

**In-situ Surface Chemistries and Catalytic Performances of Ceria  
Doped with Palladium, Platinum and Rhodium in Methane Partial  
Oxidation for Production of Syngas**

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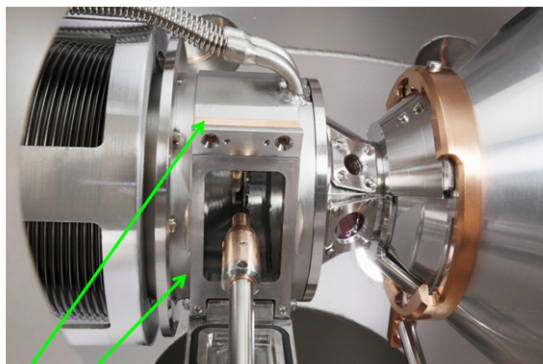
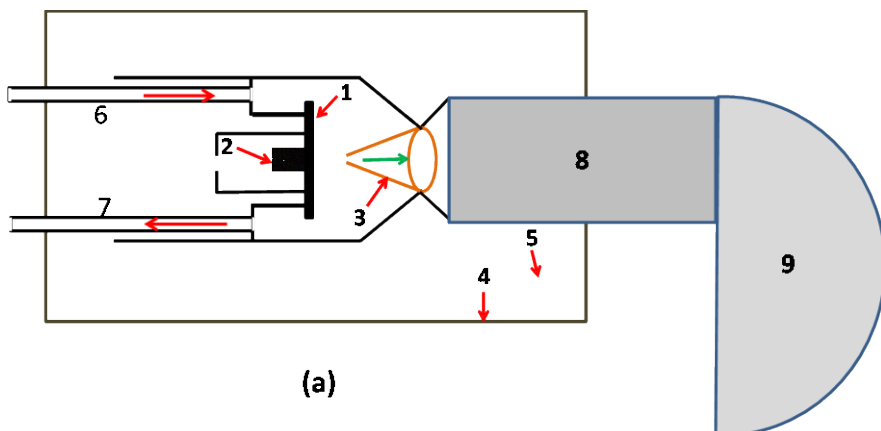
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**1. Schematic showing gas flow and heating in catalysis reactor integrated to the AP-XPS system**



Gas inlet and outlet tubes are embedded in the reaction cell.

**(b)**

Figure S1 (a) Schematic showing gas flow and sample heating. 1. Sample stage. 2. E-beam heating from vacuum-side. 3. Aperture interfacing reactive environment and pre-lens. 4. UHV chamber. 5. UHV between catalysis reactor and UHV chamber of AP-XPS. 6. Port and tube for introducing gas to the reaction cell. 7. Port and tube for flowing gas out of the reaction cell. 8. Differentially pumping system between reaction cell and energy analyzer. 9. Electrostatic energy analyzer. (b) Photo of reaction cell.

## 2. Catalysis on pure $\text{CeO}_2$

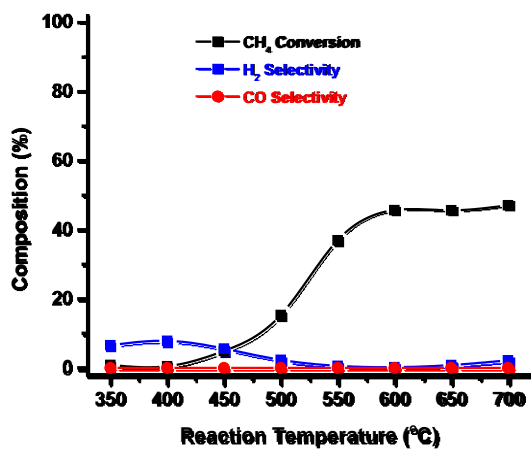


Figure S2 Catalytic performance of pure  $\text{CeO}_2$  for methane partial oxidation. Measurements of catalytic conversion and selectivity were done under the same condition as that of  $\text{CeO}_2$  doped with Pd, Pt, or Rh.  $\text{CeO}_2$  has the same average size as that of  $\text{CeO}_2$  doped with noble metal ions.

### 3. XRD pattern of catalysts

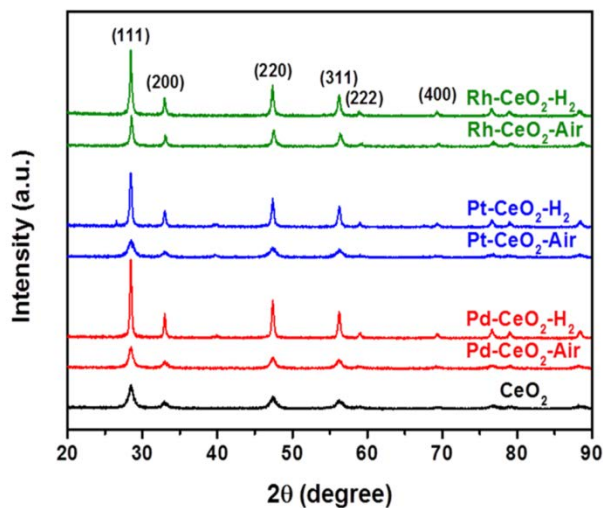


Figure S3 XRD patterns of catalysts after catalysis.

The sizes of Pd-CeO<sub>2</sub>-H<sub>2</sub>, Pd-CeO<sub>2</sub>-air, Pt-CeO<sub>2</sub>-H<sub>2</sub>, Pt-CeO<sub>2</sub>-air, Rh-CeO<sub>2</sub>-H<sub>2</sub>, Rh-CeO<sub>2</sub>-air calculated with Scherrer's equation based on the width of diffraction peaks in XRD are 32.0 nm, 14.0 nm, 26.5 nm, 9.5 nm, 28.8 nm, and 20.3 nm, respectively.

### 4. Atomic ratio of noble metal atoms to Ce of the topmost layer of catalysts during catalysis

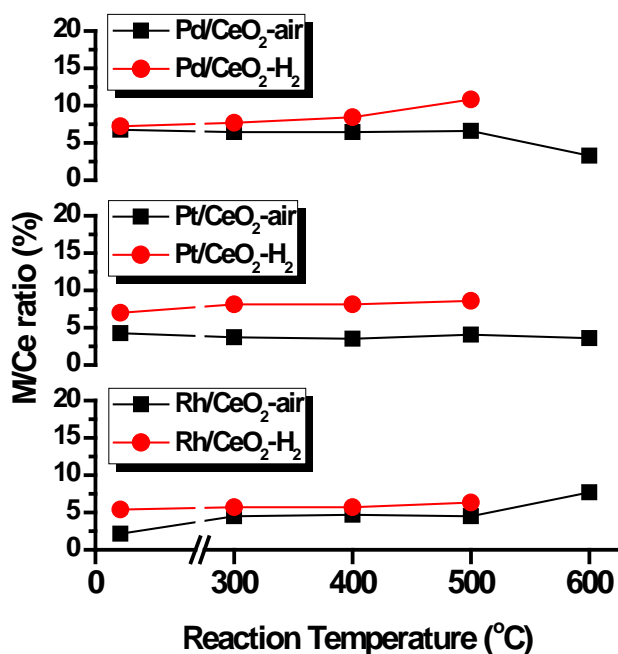


Figure S4 Atomic ratio of Pd, Pt, or Rh in the topmost surface layer to Ce of the topmost surface layer of catalysts during catalysis.

## 5. Calculation of turn-over frequency

### 5.1 Density of a unit cell of the catalyst (Pd, Pt, or Rh–CeO<sub>2</sub>)

#### 5.1.1 Weight of a unit cell of doped CeO<sub>2</sub>

Since the amount of doped metal M (= Pd, Pt, or Rh) is **5 at%** relative to the total of Ce and dopant in each catalyst, the chemical formula of one unit cell of each catalyst can be expressed as **M<sub>0.2</sub>Ce<sub>3.8</sub>O<sub>8</sub>** (the unit cell of pure CeO<sub>2</sub> is Ce<sub>4</sub>O<sub>8</sub> with O filling tetrahedral sites among the cubic close packed Ce). Based on high resolution TEM images, doped CeO<sub>2</sub> exhibit almost the same inter-planar distances. We consider the lattice constant of doped catalyst is the same as CeO<sub>2</sub> nanoparticles. Thus, the weight of a unit cell **M<sub>0.2</sub>Ce<sub>3.8</sub>O<sub>8</sub>** of the doped catalyst is calculated to be  $1.1320 \times 10^{-21}$  g for Pd–CeO<sub>2</sub>  $1.1615 \times 10^{-21}$  g for Pt–CeO<sub>2</sub>, and  $1.1308 \times 10^{-21}$  g for Rh–CeO<sub>2</sub> respectively, which are in fact very close to the weight of a unit cell of CeO<sub>2</sub> nanocrystal.

#### 5.1.2 Volume of a unit cell of doped CeO<sub>2</sub>

The volume of one unit cell of CeO<sub>2</sub> nanocrystal according to the lattice parameters of CeO<sub>2</sub> ( $a = 0.5411$  nm) and face-centered cubic structure feature of CeO<sub>2</sub> can be calculated:

$$V_{cell} = a^3 = (0.5411 \text{ nm})^3 = 0.1584 \text{ nm}^3.$$

#### 5.1.3 Density of a unit cell of doped CeO<sub>2</sub>

Thus, the density ( $\rho$ ) of a unit cell of doped CeO<sub>2</sub> is calculated:

$$\rho_{Pd-CeO_2} = m_{Cell/Pd-CeO_2} / V_{cell} = 7.146 \times 10^{-21} \text{ g nm}^{-3},$$

$$\rho_{Pt-CeO_2} = m_{Cell/Pt-CeO_2} / V_{cell} = 7.333 \times 10^{-21} \text{ g nm}^{-3},$$

$$\rho_{Rh-CeO_2} = m_{Cell/Rh-CeO_2} / V_{cell} = 7.139 \times 10^{-21} \text{ g nm}^{-3}.$$

They are quite close to the density of a pure CeO<sub>2</sub> nanocrystal.

### 5.2 The number of the nanoparticles in 0.010 g catalyst (Pd, Pt, or Rh–CeO<sub>2</sub>)

The volume ( $V_{M-CeO_2}$ ) and weight ( $m_{M-CeO_2}$ ) of a catalyst particle are calculated according to the size and shape of catalyst particles identified with TEM (Pd-CeO<sub>2</sub>-air: 13 nm; Pt-CeO<sub>2</sub>-air: 9.5 nm; Rh-CeO<sub>2</sub>-air: 22.5 nm; Pd-CeO<sub>2</sub>-H<sub>2</sub>: 34 nm; Pt-CeO<sub>2</sub>-H<sub>2</sub>: 28.5 nm; Rh-CeO<sub>2</sub>-H<sub>2</sub>: 30.5 nm) and CeO<sub>2</sub> particles are dominated by the octahedral shape with flat (111) surfaces. It is noted that it is very challenging in controlling shape of nanoparticles. There must be some error since we don't know the exact shape of each nanoparticle (it is impossible). But for the three catalysts prepared with the same method, we assume they have similar shapes. From the shape point of view, we can just use octahedral shape to represent the three catalysts. The sizes of these catalysts are consistent with those calculated with Scherrer's equation (P. Scherrer, *Göttinger Nachrichten Gesell.*, 1918, 2, 98.) based on the width of diffraction peaks in XRD of catalysts.

### 3.2.1 Volume of a catalyst particle with the average size identified with TEM and XRD

*In the following equation we use  $l$  and  $h$  to represent the average edge length and height of the octahedral CeO<sub>2</sub> nanoparticles, respectively.*

$$V_{Pd-CeO_2-air} = l^2 \times h \times 1/3 = (13 \text{ nm})^2 \times 18.4 \text{ nm} \times 1/3 = 1.036 \times 10^3 \text{ nm}^3,$$

$$V_{Pt-CeO_2-air} = l^2 \times h \times 1/3 = (9.5 \text{ nm})^2 \times 13.4 \text{ nm} \times 1/3 = 0.403 \times 10^3 \text{ nm}^3,$$

$$V_{Rh-CeO_2-air} = l^2 \times h \times 1/3 = (22.5 \text{ nm})^2 \times 31.8 \text{ nm} \times 1/3 = 5.366 \times 10^3 \text{ nm}^3,$$

$$V_{Pt-CeO_2-H_2} = l^2 \times h \times 1/3 = (28.5 \text{ nm})^2 \times 40.3 \text{ nm} \times 1/3 = 10.911 \times 10^3 \text{ nm}^3,$$

$$V_{Rh-CeO_2-H_2} = l^2 \times h \times 1/3 = (30.5 \text{ nm})^2 \times 43.1 \text{ nm} \times 1/3 = 13.364 \times 10^3 \text{ nm}^3.$$

### 3.2.2 Weight of a catalyst particle with the average size identified with TEM and XRD

*Then, weight of each nanoparticle is*

$$m_{Pd-CeO_2-air} = V_{Pd-CeO_2} \times \rho_{Pd-CeO_2} = 1.036 \times 10^3 \text{ nm}^3 \times 7.146 \times 10^{-21} \text{ g nm}^{-3} = 7.403 \times 10^{-18} \text{ g},$$

$$m_{Pt-CeO_2-air} = V_{Pt-CeO_2} \times \rho_{Pt-CeO_2} = 0.403 \times 10^3 \text{ nm}^3 \times 7.333 \times 10^{-21} \text{ g nm}^{-3} = 2.955 \times 10^{-18} \text{ g},$$

$$m_{Rh-CeO_2-air} = V_{Rh-CeO_2} \times \rho_{Rh-CeO_2} = 5.366 \times 10^3 \text{ nm}^3 \times 7.139 \times 10^{-21} \text{ g nm}^{-3} = 38.308 \times 10^{-18} \text{ g},$$

$$m_{Pt-CeO_2-H_2} = V_{Pt-CeO_2} \times \rho_{Pt-CeO_2} = 10.911 \times 10^3 \text{ nm}^3 \times 7.333 \times 10^{-21} \text{ g nm}^{-3} = 0.800 \times 10^{-16} \text{ g},$$

$$m_{Rh-CeO_2-H_2} = V_{Rh-CeO_2} \times \rho_{Rh-CeO_2} = 13.364 \times 10^3 \text{ nm}^3 \times 7.139 \times 10^{-21} \text{ g nm}^{-3} = 0.954 \times 10^{-16} \text{ g}.$$

(Density,  $\rho$  was calculated in Section 2.1.3)

### 3.2.3 Number of Pd, Pt, or Rh–CeO<sub>2</sub> nanoparticles that 0.010 g catalyst contains

The number of Pd, Pt, or Rh–CeO<sub>2</sub> nanoparticles that 0.010 g catalyst contains:

$$N_{Pd-CeO_2-air} = 0.010 \text{ g} / (7.403 \times 10^{-18} \text{ g}) = 1.351 \times 10^{15},$$

$$N_{Pt-CeO_2-air} = 0.010 \text{ g} / (2.955 \times 10^{-18} \text{ g}) = 3.384 \times 10^{15},$$

$$N_{Rh-CeO_2-air} = 0.010 \text{ g} / (38.308 \times 10^{-18} \text{ g}) = 0.261 \times 10^{15},$$

$$N_{Pt-CeO_2-H_2} = 0.010 \text{ g} / (0.800 \times 10^{-16} \text{ g}) = 1.250 \times 10^{14},$$

$$N_{Rh-CeO_2-H_2} = 0.010 \text{ g} / (0.954 \times 10^{-16} \text{ g}) = 1.048 \times 10^{14}.$$

## 5.3 Number of the exposed Pd, Pt, or Rh atoms of 0.010 g Pd, Pt, or Rh–CeO<sub>2</sub>

### 5.3.1 Atomic ratio of Pd, Pt or Rh atoms on surface of a catalyst particle to Ce atoms of a catalyst particle

Based on XPS analyses, atomic ratios Pd/Ce, Pt/Ce, and Rh/Ce do not change obviously in the temperature regime of 25°C-600°C. Number of the exposed Pd ( $N_{Pd}$ ), Pt ( $N_{Pt}$ ), or Rh ( $N_{Rh}$ ) atoms on the (111) surfaces of the M–CeO<sub>2</sub> catalyst nanoparticles could be calculated as follows:

*Pd/(Pd+Ce) molar ratio in Pd-CeO<sub>2</sub>–air:*

$$M_{Pd/(Pd+Ce)} = 0.0634,$$

*Pt/(Pt+Ce) molar ratio in Pt-CeO<sub>2</sub>–air:*

$$M_{Pt/(Pt+Ce)} = 0.0407,$$

*Rh/(Rh+Ce) molar ratio in Rh-CeO<sub>2</sub>–air:*

$$M_{Rh/(Rh+Ce)} = 0.0427,$$

*Pt/(Pt+Ce) molar ratio in Pt-CeO<sub>2</sub>–H<sub>2</sub>:*

$$M_{Pt/(Pt+Ce)} = 0.0653,$$

*Rh/(Rh+Ce) molar ratio in Rh-CeO<sub>2</sub>–H<sub>2</sub>:*

$$M_{Rh/(Rh+Ce)} = 0.0401.$$

### 5.3.2 Number of Ce<sup>4+</sup> ion on surface of a catalyst particle

$$N_{Ce\ ion\ (for\ Pd-air)} = S \times 8 / (a^2 \times 0.5) = 73.2\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5$$

$$N_{Ce\ ion\ (for\ Pt-air)} = S \times 8 / (a^2 \times 0.5) = 39.1\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5$$

$$N_{Ce\ ion\ (for\ Rh-air)} = S \times 8 / (a^2 \times 0.5) = 219.2\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5$$

$$N_{Ce\ ion\ (for\ Pt-H_2)} = S \times 8 / (a^2 \times 0.5) = 351.7\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5$$

$$N_{Ce\ ion\ (for\ Rh-H_2)} = S \times 8 / (a^2 \times 0.5) = 402.8\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5$$

### 5.3.3 Number of Pd, Pt or Rh atom on surface of 0.010 gram catalyst

$$N_{Pd\ atoms\ on\ surface\ of\ Pd-CeO_2-air} = N_{Ce\ ion\ (for\ Pd-air)} \times M_{Pd/(Pd+Ce)} \times N_{Pd-CeO_2} = (73.2\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5) \times 0.0634 \times 1.351 \times 10^{15} = 8.565 \times 10^{16}.$$

$M_{Pd/(Pd+Ce)}$ ,  $N_{Pd-CeO_2}$  and  $N_{Ce\ ion\ (for\ Pd-air)}$  were calculated in sections 3.1, 3.2, and 3.3, respectively.

$$N_{Pt-air} = N_{Ce\ ion\ (for\ Pt-air)} \times M_{Pt/(Pt+Ce)} \times N_{Pt-CeO_2} = (39.1\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5) \times 0.0407 \times 3.384 \times 10^{15} = 7.357 \times 10^{16},$$

$$N_{Rh-air} = N_{Ce\ ion\ (for\ Rh-air)} \times M_{Rh/(Rh+Ce)} \times N_{Rh-CeO_2} = (219.2\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5) \times 0.0427 \times 0.261 \times 10^{15} = 3.337 \times 10^{16},$$

$$N_{Pt-H_2} = N_{Ce\ ion\ (for\ Pt-H_2)} \times M_{Pt/(Pt+Ce)} \times N_{Pt-CeO_2} = (351.7\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5) \times 0.0653 \times 1.250 \times 10^{14} = 3.922 \times 10^{16},$$

$$N_{Rh-H_2} = N_{Ce\ ion\ (for\ Rh-H_2)} \times M_{Rh/(Rh+Ce)} \times N_{Rh-CeO_2} = (402.8\ nm^2 \times 8 / 0.2928\ nm^2 \times 0.5) \times 0.0401 \times 1.048 \times 10^{14} = 2.312 \times 10^{16}.$$

## 5.4 Calculation of the TOF



The number of converted CH<sub>4</sub> molecules ( $N_{\text{Conv}}$ ) per one second for 0.010 g catalyst can be calculated according to the number of the fed CH<sub>4</sub> molecules ( $N_{\text{CH}_4}$ ) per one second and the conversion rate of CH<sub>4</sub> ( $X_{\text{M-CH}_4}$ ) at certain reaction temperature. CH<sub>4</sub> concentration of 5% balanced with Ar.

$$N_{\text{Conv}} = N_{\text{CH}_4} \times X_{\text{M-CH}_4} = N_A \times (p \times V) / (R \times T) \times 0.05 \times X_{\text{M-CH}_4} = 6.022 \times 10^{23} \text{ mol}^{-1} \times (101325 \text{ Pa} \times 1.67 \times 10^{-6} \text{ m}^3) / (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293.15 \text{ K}) \times 0.05 \times X_{\text{M-CH}_4} = 2.09 \times 10^{18} \times X_{\text{M-CH}_4}$$

where  $N_A$  is the Avogadro constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ),  $p$  is the pressure of the gas,  $R$  is the ideal gas constant,  $T$  is the temperature of the gas, and  $V$  is the volume of the fed total gases that pass the catalyst in one second ( $1 \times 10^{-4} \text{ m}^3 \text{ min}^{-1} \times 1 \text{ min} / 60 \text{ s} \times 1 \text{ s} = 1.67 \times 10^{-6} \text{ m}^3$ ).

Then, the TOF can be calculated as:

$$\text{TOF}_{\text{Pd-CeO}_2\text{-air}} = (N_{\text{conv}}/N_{\text{Pd-air}}) / t = (2.09 \times 10^{18} \times X_{\text{Pd-CH}_4} / (8.565 \times 10^{16})) / 1 \text{ s} = 24.40 \times X_{\text{Pd-CH}_4} \text{ s}^{-1},$$

$$\text{TOF}_{\text{Pt-CeO}_2\text{-air}} = (N_{\text{conv}}/N_{\text{Pt-air}}) / t = (2.09 \times 10^{18} \times X_{\text{Pt-CH}_4} / (7.357 \times 10^{16})) / 1 \text{ s} = 28.41 \times X_{\text{Pt-CH}_4} \text{ s}^{-1},$$

$$\text{TOF}_{\text{Rh-CeO}_2\text{-air}} = (N_{\text{conv}}/N_{\text{Rh-air}}) / t = (2.09 \times 10^{18} \times X_{\text{Rh-CH}_4} / (3.337 \times 10^{16})) / 1 \text{ s} = 62.63 \times X_{\text{Rh-CH}_4} \text{ s}^{-1},$$

$$\text{TOF}_{\text{Pt-CeO}_2\text{-H}_2} = (N_{\text{conv}}/N_{\text{Pt-H}_2}) / t = (2.09 \times 10^{18} \times X_{\text{Pt-CH}_4} / (3.922 \times 10^{16})) / 1 \text{ s} = 53.29 \times X_{\text{Pt-CH}_4} \text{ s}^{-1},$$

$$\text{TOF}_{\text{Rh-CeO}_2\text{-H}_2} = (N_{\text{conv}}/N_{\text{Rh-H}_2}) / t = (2.09 \times 10^{18} \times X_{\text{Rh-CH}_4} / (2.312 \times 10^{16})) / 1 \text{ s} = 90.40 \times X_{\text{Rh-CH}_4} \text{ s}^{-1}$$

Therefore, the TOF of Pd, Pt, or Rh–CeO<sub>2</sub> catalysts at different reaction temperatures were calculated according to the conversion of CH<sub>4</sub> at the corresponding temperatures. The calculated TOF were presented in Figure 17. It is noted it is challenging to have a comparison of TOF from catalysts synthesis different methods since there are many assumption made in the calculation of TOF. But a comparison of the TOFs of these catalysts is still reasonable since these catalysts are synthesized with the same method and the data used to calculate the TOF were measured under the same condition.