Supporting Information

Single-Atom High-Temperature Catalysis on a Rh₁O₅ Cluster for Production of Syngas from Methane

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Table of Contents

Sections	Page					
Section 1: Size and morphology of 6.3wt%Rh/TiO ₂						
Section 2: Chemisorption of CO on 0.037wt%Rh/TiO ₂ and 6.3wt%Rh/TiO ₂						
Section 3: Evaluation of catalytic performances of bare TiO ₂ , 0.037wt%Rh/TiO ₂	3					
and 6.3wt%Rh/TiO ₂						
Section 4: Measurement of reaction rate under kinetics-controlled regime	4					
Section 5: Ex-Situ, In-Situ and Operando Characterizations	5					
Section 6: Calculations of the amount of Rh (in mol) exposed to surface of 50 mg of	7					
0.037wt%Rh/TiO2 and 50 mg of 6.3wt%Rh/TiO2						
Section 7: Calculations of turn-over rates (TOR) of 0.037wt%Rh/TiO ₂ (Rh ₁ /TiO ₂)						
and 6.3wt%Rh/TiO ₂ (Rh NP/TiO ₂)						
Section 8: Note on the difference in coordination environment of Rh atoms in	12					
0.037wt%Rh/TiO ₂ (Rh ₁ /TiO ₂) and 6.3wt%Rh/TiO ₂ (Rh NP/TiO ₂)						
Section 9: Note on single dispersion of 0.037wt% Rh/TiO ₂ evidenced in DRIFTS						
Section 10: Note on AP-XPS studies						
Section 11: Detail on DFT study	13					

Figure	S 1	S2	S3	S4	S5	S6	S7	S 8	S9	S10	S11	S12	S13	S14	S15
Page	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28

Figure	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26
Page	29	30	31	32	33	34	35	36	37	38	39

References:

Page 40

1. Size and morphology of 0.037wt%Rh/TiO₂ and 6.3wt%Rh/TiO₂

Size and morphology of these as-synthesized and used 6.3wt%Rh/TiO₂ samples were studied by TEM systems at overseas. In addition, the size and morphology of some of the assynthesized and used 0.037wt%Rh/TiO₂ samples were investigated with TEM systems at overseas. Before a typical TEM characterization, a small amount of catalyst power was dispersed in anhydrous ethanol; then a drop of the ethanol was casted on copper grid for TEM (coated with ultrathin carbon film, 400 mesh). Upon the copper grid loaded with catalyst was dried in air, TEM studies were performed. To obtain a meaningful size distribution, size of 500 Rh nanoparticles of this TEM copper grid were measured. It was found that the average size of Rh NPs on the 6.3wt%Rh/TiO₂ after catalysis at 650°C for 240 hrs is 3.0 nm.

2. Chemisorption of CO on 0.037wt%Rh/TiO₂ and 6.3wt%Rh/TiO₂

Dispersions of Rh atoms on the used 0.037wt%Rh/TiO₂ and used 6.3wt%Rh/TiO₂ were measured by CO chemisorption on an AutoChem II Chemisorption Analyzer (Micrometrics). In a typical test, a used catalyst powder (500 mg for Rh₁/TiO₂, or 100 mg for RhNP/TiO₂) was loaded in the cell and pretreated in flowing Ar gas (99.999%) at 300°C for 30 min. After cooled to room temperature, the catalyst was purged by pulses of CO flow (calibrated to be 10.989% in He). The amount of adsorbed CO was determined by TCD detector. The dispersions of Rh on 0.037wt%Rh/TiO₂ and 6.3wt%Rh/TiO₂ are 97.5% and 30.0%, respectively.

3. Evaluation of catalytic performances of bare TiO₂, 0.037wt%Rh/TiO₂ and 6.3wt%Rh/TiO₂

Catalytic performances of partial oxidation of methane (POM), $2CH_4+O_2\rightarrow 2CO+4H_2$ on $0.037wt\%Rh/TiO_2$ and $6.3wt\%Rh/TiO_2$ were studied in a fixed bed reactor. Typically, 50 mg catalyst was mixed with 300 mg of quartz sand (40-60 mesh) and then was loaded into a quartz tube reactor. A mixture of 25 mL/min 10% CH₄/Ar and 25 mL/min 5% O₂/Ar was flowing through the reactor. Catalysis temperature was measured by a K-type thermocouple inserted to the middle of the catalyst bed. The catalysis temperature was maintained at a set point through a proportional–integral–derivative (PID) temperature controller. The POM process was performed in the temperature range of 300°C to 650°C or 700°C with an interval of 50°C.

Reactants and products of this catalysis were monitored by using an online gas chromatography equipped with a HayeSep D ($6' \times 1/8''$) packed column, a molecular sieve $13 \times (6' \times 1/8'')$ packed column, with two thermal conductivity detector (TCD) and one flame ionization detector (FID). The conversion of methane (X_{CH_4}) and selectivities for producing hydrogen (S_{H_2}) and carbon monoxide (S_{CO}) were calculated using the following equations:

$$X_{CH_4}(\%) = \frac{C_{CH_4\,(inlet)} - C_{CH_4\,(outlet)}}{C_{CH_4\,(inlet)}} \times 100\%$$
(1)

$$S_{H_2}(\%) = \frac{\frac{1}{2}n_{H_2(outlet)}}{n_{CH_4(consumed)}} \times 100\%$$
(2)

$$S_{CO}(\%) = \frac{n_{CO \ (outlet)}}{n_{CH_4 \ (consumed)}} \times 100\%$$
(3)

where $C_{CH_4 (inlet)}$ and $C_{CH_4 (outlet)}$ are defined as the molar fractions of CH₄ at the reactor inlet and outlet, respectively.

4. Measurement of reaction rate under kinetics-controlled regime

The kinetic experiments of POM on 0.037wt%Rh/TiO₂ and 6.3wt%Rh/TiO₂ were conducted in the fixed bed reactor, 2.2 mg 0.037wt%Rh/TiO₂ or 6.3wt%Rh/TiO₂ mixed with quartz sand was loaded into a quartz tube. 25 mL/min 10% CH₄/Ar and 25 mL/min 5% O₂/Ar were pre-mixed and then flew to the reactor. The catalyst temperature was maintained at a set point through a PID temperature controller. Catalyst temperature was measured by using a K-type thermocouple inserted into the middle of the catalyst bed. Reactants and products of this catalysis process in the kinetics-controlled regime were separated and measured by using an online gas chromatography with two TCDs and one FID and data was collected twice at each temperature.

The kinetics studies of POM were performed in the temperature range of 590°C to 670°C, while kinetic process on the catalyst of 6.3wt%Rh/TiO₂ was performed in the temperature range of 610° C- 670° C. In these temperature ranges, conversions of CH₄ in POM are lower than 10%. With the measured conversion of CH₄ and selectivity for producing H₂, the yield for producing H₂ can be readily calculated. For example, here the measured conversion of CH₄ on 2.2 mg of 0.037wt%Rh/TiO₂ at 650° C is 9.0% and the selectivity for H₂ is 95%; thus, the yield of H₂ at 650° C on 2.2 mg of 0.037wt%Rh/TiO₂ at 650° C is 8.55%. The conversion of CH₄ and selectivity for H₂ at 650° C on 2.2 mg of 6.3wt%Rh/TiO₂ are 8.8% and 90.5%, respectively. The yields of H₂,

[X] at temperatures lower than 650°C were calculated and ln[X] was plotted in Figure S22. With this yield, reaction rate on 2.2 mg 0.037wt%Rh/TiO₂ or 6.3wt%Rh/TiO₂ in terms of the number H₂ molecules produced from each catalyst was calculated in the following **Section 7.** By dividing the number of active sites of 2.2 mg of 0.037wt%Rh/TiO₂ or 2.2 mg of 6.3wt%Rh/TiO₂, the turnover rates in terms of the number of H₂ molecules produced from each Rh atom at a specific temperature such as 650°C were calculated in Section 7. The details of the calculations of TORs of the two catalysts can be found in the following Section 7.

5. Ex-Situ, In-Situ and Operando Characterizations

Rh concentration of the catalyst with nominal loading of 0.20wt% on TiO₂ was measured with inductively coupled optical atomic emission spectroscopy (ICP-AES, Horiba Jobin Yvon JY 2000). Based on the ICP-AES measurements, the actual loading of Rh on TiO₂ is 0.037wt%. Thus, it is termed 0.037wt%Rh/TiO₂. For convenience of emphasizing different features of this catalyst, Rh₁/TO₂ or Rh₁O₅/TiO₂ was interchangeably used in the main text or SI. They refer to the same catalyst.

In-situ X-ray Absorption Nar Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) studies were performed at the Beamline 2-2, Stanford Synchrotron Radiation Light source at SLAC National Accelerator Laboratory, Beamline 8-ID (ISS), National Synchrotron Light Source II (NSLS-II) at Brookhaven National Lab, a couple of synchrotron centers overseas including Beamline 36XU, SPring-8. The Rh K-edge spectrum of the catalyst (0.037wt%Rh/TiO₂) was measured in fluorescence mode under ambient conditions. 20 mg of 0.037wt%Rh/TiO₂ catalyst was loaded to a quartz tube which is almost transparent for transmitted X- ray and generated fluorescence due to absorption of X-ray by K-edge of Rh atoms. The Rh K-edge spectrum of a metallic Rh foil was collected at the same time for X-ray energy calibration (23220 eV) and data alignment. XANES and EXAFS data were processed and fitted with ARTEMIS and ATHENA software.[1] The amplitude of the Fourier transformed spectra of EXAFS of reference samples, such as Rh foil and TiO₂, are rescaled by 0.5 for better comparison as shown in Figure 2b and Figure S26. The wavelet transformation was performed by HAMA Fortran package.[2] In a typical WT analysis, k weight=2, Morlet function was used, kappa=5, sigma=1.

XANES and EXAFS spectroscopy studies of catalysts were based on XAS data collected at beamline station of foreign synchrotron centers instead of our own research group. A homemade XAS reactor was used. In brief, the XAS reactor used in this work is a fixed-bed flow reactor with the capability of well control of catalysis temperature, flow rate and data collection when a catalyst in the reactor is at a wide temperature range at a wide pressure range. The details and function of the XAS reactor we used can be found in our instrumentation papers.[3, 4]

For a catalyst, two sets of XAS data were collected. In method #1, a catalyst was loaded to the XAS reactor at beamline station of synchrotron center. The loaded catalyst was pretreated at beamline end-station under the same condition as that of measurement of catalytic performance in our own research group. The GHSV of XAS reactor at beamline end-station is the same as that of catalysis measurement performed in our own group. Then, the catalyst was heated in flowing mixture of reactants to 650°C; XAS data was collected during catalysis at 650°C. This is the first set of XAS data (Set I). Then, the catalyst was cooled down to 120-150°C in the mixture of the reactants and then XAS data were collected at a temperature of 120-150°C to avoid Debye-Waller thermal vibrations of crystals at high temperature;[5] this is the second set of data (Set II). We found that the energy space spectra of the two sets of XAS data (Set I collected at 650°C in the mixture of reactants of POM and Set II collected at 120-150°C in the mixture of reactants of POM) are the same. Thus, the XAS data of Set II can completely represent the Set I which was collecting from a catalyst catalyzing POM.

In terms of r-space spectrum, the peak positions of the two sets of spectra are the same but their magnitudes of Y-axis |X(R)| (Å⁻³) are very different. Thus, we used the data of set II to generate the experimental spectra of r-space spectrum of Rh K-edge since the XAS data collected at the lower temperature do not have the issue of Debye-Waller factor of thermal vibrations (shown in Figure 2 and 4).[5]

High-angle annular dark-field scanning transmission electron microscopy images of the used Rh₁/TiO₂ catalyst were obtained on domestic and overseas aberration-corrected STEM (AC-STEM) systems operated at 200 kV with a nominal spatial resolution of 0.08 nm in the STEM mode. Before microscopy examination, the catalyst powders were ultrasonically dispersed in ethanol and a drop of the resulting suspension was placed onto a 200-mesh lacey carbon coated copper grid. Both low and high magnification images were extensively screened to extract reliable information on the dispersion of the Rh atoms on TiO₂.

Surfaces of catalysts during catalysis were studied by Lab-based ambient-pressure X-ray photoelectron spectrometer (NAP-XPS) systems. The catalyst powder was drop-casted on one

piece of Au foil with rough surface. For in-situ study of surface chemistry of Rh₁/TiO₂ for POM, methane and oxygen were mixed and then introduced into the reaction cell. The pressure was controlled at 0.8 and 0.4 Torr for methane and oxygen, respectively with a flow rate of about 4 mL/min. Gas composition during catalysis in the catalysis reactor was on-line analyzed by using the online quadrupole mass spectrometer (RGA-100, SRS Instrument).

Diffuse Reflectance Infrared Fourier Transform spectra (DRIFTS) of CO adsorption on Rh₁/TiO₂ and Rh NP/TiO₂ were obtained on domestic and overseas FTIR systems equipped with a linearized MCT detector and a Harrick diffuse reflectance accessory. The used catalyst was pretreated at 300°C for 30-60 min by 5% O₂, then purged with Helium at 300°C for 5 min. After cooled down to 30°C in flowing Helium (99.999%), a spectrum was obtained as background. Then CO was introduced, the excess CO was purged with Helium (99.999%). For the used Rh NP/TiO₂, it was reduced in 5% H₂ at 300°C for three hrs for reducing the potentially oxidized surface before performing CO chemisorption experiment.

Based on literature [6], v(CO) frequencies of free CO molecules in gas phase, CO adsorbed in μ_1 mode (a CO molecule adsorbed on top of a metal atom), CO adsorbed in μ_2 mode (a CO molecule bridging on two metal atoms), and CO adsorbed in µ3 mode (CO bridging on three metal atoms) are 2143 cm⁻¹, 2120-2000 cm⁻¹, 1900-1750 cm⁻¹ and 1730-1620 cm⁻¹, respectively. µ₁ mode is also called a terminal binding mode in which a CO molecule is adsorbed on top of a metal atom; it is the binding configuration of a single CO molecule bonded on a metal atom referred to atop in surface science or/and the germinal-dicarbonyl binding configuration. In the case of the germinaldicarbonyl binding configuration, two CO molecules are simultaneously bound to one metal atom; this binding configuration leads to the presence of symmetric and asymmetric stretching peaks of two C=O bonds. For a surface consisting of continuously packed metal atoms, CO molecules are adsorbed through μ_2 or/and μ_3 binding modes instead of μ_1 . μ_2 or/and μ_3 mode is typically observed on surface consisting of continuously packed metal atoms. Whether v(CO) bands of μ_1 mode is observed or not is an approach for distinguishing the singly dispersed metal atoms from continuously packed metal atoms on surface of metal nanoparticles. More straightforward, the appearance of only atop and/or germinal dicarbonyl bands but not μ_2 or/and μ_3 signifies the presence of singly dispersed metal atoms on surface of a catalyst.

6. Calculations of the amount of Rh (in mol) *exposed to surface* of 50 mg of 0.037wt%Rh/TiO₂ and 50 mg of 6.3wt%Rh/TiO₂

6.1 The amount of Rh atoms (in mol) exposed on surface of 50 mg of 0.037wt%Rh/TiO2

For 50 mg of 0.037wt%Rh/TiO₂, the amount of the exposed Rh atoms is 1.75×10^{-7} mol. This is calculated on the basis of dispersion of Rh atoms on surface, 97.5%. Thus, the amount of Rh atoms (in mol) exposed to surface of 50 mg of 0.037wt%Rh/TiO₂ is $\frac{0.050 \times 0.037\% \times 0.975 \text{ gram}}{102.9 \text{ gram/mol}} = 1.75 \times 10^{-7} \text{ mol}$.

6.2 The amount of Rh atoms (in mol) exposed on surface of 50 mg of 6.3wt%Rh/TiO₂

For 50 mg of $6.3wt\%Rh/TiO_2$, the amount of the exposed Rh atoms on surface in mol is 1.07×10^{-5} mol. The dispersion of Rh atoms on surface of Rh NPs, 35% was evaluated by assuming a hemisphere shape for these Rh NPs. This method was successfully used in our previous publication.[7] The following is the details of the evaluation.

First, we assumed each Rh nanoparticle is *hemisphere* on oxide support. Then, the volume of a 3.0 nm Rh nanoparticle, $V_{Rh NP}$, can be calculated with equation (11):

$$V_{Rh NP (hemisphere)} = \frac{2}{3}\pi r^3 = \frac{2}{3} \times 3.14 \times (\frac{3}{2}nm \times \frac{10^{-7}cm}{nm})^3 = 7.07 \times 10^{-21}cm^3$$

As the density of Rh metal (ρ) is 12.41 g cm^{-3} , the weight of each 3.0 nm Rh *hemisphere* nanoparticles ($W_{Each Rh NP}$) can be calculated:

$$W_{Each Rh NP} = \rho \times V_{Rh NP} = 12.41 \frac{g}{cm^3} \times 7.07 \times 10^{-21} cm^3 = 8.77 \times 10^{-20} g$$

Since the molecular weight of Rh metal is 102.91 g/mol, the total atoms in each 3 nm Rh nanoparticle with a hemisphere shape ($N_{Rh atoms}$) can be calculated with the following equation:

$$N_{Rh atoms} = \frac{W_{Each Rh Np}}{M} \times N_A = \frac{8.77 \times 10^{-20} g}{102.91 g/mol} \times 6.022 \times 10^{23} mol^{-1} = 513$$

Surface area of a *hemisphere* Rh NP can be calculated in the following:

 $A = 2\pi r^2 = 2 \times 3.14 \times (1.5nm)^2 = 14.14 \ nm^2$

Area occupied by one Rh atom on (100) surface is:

$$A_{(100)} = (2r)^2 = (0.278 \, nm)^2 = 0.07728 \, nm^2$$

Thus, the proposed Rh atoms (i.e. the number of the active sites) on surface of a Rh nanoparticle, $N_{exposed Rh atoms}$ is:

$$N_{exposed Rh atoms of (100) of Rh NP} = \frac{14.14}{0.07728} = 182$$

Thus, the dispersion of Rh atoms of Rh NPs of 6.3wt%Rh/TiO₂ is $D = \frac{182}{513} = 35\%$.

The evaluated dispersion of Rh atoms on Rh NPs of 6.3wt%Rh/TiO₂ with average size of 3.0 nm is 35%, consistent with CO chemisorption measurement of the dispersion of Rh atoms of 6.3wt%Rh/TiO₂, 30%. Thus, the amount of Rh atoms (in mol) exposed on surface of Rh NPs of 50 mg 6.3wt%Rh/TiO₂ is: $\frac{0.050 \times 6.3\% \times 0.35 \text{ (gram)}}{102.9 (\frac{\text{gram}}{\text{mol}})} = 1.07 \times 10^{-5} \text{ mol}.$

6.3 Ratio of number of exposed Rh atoms of 50 mg of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) to that of 50 mg of 6.3wt%Rh/TiO₂ (Rh NP/TiO₂)

Based on the dispersion of Rh on the two catalysts derived from CO chemisorption measurements, the ratio of Rh atoms participated into the POM of 50 mg of 6.3wt%Rh/TiO₂ to 0.037wt%TiO₂ is about 61 ($\frac{1.07 \times 10^{-5}}{1.75 \times 10^{-7}} = 61$). Thus, the number of active sites of 50 mg of 6.3wt%Rh/TiO₂ (Rh NP/TiO₂) is over 60 times of 50 mg of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂).

Although the conversions of CH₄ of the first 100 hrs for 50 mg of 0.037wt%Rh/TiO₂ (Figure 1a) and for 50 mg of 6.3wt%Rh/TiO₂ (Figure S23a) are similar, the activities of the two catalysts are distinctly different. Notably, in the field of catalysis science, activity of a catalyst defined on the activity of a catalytic site on surface of a catalyst instead of activity of a gram of catalyst is used for comparison of activities of two catalysts. The distinctly different activity of the two catalysts was confirmed by the turn-over rate (TOR) measured under kinetics-controlled regime; the calculation of TORs of the two catalysts was described in Section 7.

7. Calculations of turn-over rates (TORs) of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) and 6.3wt%Rh/TiO₂ (Rh NP/TiO₂)

7.1 General method of calculating turn-over rate based on yield of product molecules obtained under kinetic controlled regime

Reaction rate in terms of the number of produced H₂ molecules per minute on a catalyst $(0.037 \text{wt}\%\text{Rh}/\text{TiO}_2 \text{ or } 6.3 \text{wt}\%\text{Rh}/\text{TiO}_2)$ was calculated according to the number of the fed CH₄ molecules (N_{CH_4}) per minute, conversion rate of CH₄ (X_{CH_4}) and the selectivity of H₂ (S_{H_2}) at certain reaction temperature while the conversion of CH₄ is lower than 10%.

Since the volume concentration of the fed CH₄ is 10%, the number of the produced H₂ molecules per minute can be calculated by equation (5) based on the stoichiometry of POM: $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ (4)

 $N_{number of produced H_2} = 2 * N_{CH_4} * X_{CH_4} * S_{H_2} = 2 * N_A * \frac{pV}{RT} * 0.1 * X_{CH_4} * S_{H_2}$ (5)

where N_A is the Avogadro constant (6.022 × 10²³ mol⁻¹), P is the pressure of the gas, R is the ideal gas constant, T is the temperature of the gas, and V is the CH₄ partial volume of the total fed gases that pass the catalyst in one minute by assuming that these gases follow the ideal gas law. By introducing N_A , P, V, R and T, the $N_{number of prodcued H_2 per min}$ can be calculated by equation (6):

$$N_{number of prodcued H_2 per min} = 6.022 \times 10^{23} mol^{-1} \times \frac{\frac{101325 Pa \times 25 \frac{ml}{min} \times 10^{-6} \frac{m^3}{ml}}{8.314 Pa m^3 mol^{-1} K^{-1} \times 298 K} \times 0.1 \times 2 \times X_{CH_4} \times S_{H_2} = 1.25 \times 10^{20} \times X_{CH_4} \times S_{H_2}$$
(6)

Turn-over rate (TOR) can be calculated through dividing $N_{Number of produced H_2 per min}$ (the number of H₂ molecules produced per minutes) with the number of catalytic sites within kinetic control regime.

7.2 Turn-over rate (TOR) of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂)

In the kinetics studies, 2.2 mg Rh₁/TiO₂ catalyst was mixed with 50 mg of purified quartz. The weight concentration is 0.037 wt%. Thus, the number of Rh active sites ($N_{Rh \ sites}$) can be calculated as:

$$N_{Rh\,sites} = 6.022 \times 10^{23} \, mol^{-1} \times \frac{2.2 \, mg \times \frac{10^{-3}g}{mg} \times 0.037 \, wt\%}{102.91 \frac{g}{mol}} \times 97.5\% = 7.91 \times 10^{-9} mol \times 6.022 \times 10^{23} \, mol^{-1} \times 97.5\% = 4.64 \times 10^{15}$$
(7)

TOR of 0.037wt%Rh/TiO₂ (or Rh₁/TiO₂) under kinetics-controlled regime per minute can be calculated with the following equation (8).

$$TOF_{Rh_1/TiO_2} = \frac{N_{Number of produced H_2 permin}}{N_{Rh Sites}}$$
(8)

By introducing equations (6) and (7) to equation (8), the TOR of Rh_1/TiO_2 per minute can be directly calculated. The following is the equation for calculating TOR:

$$TOF_{Rh_1/TiO_2} = \frac{1.25 \times 10^{20} \times X_{CH_4} \times S_{H_2}}{4.64 \times 10^{15}} = 2.69 \times 10^4 \times X_{CH_4} \times S_{H_2}(min^{-1})$$
(9)

For instance, at 650°C on 2.2 mg of Rh₁/TiO₂ catalyst, the conversion of CH₄ (X_{CH_4}) is 9.0% and selectivity of H₂ (S_{H_2}) is 95% by using Rh₁/TiO₂ as catalyst under kinetic control regime condition, thus TOF_{Rh_1/TiO_2} at 650°C can be calculated:

$$TOF_{Rh_1/TiO_2} = 2.69 \times 10^4 \times X_{CH_4} \times S_{H_2}(min^{-1}) = 2.69 \times 10^4 \times 0.090 \times 0.95 = 2300 H_2 molecules per Rh site per minute$$
(10)

7.3 Turn-over rate of 6.3 wt%Rh/TiO₂ (Rh NP/TiO₂)

Based on the dispersion from CO chemisorption and the information that the average size of Rh nanoparticles anchored on the surface of TiO₂ is about 3.0 nm and the dispersion of the Rh atoms on the surface of 3.0 nm nanoparticles, dispersion of Rh atoms of 6.3wt%Rh/TiO₂ is 35%. For 2.2 mg 6.3wt%Rh/TiO₂, the number of Rh active sites ($N_{Rh Sites}$) can be calculated as the following:

$$N_{Rh \ sites} = 6.022 \times 10^{23} \ mol^{-1} \times \frac{2.2 \ mg \times \frac{10^{-3}g}{mg} \times 6.3 \ wt\%}{102.91 \frac{g}{mol}} \times 35\%$$
$$= 6.022 \times 10^{23} \ mol^{-1} \times 1.35 \times 10^{-6} \ mol \times 35\% = 2.85 \times 10^{17}$$

Then, TOR of 6.3wt%Rh/TiO₂ under measured under kinetics control regime can be calculated with the following equation:

$$TOF_{Rh_1/TiO_2} = \frac{N_{Number of produced H_2 per min}}{N_{Rh Sites}}$$

$$TOF_{Rh NP/TiO_2} = \frac{1.25 \times 10^{20} \times X_{CH_4} \times S_{H_2}}{2.85 \times 10^{17}} = 4.39 \times 10^2 \times X_{CH_4} \times S_{H_2}(min^{-1})$$

Under the kinetics-controlled regime, the conversion of CH₄ (X_{CH_4}) on 2.2 mg of 6.3wt%Rh/TiO₂ at 650°C is 8.8% and selectivity for producing H₂ (S_{H_2}) is 90.5% under kinetics control regime condition. Thus, $TOF_{Rh NP/TiO_2}$ at 650°C can be calculated the following equation:

 $TOF_{Rh NP/TiO_2} = 4.39 \times 10^2 \times 0.088 \times 0.905 = 35.0 H_2$ molecule per Rh site per minute

7.4 Comparison of TORs of Rh₁/TiO₂ and Rh NP/TiO₂

Based on the yield of product molecules measured under kinetics-controlled regime for 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) and 6.3wt%Rh/TiO₂ (Rh NP/TiO₂), the reaction rate on each Rh₁ of single-atom catalyst 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) is faster than that on each Rh atom

exposed on surface of Rh NP of 6.3wt%Rh/TiO₂ (Rh NP/TiO₂) by several tens of time. This huge difference is driven from their distinctly different electronic states; the profound difference in electronic states between the singly dispersed cationic site and continuously packed metallic site was uncovered in the theoretical simulation of this work.

8. Note on the difference in coordination environment of Rh atoms in 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) and 6.3wt%Rh/TiO₂ (Rh NP/TiO₂)

Distinctly different from 0.037wt% Rh/TiO₂ (Rh₁/TiO₂), the XANES and EXAFS studies of 6.3wt%Rh/TiO₂ (Rh NP/TiO₂) used for catalysis at 650°C for 240 hrs showed that Rh atoms of the used 6.3wt%Rh/TiO₂ are at the metallic state as evidenced by the fact that its Rh K-edge is close to the Rh foil reference in energy space spectrum of Rh K-edge and Rh-Rh bonds of metal nanoparticles were clearly observed in *r*-space spectra of Rh K-edge (Figure S26).

9. Note on single dispersion of 0.037wt% Rh/TiO₂ evidenced in DRIFTS

The singly dispersion of Rh atoms on TiO₂ of the used 0.037wt% Rh/TiO₂ were supported by studying vibrational frequency of chemisorbed CO using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). As shown in Figure 5, two peaks at 2090 cm⁻¹ and 2022 cm⁻¹ were clearly observed from the used 0.037wt% Rh/TiO₂. They are ascribed to the symmetric and asymmetric vibrations of gem-dicarbonyl doublet CO on a Rh cation, respectively. Based on the literature,[8] the simultaneous observation of the two peaks suggests the single dispersion of Rh atoms on surface of the used 0.037wt% Rh/TiO₂. Compared to the vibrational feature of CO adsorbed on Rh nanoparticle (Figure S7), the lack of peaks at 1872 cm⁻¹ and 2060 cm⁻¹ of Rh nanoparticles[9] formed on surface of 0.037 wt% Rh/TiO₂ during catalysis at 650°C since 1872 cm⁻¹ and 2060 cm⁻¹ are attributed to stretching of CO molecules adsorbed on surface of Rh metal nanoparticles or Rh single crystal. Thus, DRIFTS studies strongly suggest that Rh atoms in the used 0.037wt%Rh/TiO₂ are singly dispersed on TiO₂ instead of formation of Rh NPs.

10. Note on AP-XPS studies

Surface of 0.037wt%Rh/TiO2 during catalysis at different temperatures was tracked with

ambient-pressure X-ray photoelectron spectroscopy (Figure 2j) when 0.037wt%Rh/TiO₂ was catalyzing POM in the reaction cell of AP-XPS systems manufactured in European countries. 0.037wt%Rh/TiO₂ was loaded to the reaction cell. The mixture of CH₄ (0.8 Torr) and O₂ (0.4 Torr) at a total flow rate of 4.0 mL/min was continuously introduced to the reaction cell to flow through this catalyst. Formation of CO and H₂ was confirmed with an on-line mass spectrometer installed on our AP-XPS system when surface of the 0.037wt%Rh/TiO₂ was being analyzed with AP-XPS. Notably, there was no obvious shift of the binding energy of Rh 3d electrons in the whole temperature range of 300-650°C (Figure 2j). The binding energy of Rh 3d 5/2 at 310.2 eV is obviously higher that of metallic Rh at 307.4 eV, suggesting that the Rh atoms of 0.037wt%Rh/TiO₂ are definitely at cationic state.

11. Detail on DFT study

The density functional theory (DFT) calculations were performed with the Vienna ab initio Simulation Package (VASP).[10, 11] The on-site Coulomb interaction was included with the DFT+U method by Dudarev, et al.[12] in VASP using a Hubbard parameter U = 3 eV for the Ti atom, from the previous literature for TiO₂.[13, 14] The Perdew-Burke-Ernzerhof (PBE)[15] functional form of generalized-gradient approximation (GGA) was used to describe electron exchange and correlation. All calculations were performed with spin polarization. The projectoraugmented wave method was used to describe the electron-core interaction[16] with a kinetic energy cutoff of 450 eV. The Brillouin zone was sampled with the Monkhorst-Pack scheme of a 3×2×1 k-point mesh.[17] Transition states (TS) were found with the nudged elastic band (NEB)[18] method using a force convergence criterion of 0.05 eV/Å. To calculate the occupancies of the molecular bonds of methane, the periodic natural bond orbital (NBO) analysis implemented by Schmidt et al. was used. [19] The TiO₂ was purchased from Aldrich (Titania, 99.95%, Aeroxide®) P25). Its main phase is Anatase. As transition temperature of anatase to rutile is 700-1000°C in literature,²⁰ anatase is the structure used in these calculations. A specific study is that the transition temperature of 100 nm anatase to rutile occurs at 1000°C. (Pelagia I. Gouma and Michael J. Mills J. Am. Chem. Soc. 2001, 84, 619). We added this description to Section II of SI.



Figure S1. Catalytic performance of bare TiO₂ in the temperature range of 300-700°C in the first cycle (a) and the second cycle (b). The left axis and the black line show conversion of methane. The right axis and the purple line show the selectivity for producing H₂; blue line show the selectivity for producing CO. Catalysis conditions: 50 mg pure TiO₂, the gas fed to the reactor is a pre-mixed 25 ml/min of 10% CH₄ and 25 mL/min of 5% O₂.



Figure S2. Catalytic performance of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) in the temperature range of 300-650°C the first cycle and in the temperature range of 300-650°C in the 20th cycle. The left axis and the black line show conversion of methane. The right axis and the purple line show the selectivity to the production of H₂, blue line show the selectivity of production of CO. Catalysis conditions: 50 mg Rh₁/TiO₂; flow rate of 10% CH₄ is 25 mL/min and 5% O₂ is 25 mL/min.



Figure S3. Conversion of CH₄ on 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) as the function of total flow rate of reactants. The molar ratio of CH₄ and O₂ is always remained at 2:1 although the total flow rate of each experiment is different in each experiment; the total flow rate can be read from the horizontal axis; it is in the range of 10-100 mL/min. The quite similar conversions of CH₄ in the range of total flow rate at 30 mL/min to 100 mL/min show that there was no diffusion limit when the total flow rate of 50 mL/min (25 mL/min of 10% CH₄ and 25 mL/min of 5% O₂) was used in the studies of catalytic performance in this work.



Figure S4. Conversion of CH₄ on 6.3 wt%Rh/TiO₂ (Rh NP/TiO₂) as the function of total flow rate of reactants. The molar ratio of CH₄ and O₂ is always remained at 2:1 although the total flow rate of each experiment is different in each experiment; the total flow rate can be read from the horizontal axis; it is in the range of 10-100 mL/min. The quite similar conversions of CH₄ in the range of total flow rate at 30 mL/min to 100 mL/min show that there was no diffusion limit when the total flow rate of 50 mL/min (25 mL/min of 10% CH₄ and 25 mL/min of 5% O₂) was used in the studies of catalytic performance in this work.



Figure S5. Optimized geometries of four possible anchoring models of Rh_1 atom on surface of or in surface layer of Rh_1/TiO_2 . (a) Surface of TiO_2 (101) in which the topmost Ti atom was replaced by Rh atom and thus surface lattice of TiO_2 is maintained. (b-d) Surface of TiO_2 (101) with a capped Rh_1 atom.



Figure S6. *k*-space spectrum and data fitting of 0.037wt%Rh/TiO₂ (Rh₁/TiO₂) collected through in-situ study mode of EXAFS studies (see the energy space and r-space spectra in Figure 2a and 2c).



Figure S7. DRIFT studies of CO adsorbed on 6.3wt%Rh/TiO₂ (Rh NP/TiO₂). The observed vibrational signatures at 1870 cm⁻¹, 2014 cm⁻¹, 2060 cm⁻¹ and 2086 cm⁻¹ are consistent with those of CO adsorbed on Rh(111) singly crystal with a CO coverage of 0.78.[9]



Figure S8. In-situ XANES and EXAFS studies of Catalyst #2 (Catalyst #2: a Rh₁/TiO₂ catalyst used for POM at 650°C at our catalysis lab) at beamline and ex-situ studies of references samples including Rh₂O₃/Al₂O₃ at 25°C in air and Rh foil at 25°C in air. (a) Energy space spectrum of Rh K-edge of Rh foil (blue line) at 25°C in air, Rh₂O₃/Al₂O₃ (red line) at 25°C in air and Catalyst #2 under the catalytic condition of 650°C (black line); (b) r-space spectrum of Rh K-edge of Rh atoms of Catalyst #2 (black line) collected through in-situ study mode under the catalytic condition of 650°C as described in Section 5. The fitting parameters are summarized in Figure S9.

Pathway	CN	R(Å)	σ² (Ų)
Rh-O	5.29±0.28	2.05±0.01	0.00378
Rh-(O)-Ti	0.84±0.26	2.92±0.05	0.00378
Rh-(O)-Ti	1.06±0.55	3.73±0.08	0.00378

Figure S9. Structural parameters used for fitting experimental r-space spectrum of Rh K-edge of 0.037wt%Rh/TiO₂ after catalysis at 650°C (at our home lab) during catalysis at 650°C at beamline.



Figure S10. STEM images and structural model of the Rh_1/TiO_2 catalyst. (a) Large scale STEM image of used Rh_1/TiO_2 ; (b-d) High-resolution STEM images; (e) Optimized structure of (101) of bare TiO₂ catalyst. (f) Optimized (101) surface of Rh_1/TiO_2 .



Figure S11. EXAFS studies of pure TiO_2 at 25°C in air. (a) Fourier transformed *r*-space spectrum of Ti K-edge of bare TiO_2 in air. (b) Structural parameters used for fitting experimental r-space spectrum of bare TiO_2 catalyst. The coordination number is constrained according to literature.[21]



Figure S12. Optimized surface structure of Rh₁/TiO₂. This surface consists of a Rh₁O₅ cluster. Four of the five oxygen atoms are O^{α} , O^{β} , O^{γ} and O^{θ} which are on surface of TiO₂(101). One of the five oxygen atoms is in subsurface (below the Rh₁ atom) which is not marked here.

Entry	Bader charge before adsorption of CH ₄								
1		M site	0	С	Н				
2	CH ₄	/	/	-0.064	0.016				
3	TiO ₂	1.996	-1.068	/	/				
4	Rh ₁ /TiO ₂	1.430	-0.972	/	/				
5	Bader charge after adsorption of CH ₄								
6	H ₄ C····TiO ₂	2.002	-1.067	-0.103	-0.003				
7	H_4C ····Rh ₁ /TiO ₂	1.424	-0.976	-0.153	0.020				
8	Difference in Bader charge between post adsorption and pre-adsorption								
9	H_4C ····TiO ₂ vs. TiO ₂	0.006	0.001	-0.040	-0.019				
10	H_4C ····Rh ₁ /TiO ₂ vs. Rh ₁ /TiO ₂	-0.006	-0.004	-0.090	0.004				

Figure S13. Bader charges on C, H, O and Rh atoms before and after CH_4 adsorption on Rh_1/TiO_2 and bare TiO₂. Clearly, the net increase in electron density on carbon C atom of CH₄ upon adsorption on Ti atom of TiO₂ or on Rh₁ of Rh₁/TiO₂ is 0.090. More importantly, the increased amount of electron density (0.090) on the CH₄ molecule adsorbed on Rh₁ atom of Rh₁/TiO₂ is much more than the increased amount of electron density (0.040) of a CH₄ molecule adsorbed on Ti atoms of Ti₁O₅ of bare TiO₂.



Figure S14. Optimized structures of (a) free CH₄ molecule, (b) CH₄ adsorbed on Ti atom of bare $TiO_2(101)$ through the carbon atom of CH₄. (3) CH₄ adsorbed on Rh₁ atoms of Rh₁/TiO₂. The C-H distance in free CH₄, CH₄ adsorbed on Ti atom of TiO₂(101), and CH₄ adsorbed on Rh₁ of Rh₁/TiO₂ are 1.096 Å, 1.099 Å, and 1.115 Å, respectively.



Figure S15. Structure and energy of intermediates of elementary steps a to l among all 26 steps of a complete pathway of POM to produce H₂ and CO on Rh₁/TiO₂.



Figure S16. Structure and energy of intermediates of elementary steps m to z among all 26 steps of a complete pathway of POM to produce H₂ and CO on Rh₁/TiO₂.



Figure S17. Structure and energy of transition states of elementary steps *a* to *l* among all 26 steps of a complete pathway of POM to produce H_2 and CO on Rh_1/TiO_2 .



Figure S18. Structure and energy of transition states of elementary steps *m* to *z* among all 26 steps of a complete pathway of POM to produce H_2 and CO on Rh_1/TiO_2 . The energy profiles of all 25 steps are presented in Panel 1 in Figure 8 in the main text.



Figure S19. Conversion of CH₄ and selectivity for production of CO and H₂ catalyzed by 6.3wt%Rh/TiO₂ in the temperature range of 350-650°C. 50 mg catalyst was used in the test. Flow rate of 10% CH₄ or 5% O₂ is 25 ml/min. The heating and cooling rates are 2°C/min.



Figure S20. TEM studies of the used 6.3wt%Rh/TiO₂. (a-f) Representative TEM images. (g) Statistical accounting of size distribution of over 500 Rh nanoparticles of the used 6.3wt%Rh/TiO₂. The average size is 3.0 nm. Compared to Rh NPs before catalysis, the sizes of Rh NPs after catalysis did not increase obviously.



STEM of 6.3wt%RhNP/TiO₂



A bright NP is labeled with red cycle



EDX for the NP in the red cycle

Figure S21. Dark field image of HAADF-STEM mode of EDX of 6.3wt%Rh/TiO₂ and confirmation of chemical identity of nanoparticle supported on TiO₂. (a) One representative image of dark field image of HAADF-STEM mode of EDX of 6.3wt%Rh/TiO₂. (b) A single nanoparticle marked with a red circle chosen for EDX studies. (c) EDX spectrum of chemical identity of the chosen Rh nanoparticle of Figure S21b.



Figure S22. Plot of ln[Y] as a function of 1/T for 0.037wt%Rh/TiO₂ (Rh₁/TiO₂, black line) and 6.3wt%Rh/TiO₂ (Rh NP/TiO₂, red line). The yields (Y) were measured under kinetics-controlled regime where the conversions of CH₄ in POM are lower than 10%.



Figure S23. Catalytic stability of 6.3wt%Rh/TiO₂ (Rh NP/TiO₂). Catalysis condition: 50 mg 6.3wt%Rh/TiO₂, flow rate of 10% CH₄ is 25 mL/min and 5% O₂ is 25 mL/min, temperature is 650°C. (a) Conversion of CH₄ at 650°C; (b) Selectivity of H₂ at 650°C; (c) Selectivity of CO at 650°C; (d) H₂/CO mole ratio at 650°C.



Figure S24. Surface structures of surfaces of single atom catalysts and metal nanoparticle catalyst. (a) surface of Rh_1/TiO_2 . (b) Surface of Rh metal nanoparticle consisting of 79 Rh atoms representing a Rh nanoparticle of catalyst $6.3wt\%Rh/TiO_2$.



Figure S25. Structure and energy of adsorbed carbon atom on Rh₁ atom of single atom catalyst and metal nanoparticle catalyst. (a) Optimized structure of adsorbed single carbon atom on the singly dispersed Rh₁ atom of Rh₁/TiO₂ (101) and the adsorption energy of C atom; (b) Optimized structure of adsorbed single carbon atom on surface of a Rh NP consisting of 79 atoms, and the adsorption energy of C atom.



Figure S26 the Fourier transformed EXAFS spectrum of 6.3wt% Rh/TiO₂ catalyst after catalysis(red) and the corresponding Rh foil (black). The amplitude of the EXAFS spectrum of Rh foil is rescaled by 0.5.

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