Supplementary Information

Cerium modification enhances the performance of Pd/USY for formaldehyde catalytic oxidation at room temperature

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2 Texts; 1 Table; 8 Figures

Table of Contents

Text S1 Catalyst preparation

Text S2 Catalyst characterization.

Table S1 Summarized XPS results from the Ce 3d spectra.

Fig. S1 (a) HCHO conversion, (b) CO₂ yield over USY-fresh, 0.5Ce/USY-fresh,

0.5Pd/USY-fresh, 0.5Pd-0.5Ce/USY-fresh catalysts before reduction.

Fig. S2 CO₂ yield over USY-R, 0.5Ce/USY-R, 0.5Pd/USY-R and 0.5Pd-0.5Ce/USY-R catalysts.

Fig. S3 The durability test on the 0.5Pd-0.5Ce/USY-R. Reaction conditions: 150 ppm of HCHO, 20% O₂, 35% RH, He balance, WHSV 300,000 mL·g⁻¹·h⁻¹, at 25 °C.

Fig. S4 Nitrogen adsorption-desorption isotherms of USY-R, 0.5Ce/USY-R, 0.5Pd/USY-R and 0.5Pd-0.5Ce/USY-R catalysts.

Fig. S5 H₂-TPSR control experiment profiles of 0.5Pd/USY-R and 0.5Pd-0.5Ce/USY-R catalysts.

Fig. S6 In-situ DRIFTS spectra over USY-R support.

Fig. S7 In-situ DRIFTS spectra over 0.5Pd/USY-R catalyst.

Fig. S8 HAADF-STEM images and EDS elemental mapping of (a) USY-R, (b) 0.5Ce/USY-R, (c) 0.5Pd/USY-R and (d) 0.5Pd-0.5Ce/USY-R catalysts.

Text S1. Catalyst preparation.

The USY zeolites (H type, Si/Al at 11, Nankai University Catalyst Co., Ltd, China) were prepared with hydrochloric acid (HCl AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd, China) and cerium nitrate (Ce(NO₃)₃·6H₂O, AR grade, Sinopharm Chemical Reagent Beijing Co., Ltd, China). In a typical procedure, firstly, USY zeolite was dispersed into HCl solution (0.20 M) and constantly stirred in a beaker at 30 °C for 6 h. The mass ratio of solid to liquid was fixed at 1:20. After acid treatment, the mixed liquid was filtered and washed with deionized water until neutral. The resultant filter cake was then dried at 110 °C overnight in an oven. Secondly, the USY zeolites were impregnated in a cerium nitrate solution. After ultrasonication for 30 min and then impregnation under stirring for 4 h, the excess water was removed in a rotary evaporator at 60 °C. Then, the sample was dried at 110 °C and calcined at 400 °C for 4 h. The sample was denoted as 0.5 wt.%Ce/USY.

The 0.5 wt.%Pd-0.5wt.%Ce/USY and 0.5 wt.%Pd/USY catalysts were prepared by impregnation of USY, 0.5 wt.%Ce/USY and with $Pd(NO_3)_2 \cdot 2H_2O$ (Sigma Aldrich) solution, respectively. After ultrasonication for 30 min and then impregnation under stirring for 4 h, the excess water was removed in a rotary evaporator at 60 °C and the solid was dried at 110 °C overnight. Then, the sample was dried at 110 °C and calcined at 400 °C for 4 h. Before the catalytic activity testing, the samples were reduced at 350 °C with flowing 10 vol.% H₂/N₂ mixed gas at 100 mL·min⁻¹ for 1 h. After that the catalysts were denoted as 0.5Pd-0.5Ce/USY-R, 0.5Pd/USY-R, Ce/USY-R and USY-R.

Text S2. Catalyst characterization.

Before characterization, the samples were reduced in H₂ at 350 °C for 1 h. X-ray powder diffraction (XRD) patterns of the catalysts were collected with a PANalytical X'Pert PRO X-ray diffractometer (Cu K_{α} as radiation resource, $\lambda = 0.154$ nm) at 40 kV and 40 mA. The patterns were measured over the 2 θ range from 5° to 90° with a scanning step size of 0.02°. The surface areas and pore characteristics of catalysts were measured by N₂ adsorption/desorption analysis at -196 °C using a physisorption analyzer (BELSORP-max). Before the N_2 physisorption, the catalysts were degassed at 300 °C for 1 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on JEOL JEM 3200FS TEM with 300 kV acceleration voltage.

X-ray photoelectron spectra (XPS) were measured by an AXIS Ultra system, equipped with Al K α radiation (hv = 1486.6 eV) with an X-ray anode operated at 225 W and 15 kV. The C1s peak (284.8 eV) was used to calibrate the binding energy (BE) values.

Electron spin resonance (ESR) analysis was carried out on a JEOL JES-FA300 ESR spectrometer. The ESR spectra were performed at a microwave frequency of 9.85 GHz at 77 K without light irradiation.

CO chemisorption, H_2 temperature-programmed reduction (H_2 -TPR), CO temperature-programmed reduction (CO-TPR), H_2 temperature-programmed surface reduction (H_2 -TPSR) were performed in a Micromeritics AutoChem II 2920 apparatus, equipped with a thermal conductivity detector (TCD) and mass spectrometer detector (MS).

CO chemisorption was measured by a dynamic pulse method. The catalysts (50 mg) were reduced at 350 °C for 1 h in flowing 10 vol.% H₂/Ar mixed gas, followed by flushing in Ar gas (30 mL·min⁻¹) and cooled down to 30 °C. Then, pulses of 5 vol.% CO/He mixed gas (10 mL·min⁻¹) were introduced to the catalyst until uptake saturation was obtained. A CO/Pd stoichiometric ratio of 1 has been assumed for the calculation of Pd dispersion [1, 2].

For CO-TPR, the samples (50 mg, 40 – 60 mesh) were first reduced with 10% H_2/Ar at 350 °C for 1 h, followed by purging with He for 30 min to desorb H_2 . The temperature was then cooled down to 30 °C, and then the gas was switched to $H_2O + O_2$ for adsorption for 1 h. After that, He flowed over the sample for 30 min to remove weakly adsorbed $H_2O + O_2$. Then, CO-TPR was performed from 0 to 500 °C in flowing 5 vol.% CO/He mixed gas (50 mL·min⁻¹) at a heating rate of 10 °C·min⁻¹, and recording

the mass spectrometry (MS) signal of CO_2 (m/z=44) and H₂ (m/z=2).

For H₂-TPSR, the samples (50 mg, 40 – 60 mesh) were first reduced with 10% H₂/Ar at 350 °C for 1 h, followed by purging with He for 30 min to desorb H₂. The temperature was then cooled down to 25 °C, and then the gas was switched to O₂ for adsorption for 1 h. After that, He flowed for 30 min to remove weakly adsorbed O₂. Then a flow of 10% H₂/Ar was passed through the sample at a rate of 50 mL·min⁻¹. The temperature was increased from 0 to 375 °C at a rate of 10 °C·min⁻¹ and the MS signal of H₂O (m/z=18) was recorded. The H₂-TPSR control experiments and H₂-TPSR experiments followed similar experimental procedures, with the difference that after He flowed for 30 min to remove weakly adsorbed O₂.

In situ DRIFTS spectra were recorded in a Fourier transform infrared spectrometer (Thermo Fisher IS50 FT-IR) equipped with an *in situ* diffuse reflectance chamber (Harrick) and a liquid N₂ cooled MCT/A detector. Before recording each DRIFTS spectrum, the samples were reduced in flowing 10 vol.% H_2/N_2 mixed gas at 350 °C for 1 h. All spectra were measured with a resolution of 4 cm⁻¹ and an accumulation of 100 scans. A background spectrum was subtracted from each spectrum.

Table S1 Summarized XPS results from the Ce 3d spectra.

Catalysts	Ce ³⁺ (%)	Ce ⁴⁺ (%)	Ce^{3+}/Ce^{4+} (%)
0.5Ce/USY-R	16.1	83.9	19.2
0.5Pd-0.5Ce/USY-R	20.4	79.6	25.6



Fig. S1 (a) HCHO conversion, (b) CO₂ yield over USY-fresh, 0.5Ce/USY-fresh, 0.5Pd/USY-fresh and 0.5Pd-0.5Ce/USY-fresh catalysts before reduction. Reaction conditions: HCHO 150 ppm, 20 vol.% O₂, 35 % RH, He balance, WHSV 300,000 mL·g⁻¹·h⁻¹.



Fig. S2 CO₂ yield over USY-R, 0.5Ce/USY-R, 0.5Pd/USY-R, 0.5Pd-0.5Ce/USY-R and 0.5Pd/CeO₂-R catalysts. Reaction conditions: HCHO 150 ppm, 20 vol.% O₂, 35 % RH, He balance, WHSV 300,000 mL·g⁻¹·h⁻¹.



Fig. S3 The durability test on the 0.5Pd-0.5Ce/USY-R. Reaction conditions: 150 ppm of HCHO, 20% O_2 , 35% RH, He balance, WHSV 300,000 mL·g⁻¹·h⁻¹, at 25 °C.



Fig. S4 Nitrogen adsorption-desorption isotherms of USY-R, 0.5Ce/USY-R, 0.5Pd/USY-R and 0.5Pd-0.5Ce/USY-R catalysts.



Fig. S5 H_2 -TPSR control experiment profiles of 0.5Pd/USY-R and 0.5Pd-0.5Ce/USY-

R catalysts.



Fig. S6 *In-situ* DRIFTS spectra over USY-R in a flow of H₂O for 60 min (1); followed by He purging for 60 min (2) at room temperature. Reaction conditions: 150 ppm of HCHO, 20 % O_2 , 35 % RH, He balance, total flow rate of 100 mL·min⁻¹.



Fig. S7 *In-situ* DRIFTS spectra over 0.5Pd/USY-R in a flow of HCHO for 60 min (1); followed by He purging for 60 min (2); and O_2 purging for 60 min (3); and by O_2 + H₂O purging for 60 min (4) and finally by He purging for 60 min at room temperature. Reaction conditions: 150 ppm of HCHO, 20 % O_2 , 35 % RH, He balance, total flow rate of 100 mL·min⁻¹.



Fig. S8 HAADF-STEM images and EDS elemental mapping of (a) USY-R, (b) 0.5Ce/USY-R, (c) 0.5Pd/USY-R and (d) 0.5Pd-0.5Ce/USY-R catalysts.

It can be seen from the mapping images that Ce, O and Pd elements were uniformly dispersed at a scale of 50 nm.

References

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