

Role of Surface Hydroxyl Groups on Single-Atomic Rh₁/ZrO₂ Catalyst for Direct Methane Oxidation

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Experimental Section

Additional Data

Figure S1 ~ S10

Table S1

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Experimental Section

Catalyst Syntheses

Zirconium n-propoxide 14.4 mL (70 wt% in n-propanol; Sigma-Aldrich) was diluted with 38.1 mL of 1-propanol. 20 mL of ammonia water (Duksan) was injected dropwise. This solution was stirred for 1 h and then dried at 85 °C for 12 h. The white powder was collected and calcined at 450 °C for 6 h in air flow to obtain tetragonal ZrO₂. Rhodium(III) chloride (98% ; Sigma-Aldrich) 4.9 mg was dissolved in 5 mL of anhydrous ethanol (99.9%; Samcheon). 300 mg of zirconia support was dispersed in 10 mL of ethanol. These two solutions were mixed with vigorous stirring and dried at 60 °C. The dried sample was calcined at 400 °C for 1 h in air flow. The obtained Rh/ZrO₂ catalyst was hydrothermally treated in a U-shaped quartz cell. 144.5 sccm of air with 10 % H₂O was flown at 300 °C for 10, 15, and 20 h each, and they are denoted as RZH_10, RZH_15, and RZH_20, respectively.

Direct Methane Oxidation

The catalyst 30 mg was ground well and dispersed in 10 mL of targeted concentration of H₂O₂ aqueous solution, located inside a 60 mL Teflon-coated stainless-steel autoclave. The autoclave was compactly sealed, pressurized with a gas mixture of methane (95 % methane and 5 % He) and O₂ to reach the target pressure (usually 30 bar of CH₄ and 2 bar of O₂). Then the autoclave was heated to 90 °C with 850 rpm and kept for 30 min. When the reaction ends, the reactor was rapidly cooled with a dry-ice until the temperature reaches below 10 °C to minimize the volatilization of products. The liquid phase products were analyzed by ¹H NMR spectroscopy (400 MHz; Bruker) with solvent suppression method. 1 mL of liquid product was collected and centrifuged. Then 0.7 mL of supernatant was mixed with 0.1 mL D₂O (99 %; Sigma-Aldrich) and 0.01 mL of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS, 97 %; Sigma-Aldrich) solution.

Recycle tests were conducted as following; at the first cycle, the methane conversion was performed at 30 bar of methane gas (95% CH₄ balanced with He), 2 bar of O₂ using 120 mM H₂O₂ and 30 mg of RZH_10 catalyst in 10 mL solution at 90 °C for 30 min. The catalysts was then collected and dried at 85 °C. At the second cycle, this catalyst was used again for the methane conversion at the same condition. After the 2nd reaction, the catalyst was calcined at 550 °C for 1 h and hydrothermally treated at 300 °C for 10 h. This catalyst was used for the methane conversion again at the same reaction condition.

Characterizations

The crystalline structure of the catalysts was measured by powder X-ray diffractometer (XRD; SmartLab, RIGAKU). The surface Rh oxidation state of the catalysts was investigated with X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo VG Scientific) with an Al K α X-ray source (12 kV, 3 mA). C 1s peak calibration was conducted, locating the highest intensity of peak at 284.8 eV. The BET surface area of the catalysts was analyzed by a Tristar II 3020 (Micromeritics). Transmission electron microscope (TEM) images of catalysts before and after hydrothermal treatment were taken with Tecnai G2 F30 S-twin model (FEI) at 300 kV. To further confirm the highly oxidized state of Rh and single atomic structure of the catalyst, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of Rh K-edge were measured from Pohang Light Source (PLS) 10C beamline. The Rh K-edge spectra were obtained by a fluorescence mode, using a passivated implanted planar silicon (PIPS) detector (Canberra). The XANES and EXAFS data were processed with ATHENA software.

The catalysts were also analyzed with diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS; Nicolet iS-50, Thermo Scientific). The catalyst 20 mg was ground well with 80 mg of KBr, then loaded in a sample cup and set into a DRIFT cell. The temperature was raised to 300 °C by 5 °C/ min with Ar flow, while monitoring the OH peaks. The DRIFTS measurement was also performed with CO adsorption. The catalyst was pretreated in Ar for 1 h at 100 °C, then cooled to room temperature. 2 % CO with Ar balance was flown for 15 min at room temperature for CO adsorption. The DRIFT spectra were then collected under evacuation. For CH₄ adsorption, 5 % CH₄ with Ar balance was flown for 15 min and the DRIFT spectra were collected at 90 °C.

Additional Data

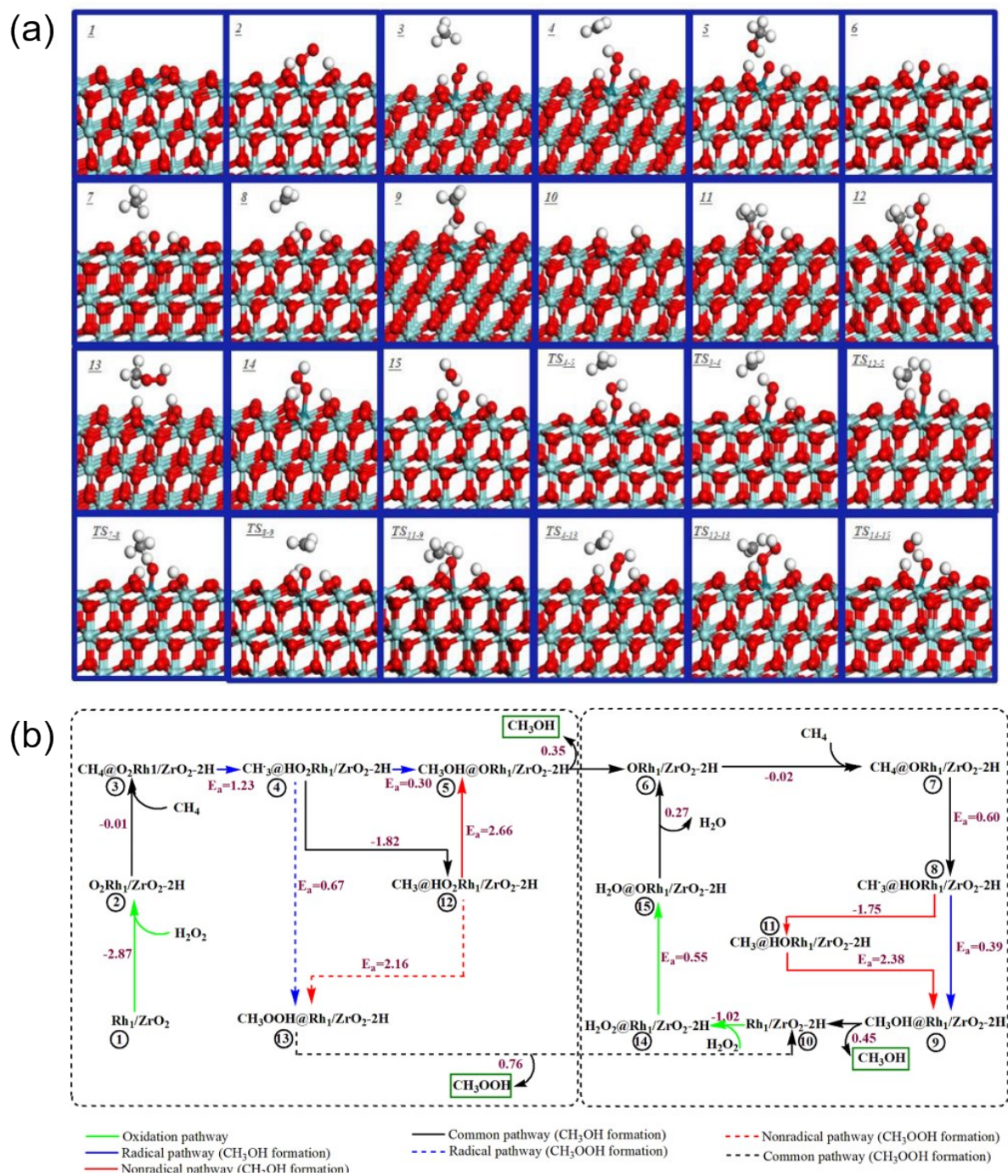


Figure S1. (a) The structures of intermediates in direct methane oxidation on Rh₁/ZrO₂. (b) Reaction network for the methane conversion on the Rh₁/ZrO₂. (adapted from ‘K. Harrath, X. Yu, H. Xiao and J. Li, ACS Catalysis, 2019, 9, 8903-8909’ with permission)

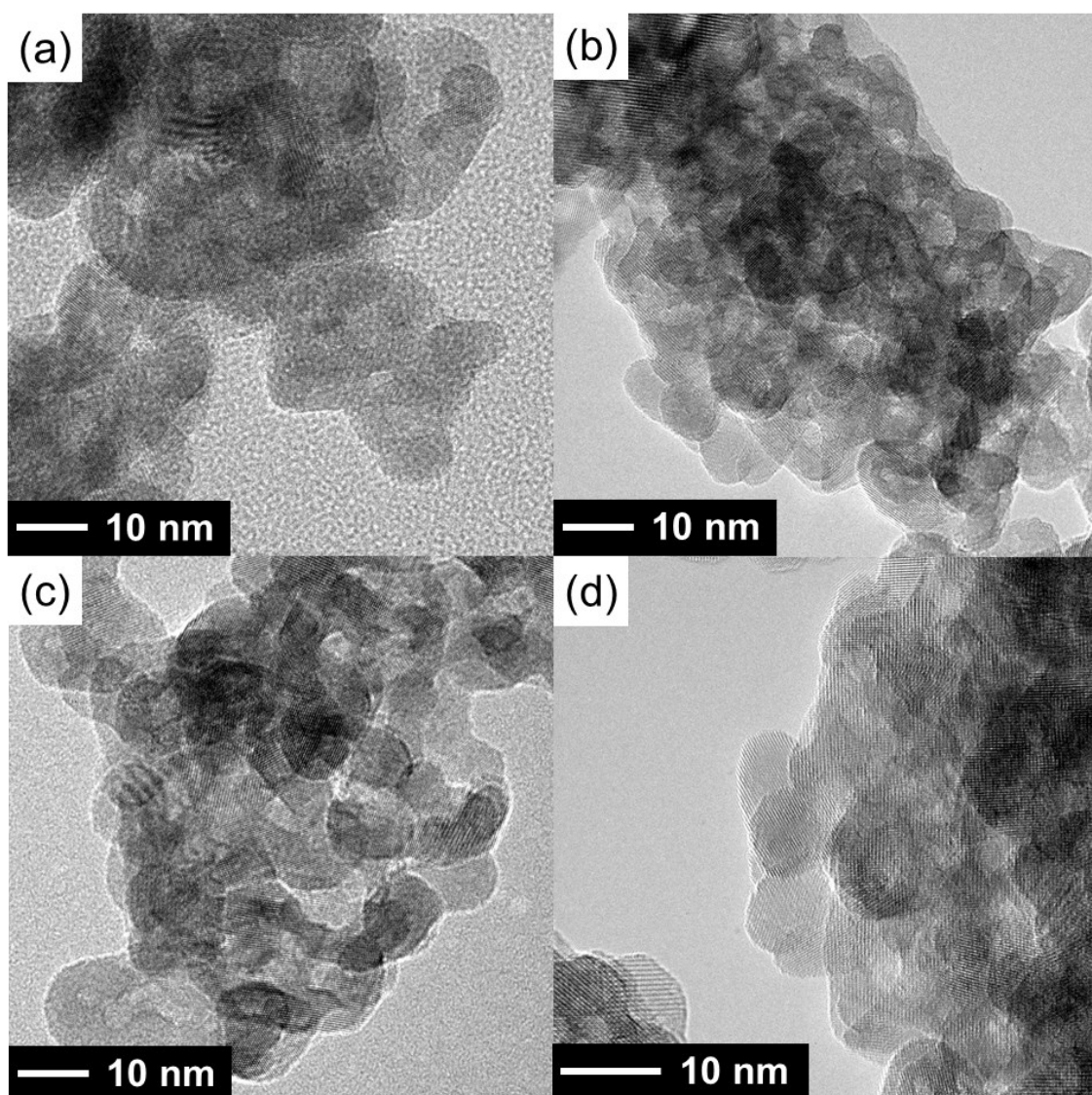


Figure S2. TEM images of (a) Rh₁/ZrO₂ (RZ), (b) Rh₁/ZrO₂ hydrothermally treated for 10 h (RZH_10), (c) Rh₁/ZrO₂ hydrothermally treated for 15 h (RZH_15), and (d) Rh₁/ZrO₂ hydrothermally treated for 20 h (RZH_20).

Table. S1 BET surface area and the analyses of Rh germinal peaks obtained in DRIFTS (Figure 1a) of RZ, RZH_10, RZH_15, and RZH_20. The angle between two CO molecules adsorbed on Rh single sites can be calculated by comparing each area of the symmetric and asymmetric peaks.^{S1-S3}

Sample	BET Surface Area (m ² /g)	Symmetric (cm ⁻¹)	A _{sym} ^a	Asymmetric (cm ⁻¹)	A _{asym} ^a	2α(°) ^b
RZ	74.1	2085	18.5	2010	17.0	87.6
RZH_10	69.7	2085	25.2	2010	28.1	93.1
RZH_15	65.4	2085	22.6	2010	22.4	89.8
RZH_20	66.1	2085	23.0	2010	23.7	90.8

^a The area of the symmetric or asymmetric peaks.

^b The angle between the adsorbed CO molecules. $A_{\text{asym}} / A_{\text{sym}} = \tan^2\alpha$

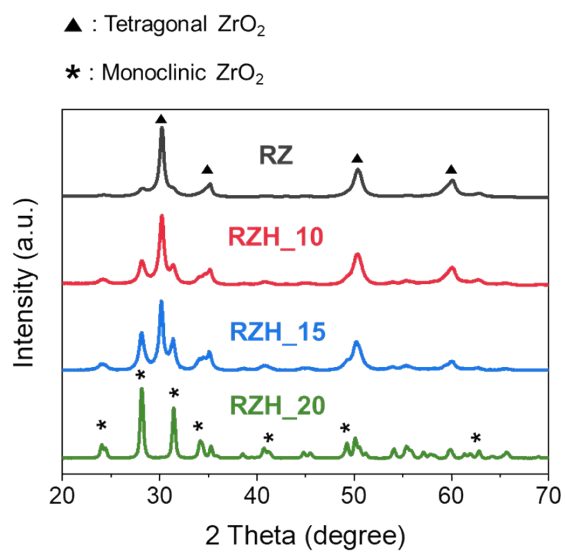


Figure S3. XRD patterns of RZ, RZH_10, RZH_15, and RZH_20. The triangle (▲) indicates tetragonal phase of ZrO₂, and the star (*) indicates monoclinic phase of ZrO₂.

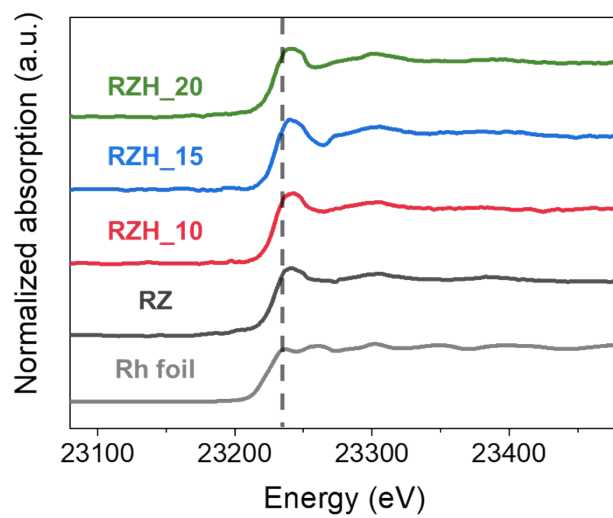


Figure S4. Rh K edge XANES spectra for RZ, RZH_10, RZH_15, RZH_20, and Rh foil.

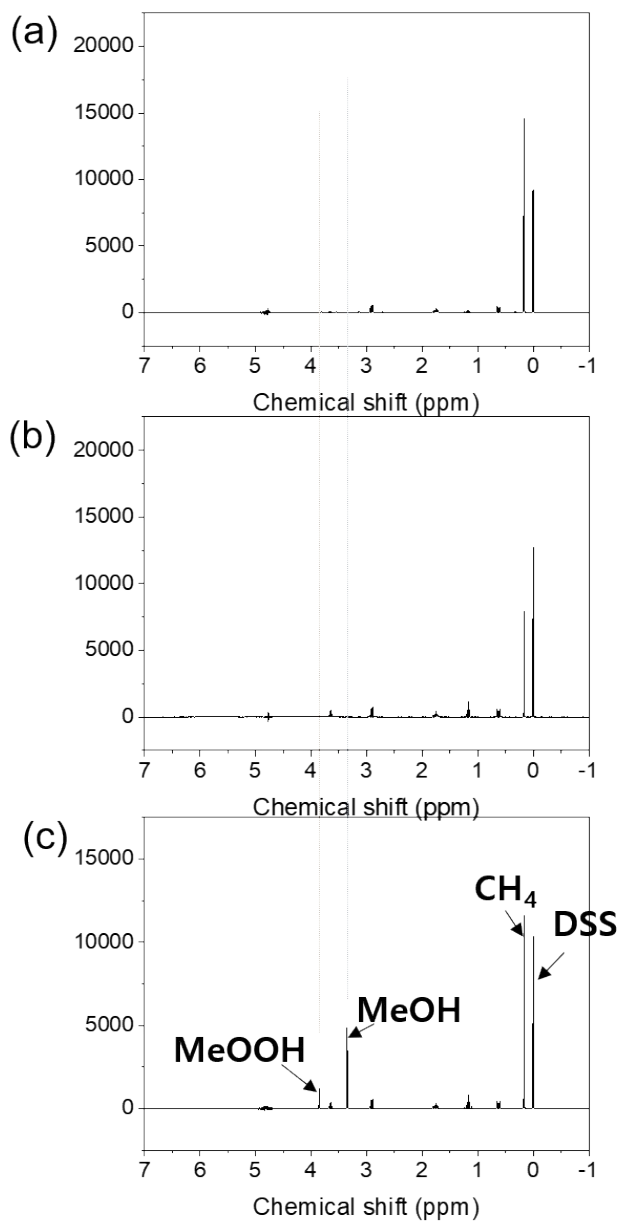


Figure S5. ^1H NMR data (a) in the absence of the catalyst, (b) in the absence of H_2O_2 , (c) in the presence of both the catalyst (RZH_10) and H_2O_2 . The reaction was performed at 30 bar of 95% CH_4/He , 2 bar of O_2 , 120 mM of H_2O_2 , and 90 $^\circ\text{C}$ for 30 min using the catalyst 30 mg in 10 mL aqueous solution.

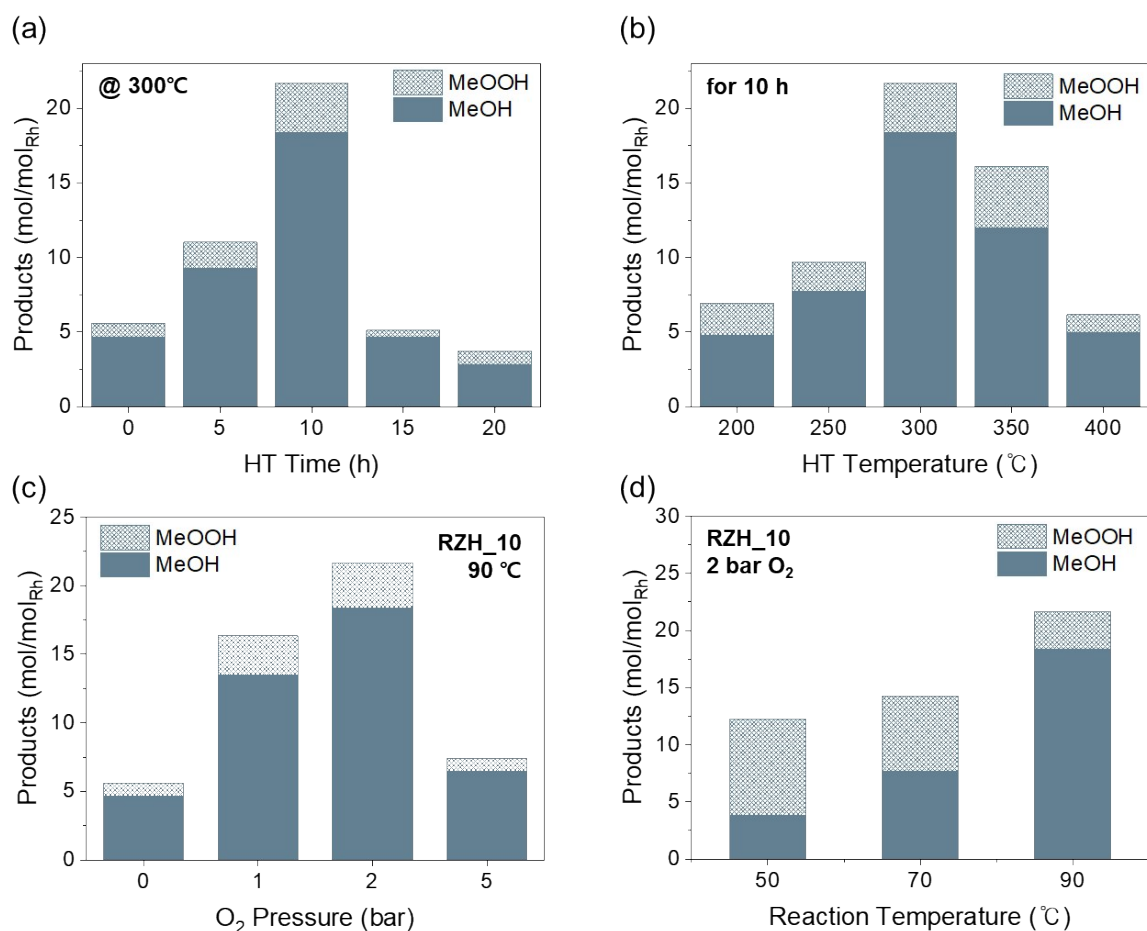


Figure S6. Production of methane oxygenates for various (a) times of hydrothermal treatment, (b) temperatures of hydrothermal treatment, (c) O₂ pressure, and (d) reaction temperatures.

Reaction conditions for (a) and (b): 30 bar of 95 % CH₄/He, 2 bar of O₂, 90 °C, 30 min, 120 mM H₂O₂ and catalyst 30 mg in 10 mL solution.

Reaction conditions for (c): Total pressure of gas is fixed with 32 bar (balanced with 95 % CH₄/He), 90 °C, 30 min, 120 mM H₂O₂ and 30 mg of RZH_10 in 10 mL solution.

Reaction condition for (d): 30 bar of 95 % CH₄/He, 2 bar of O₂, 30 min, 120 mM H₂O₂ and 30 mg of RZH_10 in 10 mL solution.

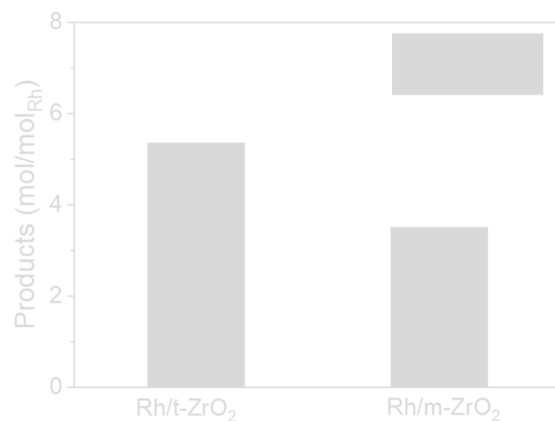


Figure S7. Reaction results for different crystalline structure of ZrO₂ support (t-ZrO₂ denotes tetragonal structure, and m-ZrO₂ denotes monoclinic structure). Reaction condition: 30 bar of 95 % CH₄/He, 30 min, 90 °C, 120 mM H₂O₂ and 30 mg of catalysts in 10 mL solution.

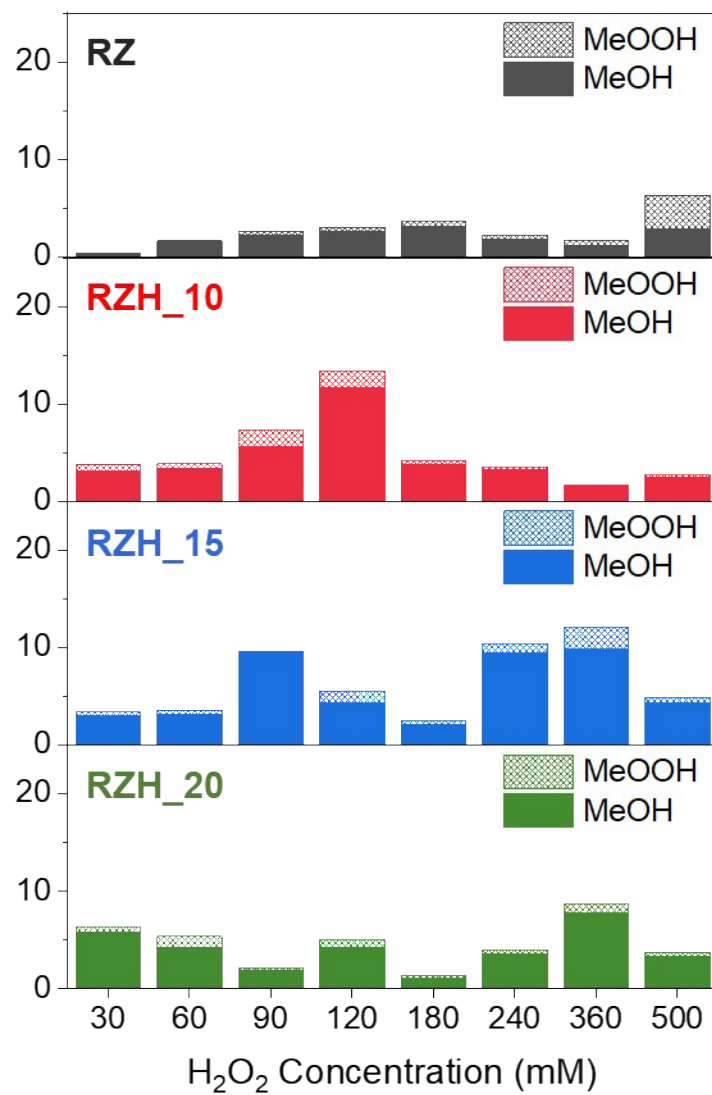


Figure S8. Production of methane oxygenates for various H₂O₂ concentrations in the absence of O₂. Reaction condition: 32 bar of 95% CH₄/He, 90 °C, 30 min, and catalyst 30 mg in 10 mL solution.

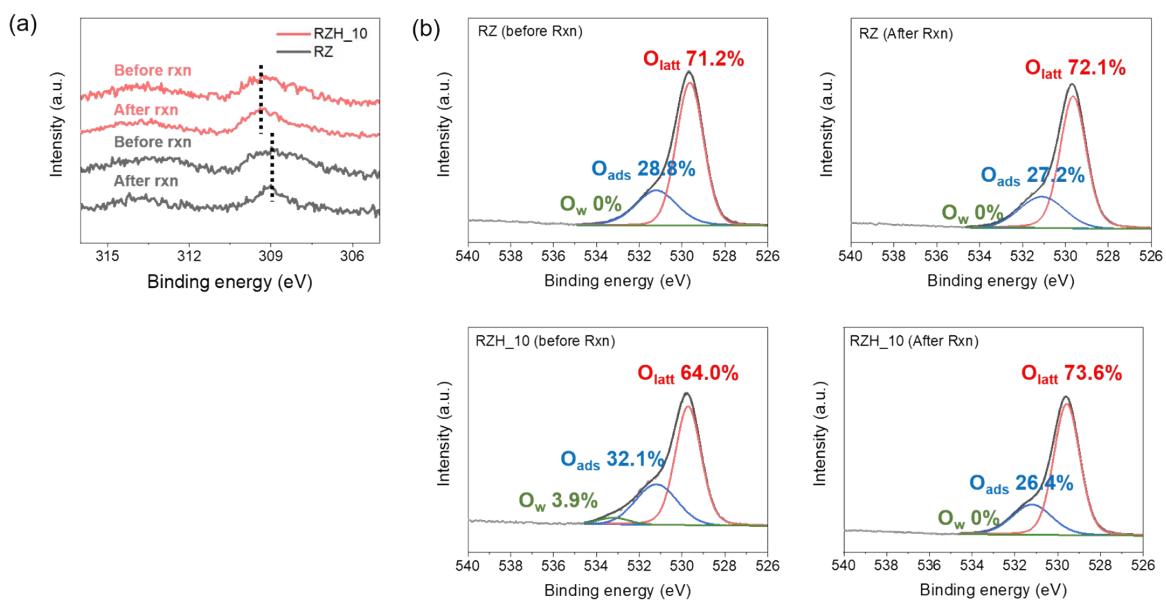


Figure S9. XPS (a) Rh 3d and (b) O 1s before and after the methane oxidation for RZ (no hydrothermal treatment) and RZH_10 (hydrothermally treated for 10 h prior to the reaction)

▲ : Tetragonal ZrO₂

* : Monoclinic ZrO₂

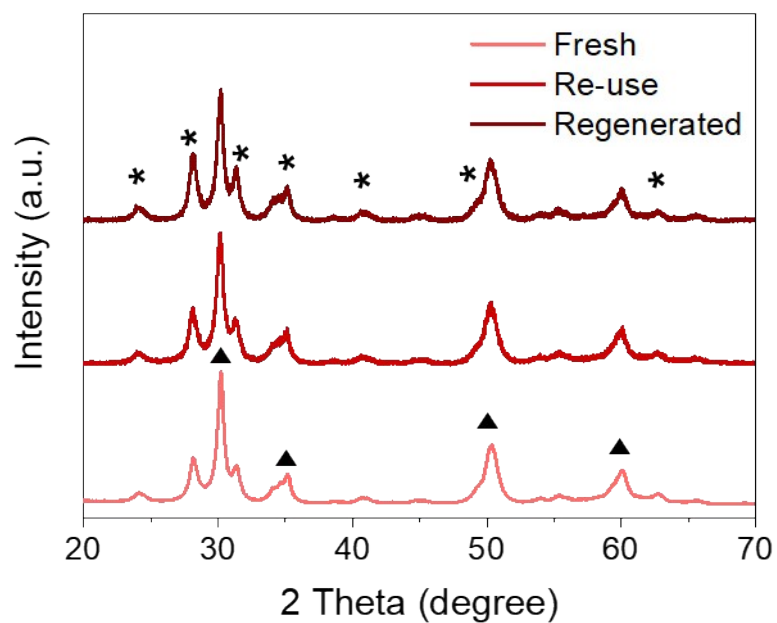


Figure S10. XRD result of fresh, re-use, and regenerated RZH_10 sample. The triangle (▲) denotes tetragonal phase of ZrO₂, with star (*) denotes monoclinic crystalline phase of ZrO₂.

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