁰ Supports influence secondary reactions of HCHO and other intermediates and also the redox properties of RuO₄ domains. ZrO₂ supports led to the highest MF rates and yields, but also to the highest selectivity to undesired CO₂.¹⁰ The specific control of structure and atomic connectivity in dispersed oxides remains a critical challenge in the improvement of catalytic performance.¹¹⁻¹⁷ Here, we probe the relationship between the structure of RuO₄ domains supported on ZrO₂ and their redox and catalytic properties during the oxidation of methanol to MF, with the aim to design more effective catalysts for MF synthesis. The structure of RuO₄ domains with a range of Ru surface densities (~0.2–4 Ru/nm²) was characterized by X-ray diffraction (XRD) and X-ray photoelectron (XPS) and Raman spectroscopies. The reducibility of RuO₄ species was probed by temperature-programmed reduction (TPR) in H₂. RuO₂⁻²⁶ structures, containing Ru⁶⁺ and likely present as Zr-RuO₄₂, were detected and found to be active and selective for MF synthesis.

Scheme 1: Primary and Secondary CH₃OH Reaction Pathways on Supported RuO₄ Catalysts

<table>
<thead>
<tr>
<th>CH₃OH</th>
<th>HCHO</th>
<th>CH₂OCH₂OH (DMM)</th>
<th>CH₃OCH₂OCH₃ (DMM)</th>
<th>HCOOCH₃(MF)</th>
</tr>
</thead>
</table>

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Experimental Methods

Synthesis and Characterization of Catalysts. ZrO$_2$-supported RuO$_x$ catalysts (denoted RuO$_x$/ZrO$_2$) were prepared by incipient wetness impregnation of ZrO$_2$ with an aqueous solution of Ru(NO)$_3$(NO$_3$)$_3$ (Alfa Aesar, 31.3% Ru) at 298 K for 3 h. The Ru concentrations in the impregnating solution were varied to change the Ru content. Impregnated samples were treated in ambient air at 398 K overnight and then at 673 K for 6 h. ZrO$_2$ was prepared by hydrolysis of aqueous ZrOCl$_2$·8H$_2$O (Beijing Chemicals, Beijing, China) with excess NH$_3$·H$_2$O (14 N, Beijing Chemicals), followed by washing of the precipitates with deionized water until Cl$^-$ was no longer detected in the filtrate. These precipitates were dried at 393 K overnight and then treated at 673 K in ambient air for 6 h.

BET surface areas were measured by $N_2$ physisorption at its normal boiling point (at 101 kPa) using an ASAP 2010 analyzer (Micromeritics) after samples were treated at 393 K for 4 h in dynamic vacuum (~2.66 Pa).

XRD patterns were obtained in the 2θ range of 10°–80° on a Rigaku D/MAX-2000 diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$) operated at 30 kV and 100 mA. The average particle sizes ($D$) were estimated by the Scherrer equation,$^{18}$

$$D = 0.9\lambda/\beta \cos \theta,$$

where $\theta$ is the diffraction angle and $\beta$ is the full width at half-maximum (fwhm).

XPS spectra were measured using an Axis Ultra spectrometer (Kratos, Manchester, U.K.) and monochromatic Al K$_\alpha$ (1486.71 eV) radiation at a source power of 225 W (15 mA, 15 kV). The binding energies were referred to a C$_1s$ peak at 284.8 eV for adventitious carbon. Surface compositions were calculated from peak intensities using the sensitivity factors provided by the spectrometer.

Raman spectra were measured at ambient temperature using a Renishaw 1000 spectrometer equipped with a He–Ne laser at a wavelength of 632.8 nm (model 127-25RP) and a CCD camera. The resolution was 2 cm$^{-1}$, and the laser power was set to 1.2 mW. Raman shifts for all of the samples were measured in the range of 100–1500 cm$^{-1}$ in ambient air.

Methanol Oxidation Rates and Selectivities. Methanol oxidation rate and selectivity data were measured in a packed-bed quartz microreactor (6 mm i.d.) using catalyst powders (80–100 mesh, 0.2 g), which were diluted with quartz (~2 g) to prevent temperature gradients and hot spots, and treated in 10% O$_2$/N$_2$ (Beijing Huayuan, 99.999%) flow (30 cm$^3$ min$^{-1}$) at 673 K for 1 h before catalytic measurements. Reactants consisted of 3.5 kPa of CH$_3$OH (Beijing Chemicals, 99.99%) and 10 kPa of O$_2$ (Beijing Huayuan, 99.99%) with 86.5 kPa of balance N$_2$ (Beijing Huayuan, 99.99%). All transfer lines between the reactor and gas chromatograph were kept above 393 K to avoid condensation of the products. Reactants and products were analyzed by on-line gas chromatography (Shimadzu 100 GC) using two packed columns (Carbosieve B, O$_2$, N$_2$, and CO; Porapak, other components) connected to thermal conductivity detectors (TCD). Steady-state kinetic data were collected after 2 h on-stream. Selectivities are reported on a carbon basis and rates as molar CH$_3$OH conversion rates per mole of Ru per hour.

Dynamics of Reduction of Dispersed RuO$_x$ Domains in H$_2$. H$_2$ temperature-programmed reduction (TPR) data were measured using a flow unit (TPS0000, Tianjin Xianquan). Samples were placed within a quartz cell, and the temperature was increased linearly from 293 to 773 K at 10 K min$^{-1}$ in flowing 5% H$_2$/N$_2$ (50 cm$^3$ min$^{-1}$; Beijing Huayuan, certified mixture). The amount of sample was varied so as to keep similar amounts of Ru (ca. 4 mg) within the cell for samples with various Ru contents. The H$_2$ concentration in the effluent was measured by on-line mass spectrometry (Hiden HPR 20). The spectrometer response was calibrated by reducing CuO powders (Beijing Chemicals, >99.0%) in H$_2$ (5% H$_2$/N$_2$).

Results and Discussion

Catalyst Characterization. BET surface areas and nominal RuO$_x$ surface densities are reported in Table 1 for all RuO$_x$/ZrO$_2$ samples. The nominal RuO$_x$ surface densities (Ru/nm$^2$) were estimated from the Ru content and BET surface area. The surface areas, specifically for the samples with Ru surface density above 1.9 Ru/nm$^2$, decreased slightly with increasing Ru content and surface density, as a result of the deposition of dispersed RuO$_x$ on top of ZrO$_2$ surfaces.

Figure 1 shows diffraction patterns for ZrO$_2$-supported RuO$_x$ catalysts with Ru surface densities of 0.2–3.8 Ru/nm$^2$ and for pure ZrO$_2$ and RuO$_x$ mixture. The amount of sample was varied so as to keep similar amounts of Ru (ca. 4 mg) within the cell for samples with various Ru contents. The H$_2$ concentration in the effluent was measured by on-line mass spectrometry (Hiden HPR 20).
concentrations (< 1.9 Ru/nm²) showed only monoclinic ZrO₂ and no crystalline RuOₓ, suggesting that RuOₓ species were well dispersed on ZrO₂. RuO₂ diffraction lines appeared at 1.9 Ru/nm² and became more intense as RuO₂ crystallites formed with increasing Ru surface density. The line breadth for the diffraction line at 2θ = 28.1° was used to estimate ZrO₂ crystallite sizes, which ranged from 6.8 to 7.9 nm (Table 1), irrespective of RuOₓ surface density.

Raman spectra (Figure 2) confirmed that only monoclinic ZrO₂ was present in the ZrO₂ support. Crystalline RuO₂ showed three Raman bands at 521, 640, and 704 cm⁻¹, corresponding to E₅, A₁g, and B₂g modes;²⁰ the band at 521 cm⁻¹ does not overlap with the ZrO₂ bands, and it can be used to detect crystalline RuO₂ in RuOₓ/ZrO₂. It was not detected for Ru surface densities of 0.2 and 0.4 Ru/nm², but emerged as a weak shoulder at 0.9 Ru/nm² and became stronger above 1.9 Ru/nm², suggesting that crystalline RuO₂ forms at surface densities > 0.9 Ru/nm². The observed red shift of this band relative to bulk crystalline RuO₂ appears to reflect the small size of supported RuO₂ crystallites.²⁰ A band was observed at ~993 cm⁻¹ in all RuOₓ/ZrO₂ samples. Taken together with the XPS spectra and stoichiometric H₂ reduction data, this new band can be tentatively assigned to terminal Ru=O stretching vibrations for RuO₂⁻² species (Ru⁶⁺) probably present in Zr(RuO₄)₂ structures formed via reactions of ZrO₂ with RuOₓ during treatment in air at 673 K.

The presence of RuO₂ and RuO₂⁻² species in RuOₓ/ZrO₂ was confirmed by XPS. At low Ru surface densities (e.g., 0.2 Ru/nm²), only a Ru3d₅/₂ signal with a binding energy of 282.7 eV corresponding to Ru⁶⁺ was observed (Table 1). The structure of the Ru⁶⁺ species remains unclear, but it is unlikely to be RuO₂ because of its thermodynamic instability and high volatility. This supports the presence of only RuO₂⁻² species in this sample. As Ru surface density increased to 0.4 Ru/nm², RuO₂ structures formed, as shown by a feature with a Ru3d₅/₂ binding energy of 281.0 eV.²¹ The surface Ru⁶⁺/(Ru⁶⁺ + Ru⁴⁺) atomic ratio was estimated to be 0.90 for this sample; this value decreased monotonically to 0.39 as the surface density increased to 3.8 Ru/nm² (Figure 3). Thus, the fraction of the Ru present as Ru⁴⁺ increases with increasing Ru surface density at ZrO₂ surfaces.

Figure 4 shows surface Ru/Zr atomic ratios (including Ru⁴⁺ and Ru⁶⁺) for these samples as a function of Ru surface density. These Ru/Zr ratios were initially proportional to the Ru surface density and then increased more slowly for surface densities above 1.9 Ru/nm². The initial linear increase indicates that RuO₂ species are highly dispersed on ZrO₂ at surface densities below 1.9 Ru/nm² and then aggregate to form RuO₂ crystallites at higher surface coverages, as also observed by XRD and Raman. Such behavior is consistent with Stranski–Krastanov (SK) growth mechanisms,²² in which RuO₂⁻² and RuO₂ are dispersed up to 0.9 Ru/nm² and then three-dimensional clusters form. The “saturation” coverage at which crystallites form is much smaller than the theoretical monolayer coverage of ~4–5 Ru/nm² [for the RuO₂ (110) plane].¹⁰ RuO₂ dispersions were estimated from...
surface Ru/Zr ratios measured by XPS using a method previously reported. Figure 4 shows that fractional dispersions of toal RuO$_x$ species were essentially constant at near unity (0.95−0.98) up to 0.9 Ru/nm$^2$ and then decreased monotonically to a value of 0.34 as surface densities reached 3.8 Ru/nm$^2$. This is consistent with the growth of RuO$_2$ crystallites, as shown from the respective dispersions of the coexisting RuO$_4^{2−}$ and RuO$_2$ species. RuO$_2$ dispersions decreased sharply above 0.9 Ru/nm$^2$, but RuO$_4^{2−}$ species remained highly dispersed (0.85) even at 3.8 Ru/nm$^2$, apparently because of their strong interactions with ZrO$_2$ surfaces.

The bulk composition and oxidation state of RuO$_x$ species in RuO$_x$/ZrO$_2$ were examined by temperature-programmed reduction (TPR) using H$_2$ as the reductant. Only one reduction peak (at ~346 K) was present for the sample with 0.2 Ru/nm$^2$ (Figure 5), and the reduction stoichiometry was 2.95 H$_2$/Ru, similar to the value expected for stoichiometric reduction of RuO$_4^{2−}$ to Ru$^0$:

$$\text{Zr(RuO}_4\text{)}_2 + 3 \text{H}_2 \rightarrow \text{ZrO}_2 + \text{Ru} + 3 \text{H}_2\text{O}$$

Another reduction peak appeared at a surface density of 0.4 Ru/nm$^2$ as a shoulder (at ~400 K). Its reduction stoichiometry is consistent with the reduction of RuO$_2$ to Ru metal. This RuO$_2$ reduction feature became more intense relative to the RuO$_4^{2−}$ reduction peak with increasing Ru surface density (Figure 5). This can also be seen clearly from the bulk Ru$^{4+/3+}$/(Ru$^{6+/4+}$ + Ru$^{6+/4+}$) atomic ratios presented in Figure 3, showing that RuO$_2$ species become prevalent on ZrO$_2$ as Ru surface density increases.

Taken together, these characterization results indicate that RuO$_x$ species evolve from dispersed RuO$_4^{2−}$ species, probably in Zr(RuO$_4$)$_2$ structures, at Ru surface densities below 0.4 Ru/nm$^2$ to dispersed and three-dimensional RuO$_2$ domains at Ru surface densities $>1.9$ Ru/nm$^2$.

**Methanol Oxidation Rates and Selectivities on RuO$_x$/ZrO$_2$ Catalysts.** Figure 6 shows methanol oxidation rates (per Ru atom) and selectivities at 373 K as a function of Ru surface density on RuO$_x$/ZrO$_2$ catalysts. The rates and selectivities were compared at similar CH$_3$OH conversions (~15%) because the extent of CH$_3$OH conversion influences the relative contributions of primary and secondary reactions. The rates and selectivities remained essentially unchanged with time (for 48 h) on all samples. CH$_3$OH oxidation rates (per Ru atom) decreased sharply as Ru surface density increased from 0.2 to 1.9 Ru/nm$^2$ and then more gradually at higher Ru surface densities. MF selectivities decreased monotonically from 96.6 to 72.6% with increasing Ru surface density (from 0.2 to 3.8 Ru/nm$^2$) while CO$_2$ selectivities concurrently increased (from 0.8 to 23.6%). HCHO selectivities were low, which initially increased slightly with increasing Ru surface density, and then reached a constant value of 4.1% above 0.4 Ru/nm$^2$ (Figure 6). By referring to the structural evolution of the RuO$_x$ domains with the Ru surface density and dispersion, these results indicate that the dispersed RuO$_4^{2−}$ species seem to be more selective for the MF synthesis relative to the RuO$_2$ species. The higher MF selectivities on samples with low Ru surface density may also be due to their higher exposed ZrO$_2$ surface areas involved in the conversion of HCHO intermediates to MF.

At Ru surface densities below 1.9 Ru/nm$^2$, especially for 0.2−0.9 Ru/nm$^2$, nearly all of the Ru atoms in RuO$_x$ domains are accessible to reactants. For these samples, rates per Ru atom correspond to turnover rates and reflect the intrinsic reactivity of exposed RuO$_x$ species. Therefore, the decrease in the rates in the Ru surface density range from 0.2 to 0.9 Ru/nm$^2$ reflects a decrease in reactivity as a result of the structural change from RuO$_4^{2−}$ species to RuO$_2$ species with lower reactivity. Above 1.9 Ru/nm$^2$, dispersed and crystalline RuO$_2$ domains became the prevalent structures. The observed decrease in methanol oxidation rates (per Ru atom) with increasing Ru surface density may reflect either the lower intrinsic reactivity of RuO$_2$ domains relative to RuO$_4^{2−}$ or merely their lower dispersion. Turnover rates [i.e., rates normalized by exposed Ru atoms (including both Ru$^{4+/3+}$ and Ru$^{6+/4+}$ species) using Ru dispersion data in Figure 4] still decreased with increasing Ru surface densities (Figure 7), suggesting that the intrinsic reactivity for RuO$_4^{2−}$ is higher than that for RuO$_2$ domains. In this case, CH$_3$OH oxidation rates (per Ru atom) should increase in parallel with the RuO$_4^{2−}$ fractions in these samples, as indeed shown by the data in Figure 8.

**Figure 5.** H$_2$ temperature-programmed reduction profiles for ZrO$_2$-supported RuO$_x$ catalysts with Ru surface densities of 0.2−3.8 Ru/nm$^2$ treated at 673 K in air.

**Figure 6.** CH$_3$OH oxidation rates normalized per Ru atom and selectivities as a function of Ru surface density at 373 K on RuO$_x$/ZrO$_2$ catalysts at conversions of ~15% (0.2−3.8 Ru/nm$^2$, 3.5 kPa of CH$_3$OH, 10 kPa of O$_2$, balance N$_2$).
The higher intrinsic reactivity of RuO$_4^{2-}$ relative to RuO$_2$ is consistent with its more reducible nature. The peak temperature for RuO$_4^{2-}$ reduction was about 50 K below that for RuO$_2$ reduction (Figure 5). The more reducible nature of RuO$_4^{2-}$ appears to reflect its higher Ru oxidation state and the atomic connectivity between Ru$^{6+}$ and the less electronegative nature of Zr$^{4+}$ cations in Zr(RuO$_4$)$_2$ relative to Ru cations in oligomeric RuO$_x$ structures, which may favor electron transfer and activation of Ru=O bonds during reduction in H$_2$ and CH$_3$OH oxidation catalysis compared with RuO$_2$ structures. Clearly, Ru$^{6+}$ species are more reducible than Ru$^{4+}$, but cannot be stabilized against autoreduction without the formation of mixed structures with ZrO$_2$. A correlation between reducibility and methanol oxidation rates is consistent with a Mars–van Krevelen cycle. It has been previously demonstrated for CH$_3$OH oxidation using kinetic and isotopic methods, which showed that HCHO and MF form on RuO$_x$ domains via redox cycles involving lattice oxygen atoms and kinetically relevant C–H bond activation steps. More facile reduction of the RuO$_2$ domains leads to faster CH$_3$OH oxidation turnovers, because transition states required for C–H bond activation steps involve electron transfer and the local reduction of cationic centers in reducible metal oxides. Similar reactivity–reducibility correlations were observed for selective oxidation reactions of alcohols, dimethyl ether, and light alkanes on MoO$_x$- and VO$_x$-based materials, which also catalyze oxidation reactions via Mars–van Krevelen redox cycles.

The higher intrinsic reactivity of RuO$_4^{2-}$ structures was also evident from transient anaerobic CH$_3$OH reactions on dispersed RuO$_2$ and RuO$_2$ structures that coexist in nearly equimolar amounts in the sample with 0.9 Ru/nm$^2$. These transient experiments were conducted by controlled exposure of samples to CH$_3$OH to attain a given extent of reduction via reactions between RuO$_x$ domains and CH$_3$OH under anaerobic conditions. Samples were then reduced in H$_2$ by increasing the temperature from 298 to 673 K after removal of CH$_3$OH from the bed with a pure N$_2$ purge. Figure 9 shows that exposure to a CH$_3$OH/N$_2$ (3.5 kPa of CH$_3$OH/96.5 kPa of N$_2$) stream for 10 s led to the complete disappearance of the lower temperature RuO$_4^{2-}$ reduction peak, present in the fresh sample, during subsequent reduction, whereas the peak corresponding to RuO$_2$ reduction remained essentially unchanged. These data show that RuO$_4^{2-}$ species react with CH$_3$OH preferentially over RuO$_2$ species. After prolonged contact with the CH$_3$OH stream, the RuO$_2$ reduction peak also decreased in intensity (Figure 9), indicating that the RuO$_2$ species can also participate in the CH$_3$OH reactions, albeit with lower reactivity. Steady-state catalytic reactions of CH$_3$OH/O$_2$ mixtures led to a H$_2$ reduction profile (not shown in Figure 9) similar to that for the fresh sample, indicating that the reoxidation is fast and kinetically irrelevant during methanol oxidation catalysis and that Ru atoms exist predominately in their higher oxidation state during catalytic turnovers. This is consistent with the involvement of the redox cycles using lattice oxygen atoms in the CH$_3$OH conversion to MF on RuO$_x$ domains, as discussed above, and with the slow nature and kinetic relevance of the reduction part of the cycle—the activation of C–H bonds in chemisorbed methoxide species. These observed effects of RuO$_x$ structure on reducibility and...
Ru/nm\(^2\) ). RuO\(_2\) domains in the activation of C

...and the synthesis of new catalysts for the CH\(_3\)OH conversion

...catalytic properties may provide a fundamental basis for the design and synthesis of new catalysts for the CH\(_3\)OH conversion to MF and other products and also for light alkane selective oxidations, for example, via the synthesis of more complete Zr-(RuO\(_4\))\(_2\) monolayers on ZrO\(_2\) or on other support structures with higher surface areas.

**Conclusions**

ZrO\(_2\)-supported RuO\(_4\) domains catalyze the oxidation of methanol to methyl formate at low temperatures (e.g., 373 K). CH\(_3\)OH oxidation rates and selectivities strongly depend on RuO\(_2\) structure, which varied with Ru surface density (0.2–3.8 Ru/nm\(^2\)). RuO\(_2\), was preferentially dispersed as isolated RuO\(_2\)\(^{2-}\) species below 0.4 Ru/nm\(^2\), probably as Zr(RuO\(_4\))\(_2\). At higher Ru surface densities, highly dispersed RuO\(_2\) domains formed, and then three-dimensional RuO\(_2\) clusters became prevalent above 1.9 Ru/nm\(^2\). Such structural evolution of RuO\(_2\), structures from RuO\(_4\)\(^{2-}\) to RuO\(_2\) with increasing Ru surface density led to a linear decrease in methanol oxidation rates per Ru atom and per exposed Ru atom (turnover rates) as the RuO\(_4\)\(^{2-}\) fraction decreased, indicating that RuO\(_4\)\(^{2-}\) species are more reactive than RuO\(_2\) domains in the activation of C−H bonds in methoxide intermediates, previously shown to control methanol oxidation rates on RuO\(_2\). These conclusions are consistent with transient anaerobic CH\(_3\)OH reactions and H\(_2\) temperature-programmed reduction data, which show that RuO\(_4\)\(^{2-}\) is more reducible than RuO\(_2\). The more reactive nature of RuO\(_4\)\(^{2-}\) species and the higher exposed ZrO\(_2\) surface area on samples with low Ru surface density led to very high methyl formate selectivities (~96% at 0.2 Ru/nm\(^2\)). Taken together, these results show that RuO\(_4\)\(^{2-}\) structures exhibit unprecedented reaction rates and selectivities for the synthesis of methyl formate from methanol−O\(_2\) co-reactants.

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