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Zr 掺杂对 PdO/$Ce_{1-x}Pd_xO_{2-\delta}$ 催化剂 CO 和 CH_4 催化氧化的影响

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Effects of Zr Addition on CO and CH_4 Catalytic Oxidation over PdO/$Ce_{1-x}Pd_xO_{2-\delta}$ Catalyst

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Table S1 Pd contents, difference in value of Pd contents in catalysts

Catalyst	Pd Content (*w*/%) [a]	$\triangle C_{Pd}$ (*w*/%) [b]
PdO/CP	1.70	0.20 [c]
CP	1.50	
PdO/CPZ	1.65	0.28 [d]
CPZ	1.37	

[a] determined by XRF technique; [b] difference in value of Pd contents in PdO/CP and CP catalysts, PdO/CPZ and CPZ catalysts; [c] $\Delta C_{Pd} = 1.70 - 1.50 = 0.20\ (\mathrm{wt.\%})$

[d] $\Delta C_{Pd} = 1.65 - 1.37 = 0.28\ (\mathrm{wt.\%})$

Part Ⅰ The calculation of TOF of PdO species on the surface of PdO/CP and PdO/CPZ catalysts for CO oxidation.

Table S2. Flow rate of CO, CO conversion, amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalysts.

Catalyst	F_{CO} (μmol·s^{-1}) [a]	X_{CO}/% [b]	V_{CO} (mL·g^{-1}) [c]
PdO/CP	0.3	5.5	2.1
PdO/CPZ	0.3	19.4	2.9

[a] flow rate of CO; [b] CO conversion at 80 ℃; [c] amount of CO chemisorbed on the PdO/CP and PdO/CPZ catalysts.

The amount of PdO/CP and PdO/CPZ catalysts used in CO oxidation is 200 mg. Assuming the amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalyst are N_1 and N_2, correspondingly.

$$N_1 = \frac{0.42\times10^{-3}\ L}{22.4\ L/mol} = 1.86\times10^{-5}\ mol \qquad N_2 = \frac{0.58\times10^{-3}\ L}{22.4\ L/mol} = 2.59\times10^{-5}\ mol$$

Assuming the TOF of PdO on the surface of PdO/CP for CO oxidation is $TOF_{PdO\text{-}1}$, the TOF of PdO on the surface of PdO/CPZ for CO oxidation is $TOF_{PdO\text{-}2}$.

$$TOF_{PdO-1} = \frac{F_{CO}\times X_{CO}}{N_1} = \frac{0.3\times10^{-6}\ mol/s\times5.5\%}{1.86\times10^{-5}\ mol} = 0.09\times10^{-2}\ (s^{-1})$$

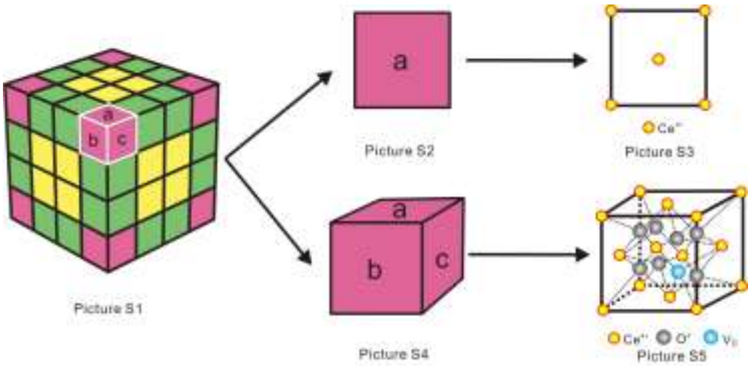
$$TOF_{PdO-2} = \frac{F_{CO}\times X_{CO}}{N_2} = \frac{0.3\times10^{-6}\ mol/s\times19.4\%}{2.59\times10^{-5}\ mol} = 0.22\times10^{-2}\ (s^{-1})$$

Part Ⅱ The calculation of TOF of Pd^{n+} cations in the CP and CPZ catalysts for CH_4 oxidation.

Table S3 Flow rate of CH_4, CH_4 conversion, crystal size and cell parameter of CeO_2, Pd content in the CP and CPZ catalysts.

Catalyst	F_{CH_4} (μmol/s) [a]	X_{CH_4} (%) [b]	Crystal size of CeO_2 (nm)	Cell parameter of CeO_2 (nm)	Pd Content (wt. %) [c]
CP	0.15	15.2	18.3	0.5407	1.50
CPZ	0.15	10.7	12.9	0.5405	1.37

[a] Flow rate of CH_4 in μmol·s^{-1}; [b] CH_4 conversion at 350 ℃; [c] Pd content in CP or CPZ solid solution



Scheme S1 Cube and Crystal particle and unit cell of CeO_2, and ball-and-stick 7model.

Picture S1 Crystal particle of CeO_2.

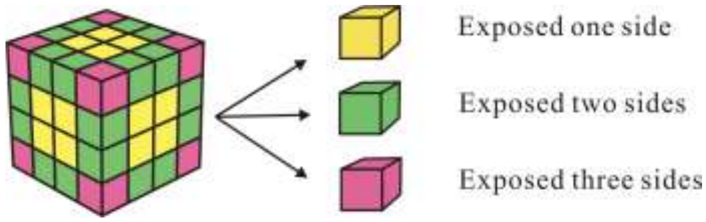
Picture S2 One side (top side) of a CeO_2 cube (denoted as side a).

Picture S3 Ball-and-stick model of one side of a CeO_2 cube.

Picture S4 Unit cell of CeO_2 (denoted as cube abc).

Picture S5 Ball-and-stick model of a unit cell of CeO_2.

In a CeO_2 crystal particle, there are three kinds of unit cell as showed in scheme S2. The yellow unit cell in the central exposed only one side (top side), the green unit cell on the edge exposed two sides (top and right sides), and the pink unit cell in the corner exposed three sides (top, front and right sides).



Scheme S2　Unit cell of CeO_2 expose different number of side.

For CP catalyst:

CeO_2 is face-centered cubic structure and a crystal particle contained many unit cell of CeO_2. For CP solid solution, the crystal size of CeO_2 is 18.3 nm, and the cell parameter of CeO_2 is 0.5407 nm. Assuming the number of unit cell in a CeO_2 crystal particle is N_1,

$$N_1 = (\frac{18.3}{0.5407})^3 = 33.8^3 \approx 34^3 = 39304$$

The number of unit cell of CeO_2 exposed one side is n_{11}, $n_{11} = (34-2)^2 \times 6 = 6144$

The number of unit cell of CeO_2 exposed two sides is n_{12},

$$n_{12} = (34-2)\times 4\times 2 + 4\times(34-2) = 384$$

The number of unit cell of CeO_2 exposed three sides is n_{13}, $n_{13} = 8$

The number of unit cell of CeO_2 exposed zero side is n_{10},

$$n_{10} = 39304 - 6144 - 384 - 8 = 32768$$

The number of sides of unit cell exposed on the surface of a CeO_2 crystal particle is S_{11}, and the number of total sides of unit cell in a CeO_2 crystal particle is S_{12}.

$$S_{11} = n_{11} \times 1 + n_{12} \times 2 + n_{13} \times 3 = 6144 \times 1 + 384 \times 2 + 8 \times 3 = 6936$$

$$S_{12} = (34 \times 34 \times 34 + 34 \times 34) \times 3 = 121320$$

The percentage of the exposed sides in the total sides in a CeO_2 crystal particle R_1,

$$R_1 = \frac{S_{11}}{S_{12}} \times 100\% = \frac{6936}{121320} \times 100\% = 5.71\%$$

The content of Pd in CP solid solution $K_1 = \frac{0.2\ \text{g} \times 1.5\%}{106.4\ \text{g/mol}} = 2.82 \times 10^{-5}\ \text{mol}$

Assuming the Pd^{n+} cations dispersed in CP solid solution uniformly. In fact, only the Pd^{n+} cations exposed on the surface of CeO_2 crystal particle contributed to the CH_4 oxidation. It should be noted that a CeO_2 crystal particle is selected as object of study in the calculation of R_1, and this value is also applicable to the whole CP solid solution.

$$TOF_{Pd^{n+}} = \frac{F_{CH_4} \times X_{CH_4}}{K_1 \times R_1} = \frac{1.488 \times 10^{-7}\ \text{mol/s} \times 15.2\%}{2.82 \times 10^{-5}\ \text{mol} \times 5.71\%} = 0.014\ \text{s}^{-1}$$

For CPZ catalyst:

The crystal size of CeO_2 is 12.9 nm, and the cell parameter of CeO_2 0.5405 nm. Assuming the number of unit cell in a CeO_2 crystal particle is N_2,

$$N_2 = \left(\frac{12.9}{0.5405}\right)^3 \approx 24^3 = 13824$$

The number of unit cell of CeO_2 exposed one side is n_{21}, $n_{21} = (24-2)^2 \times 6 = 2904$

The number of unit cell of CeO_2 exposed two sides is n_{22},

$$n_{22} = (24-2) \times 4 \times 2 + 4 \times (24-2) = 264$$

The number of unit cell of CeO_2 exposed three sides is n_{23}, $n_{23} = 8$,

The number of unit cell of CeO_2 exposed zero side is n_{20},

$$n_{20} = 13824 - 2904 - 264 - 8 = 10648$$

The number of sides of unit cell exposed on the surface of a CeO_2 crystal particle is S_{21}, and the number of total sides of unit cell in a CeO_2 crystal particle is S_{22}.

$$S_{21} = n_{21} \times 1 + n_{22} \times 2 + n_{23} \times 3 = 2904 \times 1 + 264 \times 2 + 8 \times 3 = 3456$$

$$S_{22} = (24 \times 24 \times 24 + 24 \times 24) \times 3 = 43200$$

The percentage of the exposed sides in the total sides in a CeO_2 crystal particle R_2,

$$R_2 = \frac{S_{21}}{S_{22}} \times 100\% = \frac{3456}{43200} \times 100\% = 8\%$$

The content of Pd in CPZ solid solution $K_2 = \frac{0.2\ \mathrm{g} \times 1.37\%}{106.4\ \mathrm{g/mol}} = 2.58 \times 10^{-5}\ \mathrm{mol}$

Assuming the Pd^{n+} cations dispersed in CPZ solid solution uniformly. In fact, only the Pd^{n+} cations exposed on the surface of CeO_2 crystal particle contributed to the CH_4 oxidation. It must be noted that a CeO_2 crystal particle is selected as object of study in the calculation of R_2, and this value is also applicable to the whole CPZ solid solution.

$$TOF_{Pd^{n+}} = \frac{F_{CH_4} \times X_{CH_4}}{K_2 \times R_2} = \frac{1.488 \times 10^{-7}\ \mathrm{mol/s} \times 10.7\%}{2.58 \times 10^{-5}\ \mathrm{mol} \times 8\%} = 0.008\ \mathrm{s}^{-1}$$