Tin-Promoted Platinum Supported on CeO_x nanoclusters Catalysts for CO_2-Oxidative Dehydrogenation of Propane

Rong Wang [1], Xinyi Yuan [1], Qingxiang Ma [1,*], Yan Wang [1], Jucang Ke[1], Xiaopeng Li[1], Xinhua Gao[1], Jian Sun[2,*], Tian-sheng Zhao [1]

[1] State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, PR China

[2] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

E-mail: maqx@nxu.edu.cn; sunj@dicp.ac.cn

1.Methods characterization of catalysts

Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) images were obtained from an FEI Talos F200S.

The crystal structure of the catalysts was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer, with data collected over a 2θ range of 10-85° at a scanning rate of $8°\cdot min^{-1}$.

The Raman spectra were acquired within the wavenumber range of 150-1500 cm^{-1} using a Thermo Fisher confocal microprobe laser Raman spectrometer, which was operated with a 532 nm Ar-ion laser.

N_2 physisorption isotherms were measured on an Autosorb-iQ instrument following catalyst degassing at 300 °C under vacuum for 5 h. The Brunauer-Emmett-Teller (BET) equation was applied to calculate the specific surface area, and the Barrett-Joyner-Halenda (BJH) method was used to determine the pore size distribution and volume.

Pt and Sn content in the catalysts were measured by inductively coupled plasma optical emission spectrometer (ICP-OES) on Varian ICP-OES 720.

Pt dispersion was estimated by CO pulse chemisorption performed on a BELCABT II instrument. A quantity of 50 mg of the sample was accurately weighed and placed within the reaction tube. The sample was pretreated under a stream of He flow at 150 °C for 1 h. Following pretreatment, the temperature was ramped to 500 °C at a heating rate of 10 $°C\cdot min^{-1}$ in a 10% H_2/Ar flow mixture and maintained at this temperature for 1 hour. Subsequently, the system was cooled to 50 °C under a He flow and purged for 30 min. Continuous pulses of 10% CO/He flow were then introduced onto the catalyst until CO saturation was indicated by a stable signal from the thermal conductivity detector (TCD). The quantity of adsorbed CO was determined by subtracting the total volume of CO detected at the outlet from the total volume of CO injected. The metal dispersion was calculated based on the assumption that one CO molecule adsorbs on one platinum atom (CO/Pt molar ratio = 1). The platinum particle size was then derived by applying a spherical platinum particle model to the computed dispersion. All gas flow rates mentioned above were 30 $mL\cdot min^{-1}$.

The electronic structure properties of the catalyst surface were explored by X-ray photoelectron spectroscopy (XPS) and adsorption of CO on a Spectrum Two FTIR spectrometer (PerkinElmer). The specific steps are as follows: The catalyst powder is filled into the in situ pool and lightly pressed until the surface is smooth. The catalyst was first pretreated in an Ar flow at 500 °C for 30 min, then reduced in a 10% H_2/Ar flow at the same temperature for another 30 min, and finally cooled to 50 °C in Ar and held for 30 min to collect the background signal. Then switch to 10% CO/He flow for adsorption for 30 min, turn off the CO, turn on Ar to purge the weakly adsorbed CO on the surface, and record the desorption data under the background of deduction. All gas flow rates mentioned above were 20 mL·min^{-1}.

H_2-TPR was performed using a BELCABT II system. A 50 mg catalyst sample was pretreated in Ar flow at 300 °C for 30 min and cooled to 50 °C, followed by temperature-programmed reduction in the 10% H_2/Ar flow from 50 to 650 °C at 10 °C·min^{-1}, during which the reduction profile was recorded. All gas flow rates mentioned above were 30 mL·min^{-1}.

CO_2-TPD/C_3H_8-TPD experiments were conducted on an Autochem II 2920 system. Specifically, the sample (50 mg) was first reduced in the 10% H_2/Ar flow at 500 °C for 60 min. After being cooled to 50 °C, the sample was subsequently subjected to a linear temperature program from 50 to 700 °C at a heating rate of 10 °C·min^{-1} under a 10% CO_2/He (10% C_3H_8/He) flow, while the desorbed products were monitored. All gas flow rates mentioned above were 30 mL·min^{-1}.

CO_2-C_3H_8 TPSR experiments were conducted on an Autochem II 2920 system. Specifically, the sample (50 mg) was first reduced in the 10% H_2/Ar flow at 500 °C for 60 min. The sample was cooled to 50 °C under an Ar flow. Subsequently, adsorption was carried out in a 10% C_3H_8-10% CO_2-80% Ar gas mixture for 30 min, followed by purging with Ar until a stable baseline was obtained. The gas was then switched back to the 10% C_3H_8-10% CO_2-80% Ar. The sample was heated to 550 °C at a ramping rate of 5 °C/min, while the online mass spectrometry signals were recorded. All gas flow rates mentioned above were 30 mL·min^{-1}.

The spent catalyst was subjected to thermogravimetric analysis (TG) using a Pyris 1thermogravimetric analyzer (Perkin Elmer). Approximately the spent catalyst (5 mg) was loaded into the instrument for each analysis. The catalyst was then heated from 50 °C to 800 °C under an air atmosphere (10 °C·min^{-1}).

Raman spectra of the spent catalysts were acquired using a Thermo Scientific DXR confocal microscope (532 nm excitation) to identify the nature of the deposited coke. The spectra were recorded at room temperature over the 1000-2000 cm^{-1} range.

O_2-TPO experiments were conducted on the BELCABT II system. Prior to analysis, the catalyst (50 mg) was pretreated in an Ar flow at 100 °C for 30 min to remove adsorbed species and then cooled to 50 °C. The TPO profile was recorded by heating the sample from 100 to 700 °C at 10 °C·min^{-1} under a 10%

O_2/He flow. All gas flow rates mentioned above were 30 mL·min^{-1}.

In-situ DRIFTS experiments were performed on a Bruker Tensor II FTIR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector to identify surface intermediates formed during CO_2-ODHP. Prior to the reaction, the catalyst was pretreated in a H_2/Ar flow at 500 °C. The system was then adjusted to the target reaction temperature (200-550 °C) for background collection. Subsequently, a gas mixture of C_3H_8 (10% in He) and CO_2 (10% in He) was introduced at a total flow rate of 20 mL·min^{-1}, and infrared spectra were continuously recorded over 30 min.

2. Supplementary Figures and Tables

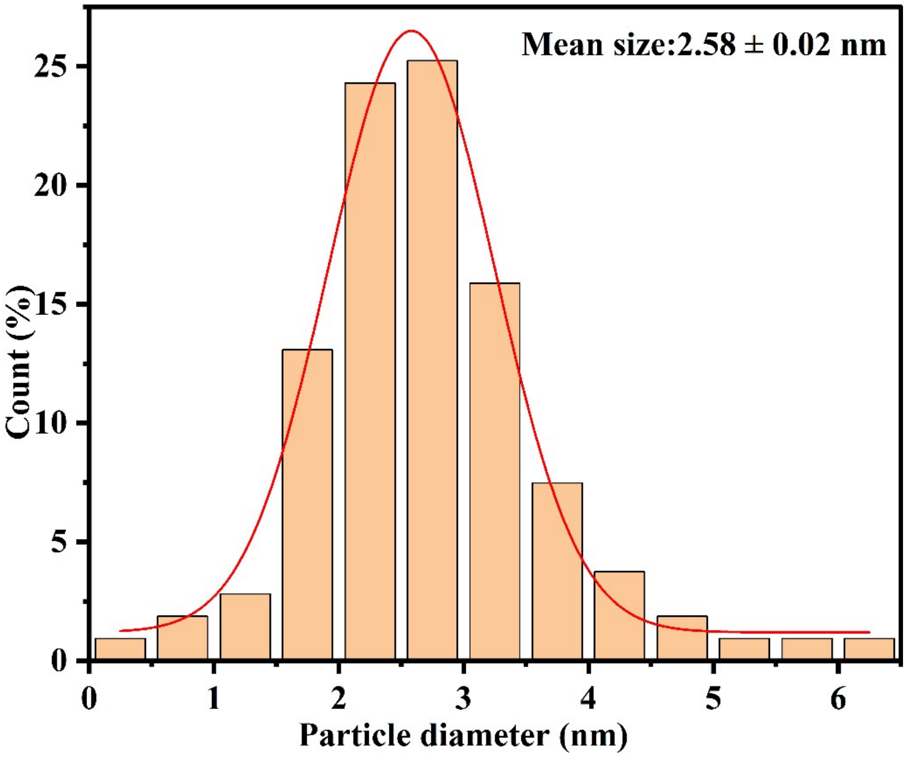

Fig. S1 Particle size statistics of CeO_x on the CeO_x-SiO_2.

Table S1 Textural structures of diverse supports and catalysts

Catalyst	S_{BET} [a] ($m^2 \cdot g^{-1}$)	V_{Total} [b] ($cm^3 \cdot g^{-1}$)	D_{BJH} [c] (nm)
CeO_x-SiO_2	275.60	0.61	4.89
0.5Pt/CeO_x-SiO_2	240.01	0.53	4.67
2.0Sn/CeO_x-SiO_2	243.33	0.58	4.56
0.5Pt 1.0Sn/CeO_x-SiO_2	253.16	0.60	4.58
0.5Pt 2.0Sn/CeO_x-SiO_2	247.78	0.56	4.52
0.5Pt 3.0Sn/CeO_x-SiO_2	265.57	0.59	4.45

[a] BET surface area. [b] Multi -point adsorption total pore volume at P/P_0 of 0.99. [c] Obtained via BJH method.

Table S2 The dispersion of Pt and the loading of Pt and Sn

Catalyst	Pt loading [a] (wt.%)	Sn loading [b] (wt.%)	Pt dispersion [c] (%)	Pt particle size (nm)
0.5Pt/CeO_x-SiO_2	0.52	-	28.91	3.70
2.0Sn/CeO_x-SiO_2	-	1.51	-	-
0.5Pt 1.0Sn/CeO_x-SiO_2	0.52	0.82	41.17	2.59
0.5Pt 2.0Sn/CeO_x-SiO_2	0.53	1.55	59.25	1.81
0.5Pt 3.0Sn/CeO_x-SiO_2	0.53	2.13	43.67	2.45

[a, b] Determined by ICP-OES. [c] Calculated according to CO uptake.