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Effect of treatment temperature on structures and properties of zirconia-supported ruthenium oxide catalysts for selective oxidation of methanol to methyl formate

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ABSTRACT

The structures of the RuO_x species supported on monoclinic ZrO₂ (m-ZrO₂) after treatment in a wide temperature range 673–1323 K were characterized by X-ray diffraction, Raman, infrared and X-ray photoelectron spectroscopies, and temperature-programmed reduction in H₂. Their catalytic properties were examined in the selective oxidation of methanol to methyl formate at 373K. The RuO_x species were present as highly dispersed RuO_4^{2-} on m-ZrO₂ with Ru surface densities of 0.2–2.2 Ru/nm², irrespective of the treatment temperatures. Their molecular structures evolved from umbrella-like dioxo (O=)₂Ru(OH)-O-Zr (containing a Ru-OH bond and a Ru-O-Zr bond to m-ZrO₂ surface) into tetrahedral dioxo $(O=)_2$ Ru- $(O-Zr)_2$ with increasing the treatment temperatures from 673 to 773 K, and into pyramidic mono-oxo $O=Ru-(O-Zr)_4$ above 1173 K, induced by the stronger interaction between the RuO_x species and underlying m-ZrO₂ surface at the higher temperatures. Following such structural changes, the turnover rates of the methanol oxidation increased markedly, and reached the greatest value (39.0 mol/mol Ru-h) on the catalyst treated at 1223 K, as a result of the parallel increase in the reducibility of the RuO_x species, consistent with the known Mars-van Krevelen redox mechanism using lattice oxygen atoms on RuO_x. These understandings may be useful for improving the reactivity of the RuO_x-based catalysts for the selective oxidation of methanol as well as of other alcohols and probably light hydrocarbons, for instance, by synthesis and tuning of the more reducible di-oxo RuO_4^{2-} structures.

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1. Introduction

Methyl formate (HCOOCH₃, MF) is a versatile intermediate in the synthesis of important formamides, carboxylic acids, and esters [1–6]. It can be synthesized by selective oxidation of methanol, which appears to be a greener and thermodynamically favorable alternative to the current industrial processes based on homogenous carbonylation and non-oxidative dehydrogenation of methanol generally using liquid sodium methoxide and Cu catalysts, respectively [1,4–6].

 V_2O_5 -TiO₂ and MoO₃-SnO₂ mixed oxides have been studied for methanol oxidation to MF [4,7,8], but significant improvements in their catalytic activities or selectivities are required for industrial applications. It is known that methanol oxidation to MF involves the kinetically relevant C-H activation step to form HCHO intermediate, and subsequent reactions of HCHO, which also competitively lead to other products, especially undesired CO_x (CO + CO₂) [3,9]. In line with the mechanism, Liu and Iglesia [10] explored more reducible RuO_x domains for methanol oxidation, and discovered their unprecedentedly superior activities relative to VO_x and MoO_x-based catalysts at lower reaction temperatures (330–400 K). Recently, we reported that the RuO_x domains present as isolated RuO₄^{2–} (containing Ru⁶⁺) structures on monoclinic ZrO₂ (m-ZrO₂) surface are efficient for the MF synthesis with a high selectivity of ~96% (at ca. 20% methanol conversion) at temperatures of as low as 373 K [11]. These RuO₄^{2–} structures are more reactive than RuO₂ domains [11], reflecting the structure-sensitivity of the methanol oxidation reaction [3].

The isolated RuO₄^{2–} structures on m-ZrO₂ are formed from the strong interaction of the RuO_x species with m-ZrO₂ surface during thermal treatment [11]. This promotes us to study the effects of the treatment temperatures on the m-ZrO₂ supported RuO_x (RuO_x/m-ZrO₂) catalysts, as part of our ongoing efforts to rationally control the active RuO₄^{2–} structures and their reactivity in the selective methanol oxidation. In this work, we characterize the RuO_x/m-ZrO₂



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catalysts treated at different temperatures (673–1323 K) by X-ray diffraction (XRD), X-ray photoelectron (XPS) and Raman spectroscopies. We probe their reducibility by temperature-programmed reduction (TPR) in H₂. Their catalytic properties in the oxidation of methanol to MF are examined and then related to the proposed evolution of the RuO₄^{2–} structures on m-ZrO₂ with the different treatment temperatures.

2. Experimental methods

2.1. Sample synthesis

 RuO_x/m -ZrO₂ catalysts with a 0.5 wt% Ru loading were prepared by incipient wetness impregnation of m-ZrO₂ with an aqueous solution of Ru(NO)(NO₃)₃ (Alfa Aesar, 31.3% Ru) at 298 K for 3 h. The samples were dried in ambient air at 398 K overnight after impregnation, and then treated in ambient air at different temperatures between 673 and 1323 K for 4 h. m-ZrO₂ was synthesized hydrothermally by hydrolysis of aqueous zirconyl nitrate (ZrO(NO₃)₂·2H₂O; >45.0% ZrO₂, Beijing Chemicals) solutions with urea (CO(NH₂)₂; >99.9%, Beijing Chemicals) at 433 K for 20 h in a Teflon-lined stainless-steel autoclave, followed by filtration of the precipitates and treatment in ambient air at 398 K overnight and subsequently at 673 K for 4 h [12].

2.2. Sample characterization

BET surface areas for the RuO_x/m - ZrO_2 samples were measured by N₂ physisorption at 78.3 K using an ASAP 2010 analyzer (Micromeritics) after they were evacuated at 393 K for 4h under dynamic vacuum (<2.66 Pa) conditions.

XRD patterns were collected in the 2θ range of $10-80^{\circ}$ using a Rigaku D/MAX-2000 diffractometer with a Cu K α radiation source ($\lambda = 1.5406$ Å) operated at 30 kV and 100 mA. The average particle sizes (*D*) were estimated by the Scherrer equation [13], $D = 0.90\lambda/\beta \cos \theta$, where θ is the diffraction angle and β is the full width at half-maximum (fwhm).

XPS measurements were preformed on an Axis Ultra spectrometer using monochromatic Al K α (1486.71 eV) radiation at a source power of 225 W (15 mA and 15 kV). The binding energies were calibrated by referring to the C 1s peak at 284.8 eV for adventitious carbon.

Raman spectra were measured in the range of $100-1500 \text{ cm}^{-1}$ on a Bruker Senterra confocal microscope spectrometer equipped with a Nd:YAG laser (532 nm) and a CCD camera. The RuO_x/m-ZrO₂ samples were placed in a quartz cell for in situ treatment and measurement without exposure to ambient air.

H₂ temperature-programmed reduction (H₂-TPR) experiments were carried out on a flow unit (TP5000, Tianjin Xianquan) in a ~5% H₂/N₂ flow (30 cm³ min⁻¹; Beijing Huayuan). The RuO_x/m-ZrO₂ samples (~0.1 g) were treated in a quartz cell in flowing air for 1 h to remove surface contaminants, and then they were switched to the H₂/N₂ flow at 298 K and heated linearly to 873 K at a ramping rate of 10 K min⁻¹. The H₂ consumption was measured using an on-line quadruple mass spectrometer (Hiden HPR 20), and the response was calibrated by the reduction of CuO powders (Beijing Chemicals, >99.0%) in H₂ (~5% H₂/N₂).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded in reflectance mode with 4 cm^{-1} resolution on a Bruker Tensor 27 FT-IR spectrometer equipped with a Harrick diffuse-reflectance attachment and a reaction chamber. The samples were treated in the reaction chamber in a N₂ flow at 573 K for 2 h before measuring the spectra in the range of 1000–4000 cm⁻¹ at ambient temperature. All the spectra were obtained by subtracting the spectrum of KBr treated under the identical conditions.



Fig. 1. X-ray diffraction patterns for RuO_x/m -ZrO₂ catalysts after treatment in flowing dry air at different temperatures between 673 and 1323 K.

2.3. Catalytic methanol oxidation reactions

Methanol oxidation reactions were carried out in a packed-bed quartz microreactor at 373 K and atmospheric pressure. The catalysts (60-80 mesh) were diluted with quartz powders to prevent temperature gradients and hot spots. The amounts of the catalysts varied with their activities to keep similar methanol conversions of about 20%. The catalysts were treated in 10% O_2/N_2 (Beijing Huayuan, 99.999%) flow (30 cm³ min⁻¹) at 673 K for 1 h before they were exposed to the reactant mixtures consisting of 3.5 kPa CH₃OH (Beijing Chemical, 99.99%), 30 kPa O₂ and balance N₂ (Beijing Huayuan, 99.999%). Methanol was introduced by bubbling N₂ through a glass saturator filled with liquid methanol (Beijing Chemical, 99.99%). All stream lines from the reactor to the detector were kept above 393 K to avoid condensation of the products. Reactants and products were analyzed by on-line gas chromatography (Shimadzu 2010 GC) using two packed columns (5A molecular sieve for O₂/N₂ and Porapak Q for other components) and TCD detectors. All data in this study were collected at steady state after 2 h on-stream. Selectivities are reported on a carbon basis and rates as molar CH₃OH conversion rates per mole of Ru per hour (mol/mol Ru-h). Blank experiments were conducted on quartz and pure m-ZrO₂ powders, showing no detectable CH₃OH conversions under all reaction conditions employed in this study.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows BET surface areas, support particle sizes and nominal surface densities for RuO_x/m -ZrO₂ samples treated from 673 to 1323 K. The surface areas decreased from 129.6 to 90.5 m²/g with increasing the treatment temperatures from 673 to 773 K, and then sharply to 52.5 and 13.3 m²/g at 873 and 1323 K, respectively. Such decrease in the surface areas indicates the thermal sintering of the ZrO₂ support, as also evidenced from the concurrent increase in its particle sizes from 7.8 to 36.0 nm (estimated from the width of the diffraction line at 28.1° shown in Fig. 1). Accordingly, the normal RuO_x surface density, calculated from the Ru content and BET sur-

Table 1

BET surface areas, average ZrO₂ crystallite sizes, nominal Ru surface densities and XPS Ru 3d_{5/2} and Ru 3d_{3/2} binding energies for monoclinic ZrO₂-supported RuO_x catalysts treated at different temperatures.

Treatment temperature (K)	Surface area (m ² /g)	Support particle size ^a (nm)	Ru surface density (Ru/nm)	Binding energy (eV)	
				Ru 3d _{5/2}	Ru 3d _{3/2}
673	129.6	7.8	0.2	282.7	286.9
723	110.9	8.3	0.3	282.6	286.8
773	90.5	8.3	0.3	282.6	286.8
873	52.5	14.9	0.6	282.7	286.9
973	38.4	16.1	0.8	282.7	286.9
1073	34.8	18.6	0.9	282.7	286.9
1173	26.6	22.7	1.1	282.7	286.9
1223	19.2	27.0	1.6	282.7	286.9
1273	15.1	33.3	2.0	282.8	287.0
1323	13.3	36.0	2.2	282.7	286.9

^a Calculated from X-ray diffraction patterns for these samples by the Scherrer equation.

face area, increased from 0.2 to 2.2 Ru/nm^2 . In this surface density range, the RuO_x domains were reported to be highly dispersed on the m-ZrO₂ surface with nearly 100% dispersion [11].

Fig. 1 shows XRD patterns for the RuO_x/m-ZrO₂ catalysts following treatment at different temperatures in the range 673–1323 K, where all diffraction peaks at $2\theta = 24.2^{\circ}$, 28.2° , 31.5° , and 34.3° are assigned to monoclinic ZrO₂. No tetragonal ZrO₂ and crystalline RuO₂ phases were detected, because of the absence of their characteristic peaks at 30.2° and 35.2° , respectively [11,12].

Raman spectra (Fig. 2) confirmed the XRD results. In the range 250–650 cm⁻¹, Raman bands appeared only at 618, 558, 504, 477, 381 and 335 cm⁻¹, which are characteristic of m-ZrO₂ with no detectable bands corresponding to tetragonal ZrO₂ and crystalline RuO₂ phases (e.g. at 271 and 521 cm⁻¹, respectively) [14,15]. In the range 900–1100 cm⁻¹, a broad band at 978 cm⁻¹ was detected on the RuO_x/m-ZrO₂ sample treated at 673 K, which is attributed to terminal Ru=O stretching vibration in the tetrahedral RuO₄^{2–} structures [11]. This band shifted from 978 to 1003 cm⁻¹ with increasing the treatment temperatures from 673 K to 1173 K, and then remained around 1003 cm⁻¹ between 1173 and 1323 K. The

progressive blue-shift may reflect the stronger interaction of the RuO_x species with m-ZrO₂ at the higher treatment temperatures, and the consequent increase in its Ru=O bond strength and stretching vibration frequencies. Along with such blue-shift, a shoulder appeared at 970 cm⁻¹ at 873 K, and became more intense at higher temperatures. Above 1173 K, a weak Raman band emerged at 1020 cm⁻¹. It also became more intense currently with the attenuation of the 1003 cm⁻¹ band with increasing the treatment temperatures, and ultimately reached the equivalent intensity of the 970 cm⁻¹ band at 1323 K. To assign the two new bands, pure m-ZrO₂ was characterized by Raman for comparison after treatment at the same temperatures (Supplementary data, Fig. S1). The two bands were also observed on m-ZrO₂ after treatment above 873 K, but essentially with equivalent intensities. These features together suggest that the two new bands in the RuO_x/m -ZrO₂ samples are attributed not only to m-ZrO₂ support itself, but also to the RuO_x species, which is indeed confirmed by the combined results of H₂-TPR and Raman characterization, as discussed below.

Fig. 3 presents H_2 -TPR profiles for the treated RuO_x/m -ZrO₂ samples. For comparison, pure m-ZrO₂ was also examined, and it shows a reduction peak at 730 K. On the RuO_x/ZrO_2 sample treated



Raman shift (cm⁻¹)

Fig. 2. Raman spectra for dehydrated $RuO_x/m-ZrO_2$ catalysts after treatment in flowing dry air at different temperatures between 673 and 1323 K.



Fig. 3. H_2 temperature-programmed reduction profiles for RuO_x/m -ZrO₂ catalysts after treatment in flowing dry air at different temperatures between 673 K and 1323 K.

at 673 K, there were two reduction peaks around 435 and 590 K. The low-temperature peak corresponds to the reduction of the RuO₄²⁻ species to Ru⁰ [11], consistent with its reduction stoichiometry of approximately 3 H₂/Ru. The peak around 590 K can be assigned to m-ZrO₂ reduction. The observed shift to lower reduction temperature relative to pure m-ZrO₂ may be due to the promoting effect of RuO_x on the mobility of the lattice oxygen atoms of m-ZrO₂ or to the effect of hydrogen spillover from metallic Ru (derived from the RuO_x reduction) to m-ZrO₂, as generally found with other supported metal catalysts [16–19]. The reduction peak of the RuO_x species shifted to lower temperatures from 435 to 357K with increasing the treatment temperatures from 673 up to 1323 K; the peak intensity decreased sharply above 1173 K. Meanwhile, a new reduction peak was noticed around a higher temperature of 429 K on the samples treated at 1173 K, which became more intense at higher treatment temperatures, apparently at the expense of the lower-temperature peak. The corresponding amounts of H₂ consumption for the two reduction peaks were estimated, and the molar fraction derived from the new peak increased from 27.7 and 51.5% to 89.0 and 89.9% with increasing the treatment temperatures from 1173 and 1223 K to 1273 and 1323 K, respectively. However, the reduction stoichiometry of the RuO_x species for the two peaks was always ca. 2.9–3.2 H₂/Ru, irrespective of the treatment temperatures, indicating the presence of only Ru⁶⁺ species, i.e. RuO₄^{2–}, as further confirmed by XPS. The XPS result exhibited only peaks at binding energies of 282.7 and 286.9 eV (Table 1), corresponding to Ru 3d_{5/2} and Ru 3d_{3/2} for the Ru⁶⁺ species, respectively [11,20].

To more clearly assign the Raman bands (Fig. 2) and H₂-TPR reduction peaks (Fig. 3), the RuO_x/m -ZrO₂ samples were characterized upon controlled reduction in H₂ by in situ Raman and TPR. Fig. 4 shows the representative results for the sample treated at 1223 K. After reduction at 403 K, i.e. only selective removal of the lowertemperature peak at 373 K, the corresponding Raman bands at 1003 and 970 cm⁻¹ disappeared and sharply attenuated, respectively, whereas the 1020 cm⁻¹ band remained essentially unchanged. Further reduction of the sample at 503 K led to a decrease of the Raman band at 1020 cm⁻¹ in intensity, and no detectable further change in the 970 cm⁻¹ band, which can be more clearly seen from the difference spectrum between b and c (Fig. 4B, curve d). Thus, we conclude that the Raman bands at 1003 and 970 cm⁻¹ correspond to the RuO₄^{2–} species with the lower reduction temperature, which can be tentatively assigned to the symmetric (v_s) and asymmetric (v_{as}) stretching vibrations of the terminal Ru=O bonds for the RuO₄²⁻ species, respectively. The band at 1020 cm⁻¹ is attributed to the RuO₄²⁻ species formed at treatment temperatures above 1173 K, which showed the higher reduction temperature. After such reduction treatment and complete removal of the RuO_x species, the two bands at 1020 and 970 cm⁻¹ were still observed, however, with similar intensity, reflecting the features of pure m-ZrO₂ support (Fig. S1). These results confirm that both RuO_4^{2-} species and m- ZrO_2 support for RuO_x/m - ZrO_2 coincidently contribute to the two Raman bands.

Clearly, the RuO_x species are present as isolated RuO₄^{2–} species in the RuO_x/m-ZrO₂ samples, but the observed changes in their H₂ reduction and Raman features (Fig. 4A and B) indicate the evolution of the molecular structures of the RuO₄^{2–} species on m-ZrO₂ induced by the thermal treatment at different temperatures. Such structural evolution of the RuO_x species has been scarcely reported to date, which, however, can be understood by referring to the extensive studies on the molecular structures of other isolated metal oxides (MO_x), e.g. MoO_x, VO_x, and WO_x [21–23]. These surface MO_x species on different supports (e.g. SiO₂, Al₂O₃, TiO₂, and ZrO₂) generally possess M=O and M–O bonds, and the number of these bonds depends on the oxidation state of the metal oxides, the surface structures of the supports, and the thermal treatment



Fig. 4. H₂ temperature-programmed reduction profiles (A) and in situ Raman spectra (B) for $\text{RuO}_x/\text{m-ZrO}_2$ after treatment in flowing dry air at 1223 K before (a) and after pre-reduction in H₂ at 403 K (b) and 503 K (c). (d) In (B) is the difference Raman spectrum between spectra (b) and (c).

conditions. Isolated VO_x species are present as the distorted tetrahedral mono-oxo structures containing one terminal V=O bond and three V–O bonds, while isolated MoO_x and WO_x species form both mono-oxo (O=Mo(–O-support)₄ and O=W(–O-support)₄) and dioxo ((O=)₂Mo(–O-support)₂ and (O=)₂W(–O-support)₂) structures on the support surfaces. These structures exhibit distinct spectroscopic features. The mono-oxo M=O bonds under dehydrated conditions show only symmetric (ν_s) vibration Raman bands at higher frequencies relative to the bands for the di-oxo O=M=O bonds that exhibit both symmetric (ν_s) and asymmetric (ν_{as}) vibrations separated by ca.10–30 cm⁻¹ [22,24,25]. The mono-oxo and di-oxo structures are known to be inter-convertible by chang-



Fig. 5. Diffuse reflectance infrared Fourier transform spectra for $RuO_x/m-ZrO_2$ catalysts after treatment in flowing dry air at different temperatures between 673 and 873 K.

ing the treatment temperatures, water vapor pressures, etc. For example, dioxo $(O=)_2$ Mo(-O-support)₂ can convert to mono-oxo O=Mo(-O-support)₄ on SiO₂ by the release of a H₂O molecule from the interaction between one Mo=O and two Si–OH bonds, although the formation of the four Mo–O–Si bonds in the mono-oxo structure results in substantial strain of the SiO₂ surfaces [22]. Similarly, we envisage the structural transformation of the RuO₄^{2–} species from tetrahedral di-oxo ($O=)_2$ Ru(-O–Zr)₂ to pyramidic mono-oxo $O=Ru(-O-Zr)_4$ with the observed Ru=O stretching frequencies around 1003 (v_s)/970 (v_{as}) and 1020 (v_s) cm⁻¹, respectively, as a result of the enhanced interaction between the RuO₄^{2–} species and m-ZrO₂ surfaces when the treatment temperatures exceed 1173 K.

As mentioned above, the Ru=O vibration band and H₂ reduction peak for the supported RuO_x species shifted sharply from 978 to 985 cm^{-1} and from 435 to 398 K, respectively (Figs. 2 and 3), with increasing the treatment temperature from 673 to 773 K, which then changed more slowly above 773 K. Such progressive shifts indicate a change in the structures of the RuO_4^{2-} species following treatment above 773 K. Fig. 5 shows the DRIFT spectra in the range $3000-4000 \text{ cm}^{-1}$ for the RuO_x/m-ZrO₂ treated at 673-873 K. All spectra exhibit a band at 3771 cm⁻¹, typical for isolated Zr–OH groups, and a shoulder around 3680 cm⁻¹ for bridging Zr-OH groups [26-28]. The two bands remained almost unaltered in the range 673-873 K. In contrast, an additional sharp band was detected at 3855 cm⁻¹ on the sample treated at 673 K, and it attenuated significantly and became nearly invisible with increasing the treatment temperatures up to 773 K. This band was tentatively assigned to Ru-OH stretching vibration. Such M-OH bonds have also been detected spectroscopically, for example, on isolated VO_x species, present as a mono-oxo O=V(OH)₂-O-M structure on the different support surfaces (e.g. SiO₂, Al₂O₃, and ZrO₂) [29,30]. By referring to these previous studies, we tentatively propose that the RuO_4^{2-} species form umbrella-like di-oxo (O=)₂Ru(OH)-O-Zr structure with a Ru-OH bond between 673 and 773 K, which tends to transform to tetrahedral di-oxo $(O=)_2$ Ru- $(O-Zr)_2$ above 773 K most likely by reaction of Ru–OH with Zr–OH and release of a H₂O



Fig. 6. CH₃OH oxidation rates normalized per Ru atom and selectivities at 373 K as a function of treatment temperatures (673–1323 K) on RuO_x/m-ZrO₂ catalysts at methanol conversions of ~20% (0.2–2.2 Ru/nm², 3.5 kPa CH₃OH, 30 kPa of O₂, balance N₂).

molecule to form a new Ru–O–Zr bond at the higher treatment temperatures.

In summary, the molecular structures of the isolated RuO_4^{2-} species on m-ZrO₂ most likely evolve from umbrella-like di-oxo $(O=)_2\text{Ru}(OH)-O_b$ -Zr to tetrahedral di-oxo $(O=)_2\text{Ru}-(O-Zr)_2$ with increasing the treatment temperatures from 673 to 773 K, and then to pyramidic mono-oxo $O=\text{Ru}-(O-Zr)_4$ above 1173 K, as depicted in Scheme 1. Such changes in the structures of the RuO_4^{2-} species led to the parallel changes in their reducibility and catalytic reactivity in the selective oxidation of methanol, as discussed below.

3.2. Methanol oxidation rates and selectivities on RuO_x/m -ZrO₂ catalysts

Fig. 6 shows CH₃OH oxidation rates (normalized per Ru atom) and selectivities at 373 K on RuO_x/m -ZrO₂ as a function of the treatment temperatures in the range 673-1323 K. The rates and selectivities were compared in the kinetic regime at similar CH₃OH conversions (~20%) to avoid the known effects of CH₃OH conversion on the primary and secondary reactions [10]. MF, HCHO and CO_2 were only detected as the products. RuO_x/m -ZrO₂ treated at 673 K was not selective, and equally formed MF and CO₂ (48.1% vs. 47.2%). By increasing the treatment temperature to 773 K, the selectivities to MF and CO2 inversely changed sharply to 73.8 and 16.0%, respectively. With further increasing the temperatures in the range 773-1323 K, the CO₂ selectivity gradually decreased to as low as 4.3%, while the MF selectivity first decreased slightly to 68.8%, then sharply to 39.6% at the treatment temperatures of 1223 and 1323 K, respectively. The HCHO selectivity gradually increased from 4.7 to 24.1% with increasing the treatment temperatures from 673 to 1223 K, and then abruptly increased to 56.1% at 1323 K, concurrently with the observed decline in the MF selectivity between 1223 and 1323 K (Fig. 6). These results show that the ${\rm RuO_4}^{\rm 2-}$ structures formed at higher temperatures are more selective for the methanol oxidation to MF and HCHO relative to CO₂. The decreased MF selectivities on the samples treated above 773 K, especially above 1273 K, appear to be relevant to their decreased ZrO₂ surfaces (Table 1) that are known to be involved in the conversion of



Scheme 1. Plausible changes in RuO_x structures on m-ZrO₂ with treatment temperatures from (a) umbrella-like dioxo (O=)₂Ru(OH)-O-Zr with two V=O bonds, one Ru-OH bond and one Ru-O-Zr bond to m-ZrO₂ surface into (b) tetrahedral dioxo (O=)₂Ru-(O-Zr)₂ with two V=O bonds and two Ru-O-Zr bonds to m-ZrO₂ surface from 673 to 773 K, and into (c) pyramidic mono-oxo O=Ru-(O-Zr)₄ with one V=O bond and four Ru-O-Zr bonds to m-ZrO₂ surface above 1173 K.

HCHO intermediates to MF [10,11], which accordingly led to the observed increase in the HCHO selectivities (Fig. 6).

The CH₃OH oxidation rates, as shown in Fig. 6, increased dramatically by a factor of 4.7 from 4.9 to 22.9 mol/mol Ru-h with increasing the treatment temperature from 673 to 773 K, and then more gradually to 39.0 mol/mol Ru-h as the temperature reached 1223 K. However, further increasing the treatment temperatures to 1273 and 1323 K led to a sharp decline in the rates to 21.9 and 15.1 mol/mol Ru-h, respectively. From the structural characterization of the RuO_x species, it is known that most of the Ru atoms, if not all, are exposed at surfaces and accessible to the reactants on the RuO_x/m-ZrO₂ catalysts following treatment throughout the whole temperature range 673-1323 K. Therefore, the rates per Ru atom for these catalysts correspond to their turnover rates (TOFs), and can be used to compare their intrinsic reactivity. Clearly, the observed changes in the rates (Fig. 6) with the treatment temperatures are not due to the change in the accessibilities of the RuO₄²⁻ species, but due to the change in their intrinsic reactivity with the structural evolution induced by thermal treatment at the different temperatures. Such change in the reactivity for the RuO₄^{2–} species is consistent with their differences in reducibility.

The reducibility of the RuO_4^{2-} species was probed by TPR using H₂ as the reductant (Fig. 3). As discussed above, the peak temperatures for the reduction of Ru^{6+} to Ru^0 in the di-oxo RuO_4^{2-} structures shifted from 435.8 to 357.2 K by 78.6 K with increasing the sample treatment temperatures from 673 to 1323 K, which shows the more reducible nature of the di-oxo structures formed at higher treatment temperatures. Our recent kinetics and isotopic studies [10] have shown that the C-H bond activation steps using lattice oxygen atoms limit the methanol oxidation rates on the RuO_x domains, involving the incipient RuO_x reduction with the formation of a low surface density of oxygen vacancies during the steady-state catalysis (around 393 K). Thus, the initial stages of the RuO_x reduction are most relevant to the redox cycles required in the methanol oxidation [10]. The initial H₂ reduction rates at 385 K for the di-oxo RuO_4^{2-} structures were extracted from Fig. 3. They increased with increasing the treatment temperature in the range 673-1223 K (Supporting information, Fig. S2), which are in parallel with the increase in the methanol oxidation rates (i.e. TOFs) at 373 K, as shown in Fig. 7. After the treatment temperatures exceeded 1223 K, the less reducible mono-oxo RuO₄²⁻ structures became the dominant RuO_x species, as estimated from the H₂ consumption above (over 89%), leading to the observed decline in the methanol oxidation rates for the two samples treated at 1273 and 1323 K (Fig. 6).

This correlation between the reducibility of the RuO_4^{2-} species and their catalytic reactivity reflects the Mars–van Krevelen redox mechanism involving the C–H bond activation in the chemisorbed species by lattice oxygen atoms as the kinetically relevant step in the methanol oxidation on RuO_x domains [3,10], as also observed with the selective oxidation reactions of methanol and other alcohols as well as hydrocarbons on MoO_x, VO_x and other oxide-based



Fig. 7. Dependence of methanol oxidation rates (per Ru atom) at 393 K on initial H_2 reduction rates (per Ru atom) at 385 K for RuO_x/m -Zr O_2 catalysts after treatment in flowing dry air at different temperatures between 673 and 1223 K (0.2–1.6 Ru/nm², 3.5 kPa CH₃OH, 30 kPa of O_2 , balance N_2).

catalysts [31–36]. Clearly, such correlation and structural understandings provide guidance for further tuning and improving the reactivity of the RuO_x-based catalysts via synthesis of the dioxo RuO_4^{2-} structures with more reducible nature for the selective oxidation of methanol as well as of other alcohols and light hydrocarbons.

4. Conclusions

Treatment temperatures of m-ZrO₂-suppored RuO_x catalysts significantly influence the structures of the RuO_x species and their catalytic performances in the methanol oxidation to methyl formate at 373 K. RuO_x exists as highly dispersed RuO₄^{2–} species on m-ZrO₂ with Ru surface densities of 0.2–2.2 Ru/nm², following treatment at different temperatures in the range 673–1323 K. The molecular structures of the RuO₄^{2–} species vary from umbrella-like dioxo (O=)₂Ru(OH)–O–Zr with a Ru–OH bond into tetrahedral dioxo (O=)₂Ru–(O–Zr)₂ by increasing the treatment temperatures from 673 to 773 K, and then into pyramidic mono-oxo O=Ru–(O–Zr)₄ above 1173 K, due to the stronger interaction between the RuO_x species and m-ZrO₂ surface at the higher temperatures, partly evident from the blue-shift of the Raman vibration frequencies for the Ru=O bonds. Such structural changes lead to a

parallel increase in the reducibility of the RuO₄²⁻ species and their methanol oxidation rates, reflecting the Mars–van Krevelen redox mechanism using lattice oxygen atoms.

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Appendix A. Supplementary data

Raman spectra for m-ZrO₂ support treated at different temperatures between 673 and 1323 K, and Initial H₂ reduction rates at 385 K for RuO_x/m-ZrO₂ catalysts as a function of treatment temperatures (673–1323 K).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.05.021.

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