

Supporting Information

Organic-free syntheses and ortho-reaction channel of monodisperse Ni incorporated CeO₂ Nanocatalysts

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1 Experimental Section

1.1 Catalysts preparation

1.1.1 CHFS route

The $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_{2-6}$ was manufactured in our laboratory using a three pump-hydrothermal flow system (CHFS). The reactor, tubing and components were all made of 316 stainless steel (Swagelok™). The apparatus (see supplementary **Fig. S1**) consists of a metal salt(s) solution HPLC pump (P2), a base solution HPLC pump (P3) and a water HPLC pump (P1). Deionized water was pumped through an electrical pre-heating coil (2.5 kW) and heated to the appropriate temperature (500 °C), which then meets a metal salt solution containing $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1M) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.02M), and a flow of NaOH solution (1 M) at a mixing point (a 1/4" counter-current mixer that was assisted by a 500 °C band heater), whereupon rapid co-precipitation of crystalline products occurred. The aqueous suspension was cooled via a water jacket cooler, passed through a 7 μm in-line filter and was collected from the exit of a back-pressure regulator (BPR). Flow rates of 7.5, 7.5 and 30 mL min^{-1} were used for metal salt solution, base solution and water stream, respectively. The system pressure was maintained at ca. 23.0 MPa. Solids were recovered by centrifuging the suspension and then freeze-dried to yield the final products.

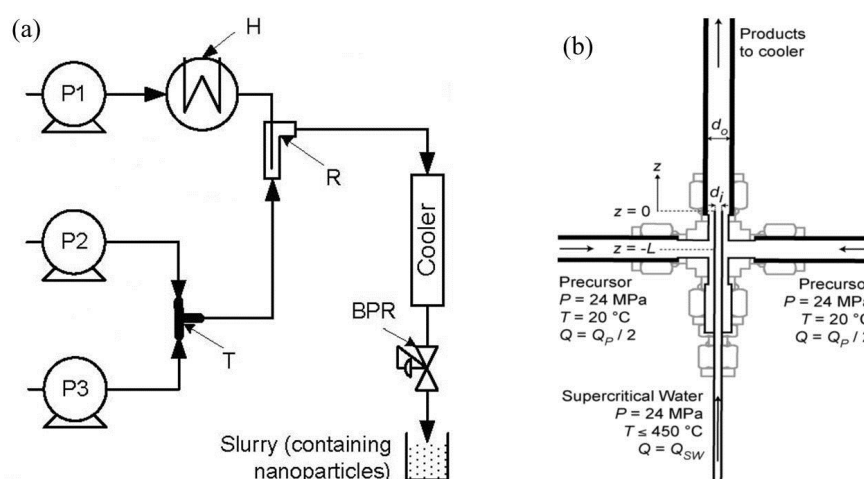


Fig. S1 (a) Schematic representation of the three-pump (P1–P3) continuous hydrothermal flow synthesis system that was used to prepare nanoparticles catalysts. Key: P = pump, BPR = back-pressure regulator, R = reactor, H = heater, T = T junction; (b) Schematic diagram of the confined jet reactor (R. I. Gruar, C. J. Tighe and J. A. Darr, *Industrial & Engineering Chemistry Research*, 2013, 52, 5270-5281).

1.1.2 Physically mixing route

Isolate CeO₂ and NiO that were synthesized via a thermal decomposition of Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O at 500 °C for 4h under air atmosphere in a furnace were loaded into a hard alloy jar and milled using a high-energy ball mill at a rotation speed of 200r/min for 10h. The nominal Ni loading of catalysts was 20 mol% of CeO₂.

1.2 Characterizations

1.2.1 XRD, XPS, SEM-EDS and TEM-EDS

XRD patterns were recorded by using a Rigaku D/Max RA diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm) at 40 kV and 150 mA. Crystal phase of the samples were identified by using the JCPDS database. Surface elemental analysis was conducted by using a Thermo ESCALAB 250 XPS instrument with a Al-K α radiation ($h\nu = 1486.6$ eV) operated at 150W. The signal of adventitious carbon (a binding energy of 284.8 eV) had been used to calibrate the binding energy scale. Curve fits were performed using a Shirley background and a Gaussian peak shape with 20 % Lorentzian character. A model JEM-ARM200F (JEOL Company, Japan) high-resolution transmission electron microscope (200 kV accelerating voltage) instrument equipped with a spherical aberration STEM was employed to analyze the morphology, XEDS mapping and elemental ratio measurements. SEM-XEDS was carried out on SU8010 FE-SEM operated at an accelerating voltage of 3 kV.

1.2.2 H₂-TPR

H₂-TPR was conducted in a TP-5089 (supplied by Tianjin Xianquan Industry and Trade Development Co., Ltd); Prior to each test, samples (0.05g) were heated to 400 °C with a dwelling time of 1 h and a purge of 3 % O₂/He gas at the flow rate of 50 mL.min⁻¹, and then cooled to 100 °C. After that, they were preheated at 100 °C for 40 min and then further heated to 900 °C at a ramp of 10 °C.min⁻¹ in a purge of 5 % H₂/N₂ gas at the flow rate of 35 mL.min⁻¹. The variation in H₂ concentration was recorded by a thermal conduction detector

(TCD).

1.2.3 In situ DRIFTS study

FT-IR was conducted using an in situ DRIFT cell with an appliance of a gas flow system. The DRIFT measurements were performed with ZnSe windows coupled to Bruker tensor 27 FTIR spectrometers. In the DRIFT cell, catalysts were pretreated at 300 °C in a He environment for 2 h, and then cooled to 100 °C. The background spectrum was recorded with flowing He and was subtracted from the catalyst spectrum.

1.2.4 Catalytic activity measurement

As for activity measurement, catalyst was placed in a fixed-bed quartz tubular flow reactor (i.d. 10mm). Before each test, catalyst was pretreated in a N₂ flow at 500 °C for 1h. The feed gas (total gas flow rate: 1.5L/min) consisted of 600 ppm NO, 1200 ppm CO with N₂ balance. The catalyst load was at 2.2 mL and the gas hourly space velocity (GHSV) was approximately at 40,000 h⁻¹. All catalysts were sieved to 40-60 meshes. The composition and concentration of input and output gases (including NO, NO₂, N₂O) concentration were monitored by using an infrared gas analyzer (Photon II, Madur Electronics, Austria) and a flue gas analyzer (Testo 350, Testo Inc., Germany). The catalytic activity and N₂O selectivity were calculated according to the following formula:

$$X(\text{NO}) = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} / [\text{NO}]_{\text{in}}) \times 100\% \quad (1)$$

$$S(\text{N}_2) = 1 - (2[\text{N}_2\text{O}]_{\text{out}} / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})) \times 100\% \quad (2)$$

In order to eliminate the effect of size, the NO conversion and N₂ selectivity was converted into X_{NO} and S_{N₂}, which were calculated as follow:

$$X_{\text{NO}} = (X * 600 \text{ ppm NO} * 10^{-6} * 1500 \text{ (mL}^3 \text{ min}^{-1}) * 10^{-3}) / (22.4 \text{ (L/mol)} * 1.6 \text{ (g)} * S \text{ (m}^2 \text{/g)}) \text{ (mol/m}^2 \cdot \text{h)}$$

$$S_{\text{N}_2} = (S_{\text{N}_2} * 1 / 2 * 600 \text{ ppm NO} * 10^{-6} * 1500 \text{ (mL}^3 \text{ min}^{-1}) * 10^{-3}) / (22.4 \text{ (L/mol)} * 1.6 \text{ (g)} * S \text{ (m}^2 \text{/g)}) \text{ (mol/m}^2 \cdot \text{h)}$$

2 Supporting data

2.1 Rietveld refinement of pure CeO₂

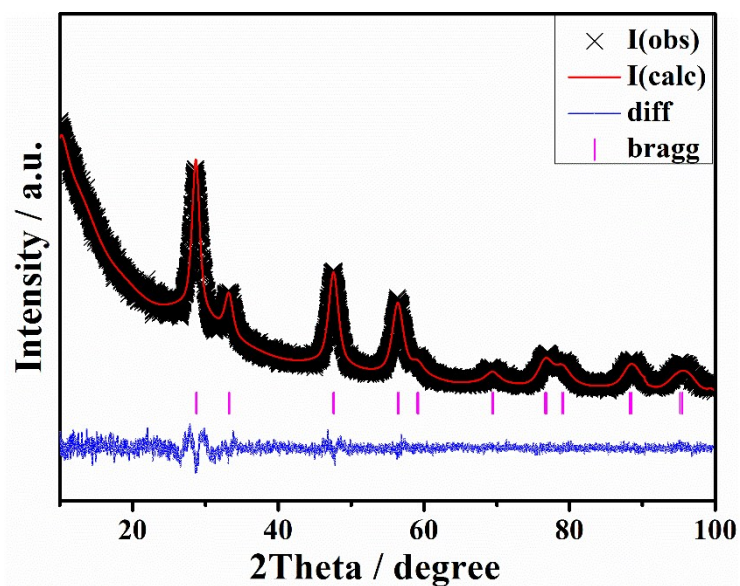


Fig.S2 Rietveld refinement patterns of pure CeO₂.

Table.S1 lattice parameters of pure CeO₂ sample as obtained from Rietveld refinement

Lattice parameter					
Crystal system	Space group	a	b	c	$\alpha=\beta=\gamma$
Cubic	Fm-3m	5.4340 (8)	5.4340 (8)	5.4340 (8)	90
Rp	Rwp	Chi2			
4.19 %	5.54%	1.115			

2.2 EDX line-scanning of sc-Ni_{0.17}Ce_{0.83}O_{2- δ} aggregated particles

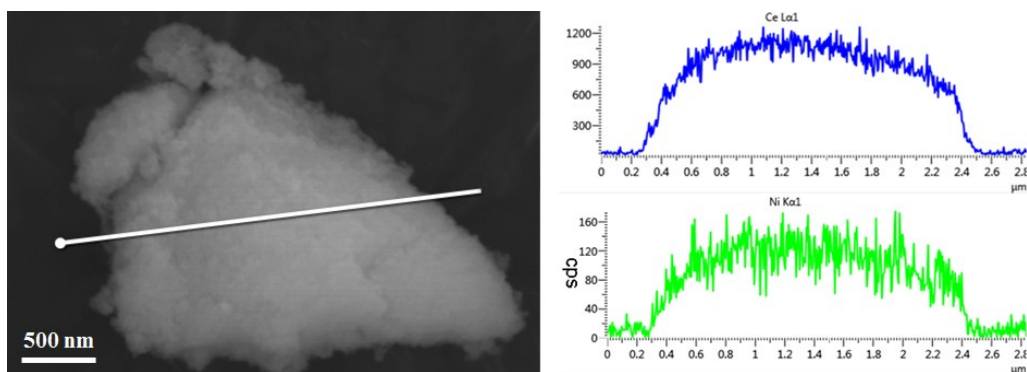
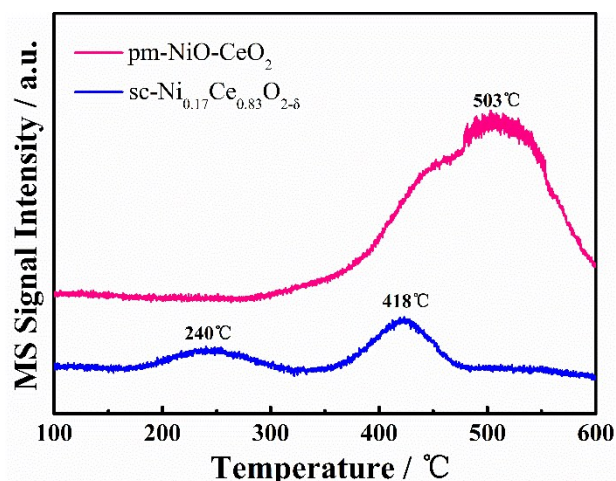


Fig.S3 EDX line-scanning of sc-Ni_{0.17}Ce_{0.83}O_{2- δ} aggregated particles.

2.3 Quantitative analysis of Ni/Ce ratio

Table.S1 The Ni/Ce ratio of quantitative analysis of ICP and EDS for $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_{2-6}$

samples	theoretical	aggregated particle	single particle	ICP value
	value	value	value	
$\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_{2-6}$	0.20	0.195	0.195	0.183



2.4 O₂-TPD profiles

Fig.S4 O₂-TPD profiles of $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_2$ and $\text{pm-NiO}_2\text{-CeO}_2$ samples.

In O₂-TPD, two distinct peaks centered at 240 and 418 °C in the $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_2$ were assigned to surface chemisorbed oxygen and surface lattice oxygen. The band at 503 °C in the pm-NiO-CeO_2 was ascribed to the lattice oxygen of NiO, which was lack in the $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_2$, further confirming the absence of NiO phase in this catalyst.

2.5 XPS O 1s spectrum

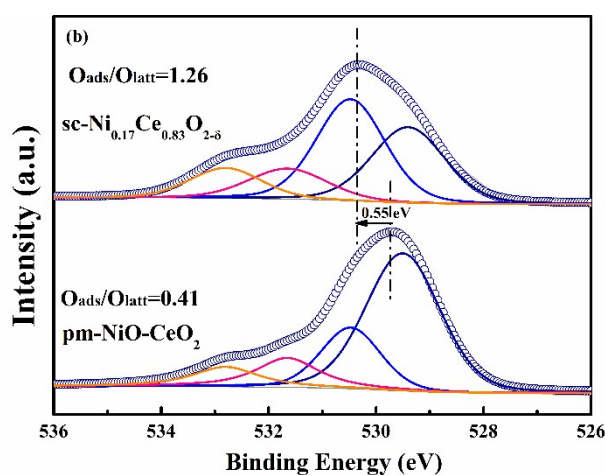


Fig.S5 XPS O 1s spectrum of sc-Ni_{0.17}Ce_{0.83}O₂ and pm-NiO₂-CeO₂ samples.

2.6 XPS Ni 2p spectrum

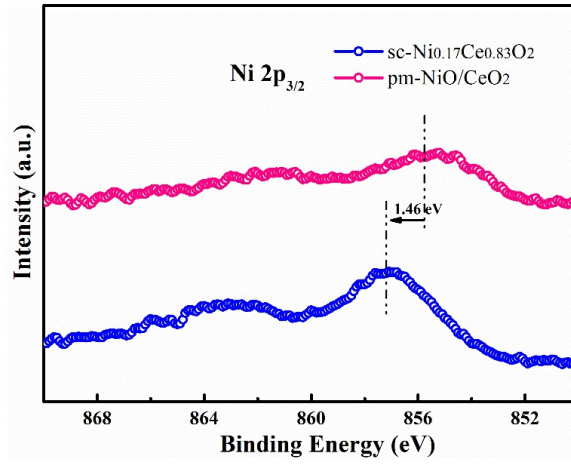


Fig.S6 XPS Ni 2p spectrum of sc-Ni_{0.17}Ce_{0.83}O₂ and pm-NiO₂-CeO₂ samples.

2.7 Raman spectrum

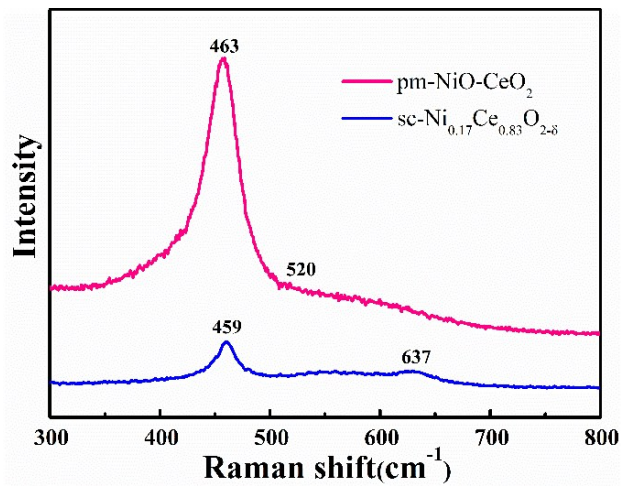


Fig.S7 Raman spectrum of sc-Ni_{0.17}Ce_{0.83}O₂ and pm-NiO₂-CeO₂ samples.

2.8 In situ DRIFTS studies on CO adsorption

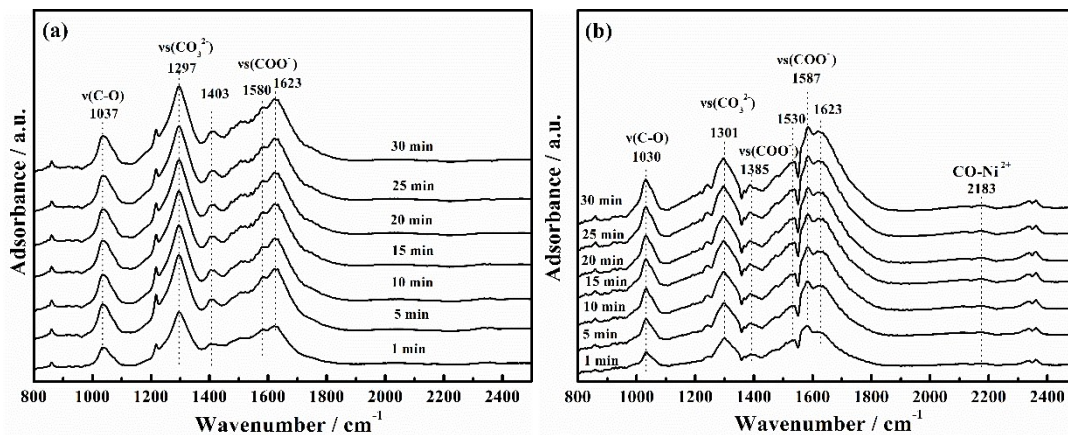


Fig. S8 In situ DRIFTS studies on CO adsorption of (a) $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_2$ and (b) $\text{pm-NiO}_2\text{-CeO}_2$ samples in a flow of 1000 ppmCO at 100 °C.

2.9 In situ DRIFTS studies on CO and NO co-adsorption

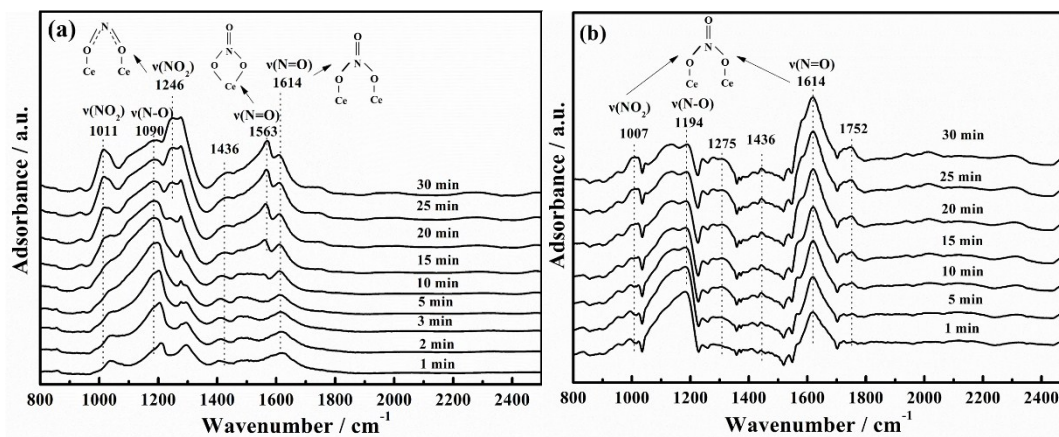


Fig. S9 In situ DRIFTS studies on CO and NO co-adsorption of (a) $\text{sc-Ni}_{0.17}\text{Ce}_{0.83}\text{O}_2$ and (b) $\text{pm-NiO}_2\text{-CeO}_2$ samples in a flow of 1000 ppmCO+ 1000 ppm NO at 100 °C.