

Supplementary Information

Significant differences of NH₃-SCR performances between monoclinic and hexagonal WO₃ on Ce- based catalyst

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Experimental section

The Preparation of WO₃

3 g H₄₀N₁₀W₁₂O₄₁·xH₂O (AR grade, Anda China) was dissolved in 80 mL aqueous solution. The solution was adjusted to pH = 1 by dropwise addition of 0.60 mol/L H₂SO₄ (AR grade, Kelong China) with constant magnetic stirring at 30 °C for 1 h. Then, the solution was transferred into a Teflon-lined 100 mL autoclave for a hydrothermal treatment at 120 °C for 20 h. After being cooled down to room temperature, the precipitates were filtrated and washed thoroughly with water, followed by drying at 90 °C for 12 h and calcination at 400 °C for 3 h. The hexagonal WO₃ was obtained.

2 g Na₂WO₄ (AR grade, Kelong China) was dissolved in 80 mL aqueous solution. The 5 mL conc. HCl (AR grade, Kelong China) and 0.91 g (AR grade, Kelong China) oxalic acid were added to the solution successively with constant magnetic stirring at 30 °C for 1 h. Then, the solution was transferred into a Teflon-lined 100 mL autoclave for a hydrothermal treatment at 200 °C for 12 h. After being cooled down to room temperature, the precipitates were filtrated and washed thoroughly with water, followed by drying at 90 °C for 12 h and calcination at 400 °C for 3 h. The monoclinic WO₃ is obtained.

The powders of hexagonal and monoclinic WO₃ were coated on honeycomb cordierites (2.5 mL, 400 cpi, Corning Ltd., USA) with the catalyst loading about 160 g/L. Pure WO₃ monolithic catalysts were obtained after calcining for 3 h at 400 °C and marked as W-h and W-m, respectively. W-h and W-m catalysts were collectively referred to as W.

The Preparation of Catalysts

CeO₂-WO₃-hexagonal and CeO₂-WO₃-monoclinic catalysts were prepared by mechanical mixing of CeO₂ (Sinocat, China) and hexagonal or monoclinic WO₃ with a molar ratio of 3:1, pure CeO₂

was used as reference sample. The three cases were dried at 90 °C for 12 h and calcined at 400 °C for 3 h to obtain catalysts powder. The powders were coated on honeycomb cordierites (2.5 mL, 400 cpi, Corning Ltd., USA) with the catalyst loading about 160 g/L. Monolithic catalysts were obtained after calcining for 3 h at 400 °C. The CeO₂-WO₃-hexagonal, CeO₂-WO₃-monoclinic and CeO₂ catalysts were labeled as Ce-W-h, Ce-W-m and Ce, respectively. Ce-W-h and Ce-W-m catalysts were collectively referred to as Ce-W.

NH₃-SCR Activity Measurements

Catalyst activity was evaluated in a fixed-bed quartz tube flow reactor. The gases flow was controlled by mass flowmeter before entering the reactor. The simulated reaction conditions were as follows: 500 ppm NO, 550 ppm NH₃, 50 ppm SO₂ (when used), 5 vol.% H₂O (when used), 5 vol.% O₂, N₂ as balance gas. The gas hourly space velocity (GHSV) was 30,000 h⁻¹, corresponding to total flow rate of 1,250 mL/min. The concentrations of N_xO_y and NH₃ were monitored by FT-IR in Antaris IGS (Nicolet, USA). The conversion of NO_x and NH₃ as well as the N₂ selectivity were calculated according to the following formula:

$$\text{NO}_x \text{ Conversion (\%)} = \frac{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}}} \times 100 \quad (1)$$

$$\text{NH}_3 \text{ Conversion (\%)} = \frac{[\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}}}{[\text{NH}_3]_{\text{inlet}}} \times 100 \quad (2)$$

$$\begin{aligned} \text{N}_2 \text{ Selectivity (\%)} = & \frac{[\text{NO}_x]_{\text{inlet}} + [\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}} - [\text{NO}_x]_{\text{outlet}} - 2 \times [\text{N}_2\text{O}]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}} \\ & + [\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}} - [\text{NO}_x]_{\text{outlet}}} \times 100 \quad (3) \end{aligned}$$

$$\text{NO}_x = \text{NO} + \text{NO}_2 \quad (4)$$

Catalysts Characterization

Powder X-ray diffraction (XRD) experiments were performed on a Rigaku DX-2500 diffractometer (Rigaku, Japan) using Cu Ka ($\lambda = 0.15406$ nm) radiation. The tube voltage and

current were 40 kV and 25 mA, respectively. XRD powder diffractograms were recorded at $0.031^{\circ}\cdot\text{s}^{-1}$ intervals in the 2θ range of $10\text{--}80^{\circ}$.

The Vis-Raman spectra of the catalysts were recorded on a LabRAM HR Laser Raman spectrometer (HORIBA JOBIN YVON, France). A diode pumped YAG laser of 532 nm excitation wavelength with power 73.5 mW is employed.

The N_2 adsorption-desorption was measured on a Quadosorb SI automated surface area and pore size analyzer (Quantachrome, USA) at 77 K, and the sample was pre-treated at 300°C for 3 h prior to the measurement. The surface areas of the catalysts were calculated by the Brunauer-Emmett-Teller.

Transmission electron microscopy (TEM) and TEM-Mapping images were obtained by a Titan G2 60-300 (AC-TEM) with 300 kV accelerating voltage (FEI Co., USA,) to observe the microstructure of samples.

The X-ray photoelectron spectra (XPS) data were recorded by the Escalab 250Xi (Thermo, American) spectrometer with 15 kV high pressure and 20 mA operating current using Mg K_{α} radiation. C 1s (284.5 eV) was used for the internal standard to calibrate the binding energy.

Temperature programmed reduction with H_2 (H_2 -TPR) experiment was carried out on a TP-5076 TPD/TPR dynamic adsorber (Xianquan, China) with a thermal conductivity detector. The samples approximately 100 mg were pre-treated in a quartz tubular microreactor in a flow of pure N_2 at 400°C for 40 min, and then cooled to 30°C . The reduction was carried out in a flow of 5 vol.% H_2 -95% N_2 from 30°C to 850°C with a heating rate of $10^{\circ}\text{C}/\text{min}$. In addition, the H_2 consumption of catalysts is calculated by the integral fitting after deconvolution (CuO acts as the standard sample).

NO oxidation of monolithic catalyst was evaluated in a fixed-bed quartz tube flow reactor. The simulated reaction conditions were as follows: 500 ppm NO, 5 vol.% O₂, N₂ as balance gas. The gas hourly space velocity (GHSV) was 30,000 h⁻¹. The concentrations of N_xO_y were monitored by FT-IR in Antaris IGS (Nicolet, USA). The conversion of NO oxidation was calculated according to the following formula:

$$\text{NO Conversion (\%)} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100 \quad (5)$$

Temperature-programmed desorption experiments of NH₃ (NH₃-TPD) experiments were carried out on a TP-5076 TPD/TPR dynamic adsorber (Xianquan, China) with a thermal conductivity detector. All samples mass about 80 mg in a quartz tubular micro-reactor were used. The experiment included four stages: (1) activate the samples in He at 400 °C for 40 min, (2) adsorption of 2 vol.% NH₃-98% N₂ at 80 °C for 40 min, (3) isothermal desorption in He at 80 °C until no NH₃ was detected, and (4) temperature programmed desorption in He (TPD stage) at 10 °C/min up to 700 °C.

In situ IR Spectra were performed using a Nicolet Nexus 6700 FTIR spectrometer (Nicolet, USA) with a diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) equipped a reaction cell with KBr window. The reaction temperature was controlled by the Omega program temperature controller, heating rate of 10 °C/min. The powder sample was activated in N₂ at 400 °C for 40 min. The background spectra of the sample were recorded in pure N₂ from 350 to 50 °C. And then exposed to NH₃ (N_xO_y) for 40 min, the NH₃ (N_xO_y) adsorption spectra at 50 to 350 °C of catalysts were collected in pure N₂. In addition, transient reactions were studied using the same Nicolet Nexus 6700 FTIR spectrometer (Nicolet, USA). The powder sample was pre-treated in N₂ at 400 °C for 40 min prior. The background spectrum of the sample was recorded in pure N₂ at 250-350 °C. And then exposed to NH₃ (N_xO_y) for 40 min, and subsequently purged

with N₂ for 20 min. The NH₃ (N_xO_y) adsorption spectra at 250-350 °C of samples were recorded in pure N₂. Afterwards, the spectra were collected when N_xO_y (NH₃) was flowed into the gas chamber to react with the pre-adsorbed NH₃ (N_xO_y) species on samples for 1 h. All spectra were recorded by accumulating 64 scans with a resolution of 4 cm⁻¹. The gas used for the experiments was a mixture of 1000 ppm NH₃, 1000 ppm NO, 5 vol.% O₂ and N₂ as the balance gas, with a total flow rate of 300 mL/min.

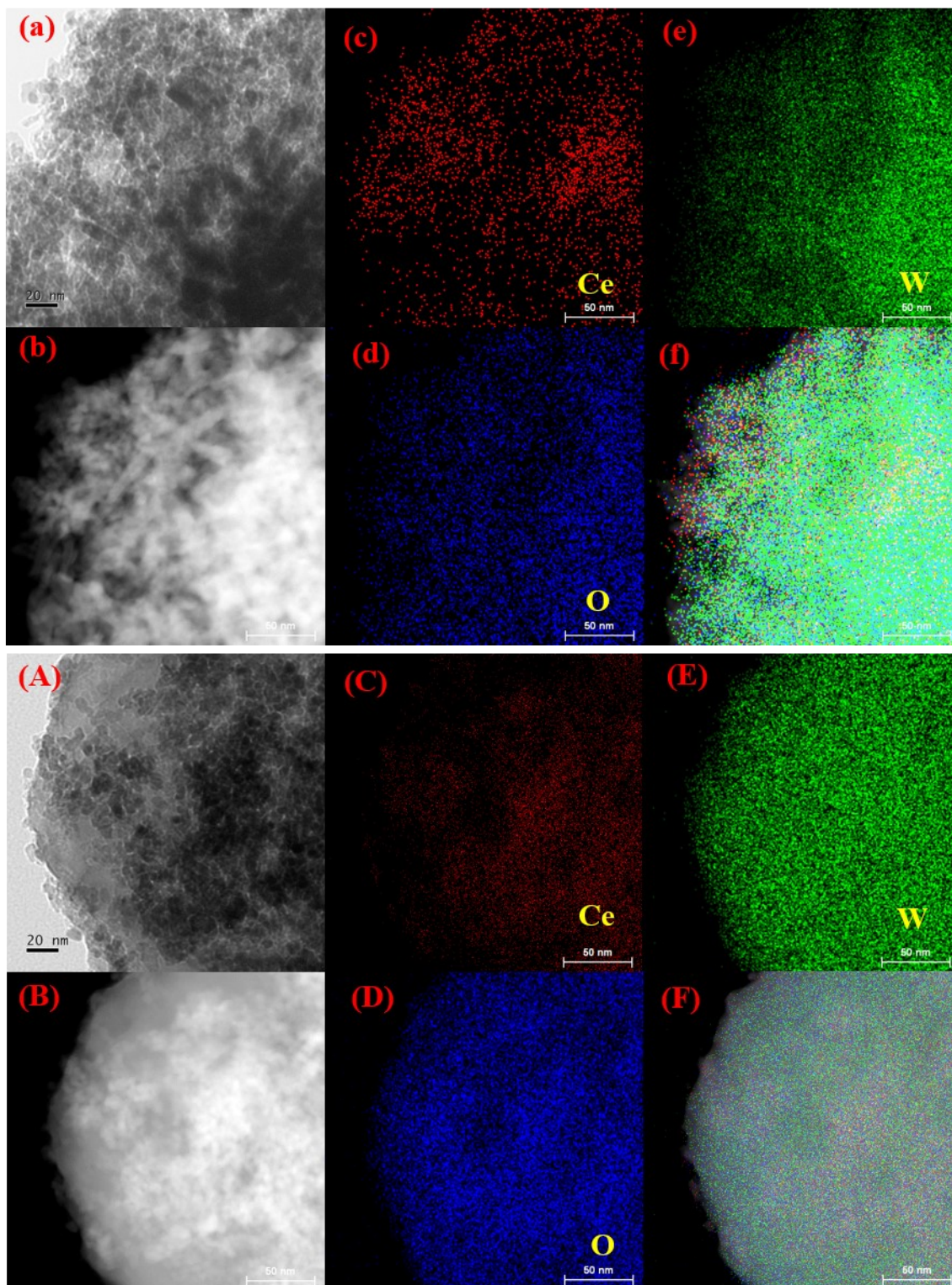


Fig. S1 TEM of Ce-W-h (a) and Ce-W-m (A) as well as Mapping images of Ce-W-h (b-f) and Ce-W-m (B-F).

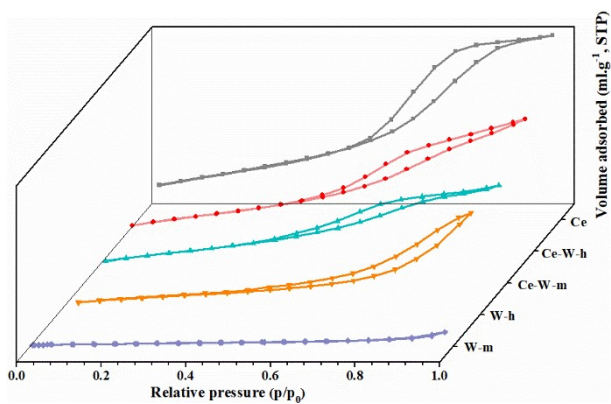


Fig. S2 N_2 adsorption-desorption isotherms and specific surface area of pure W and Ce-W catalysts.

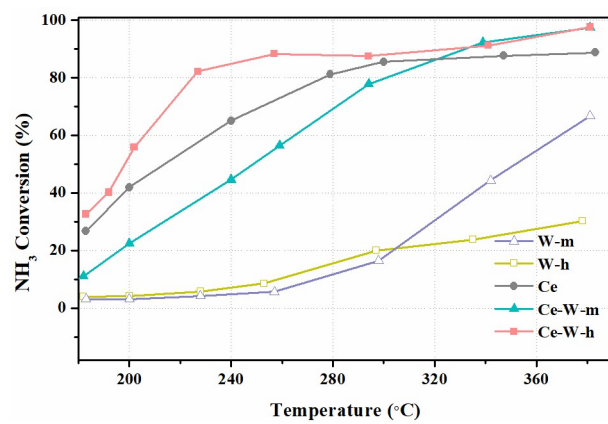


Fig. S3 NH₃ conversion of the catalysts during NH₃-SCR reaction.

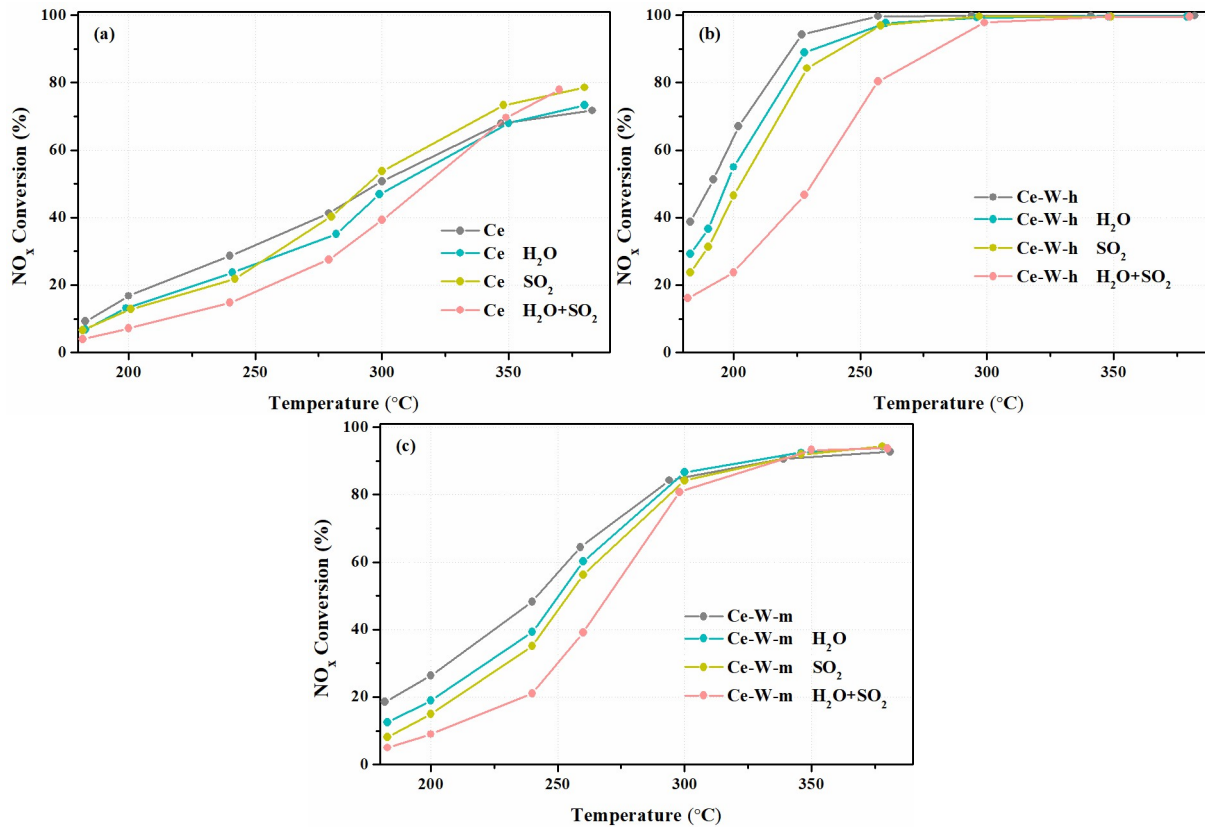


Fig. S4 NO_x conversion during NH₃-SCR reaction in the presence or absence of SO₂ and H₂O over the Ce (a), Ce-W-h (b) and Ce-W-m (c). Reaction conditions: 500 ppm NO, 550 ppm NH₃, 5 vol.% O₂, 50 ppm SO₂ (when used), 5 vol.% H₂O (when used), balance gas N₂, GHSV: 30,000 h⁻¹.

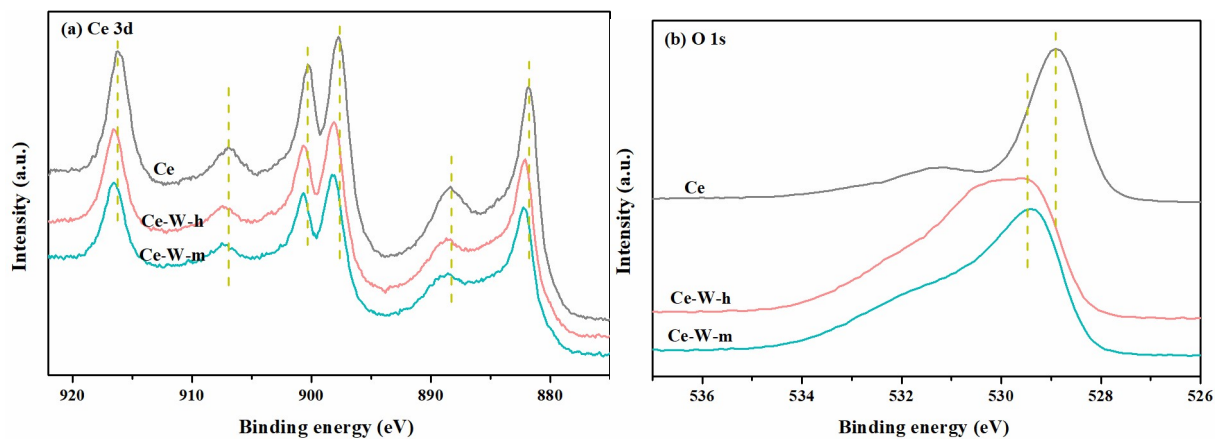


Fig. S5 The Ce 3d (a) and O 1s (b) XPS spectra of the catalysts.

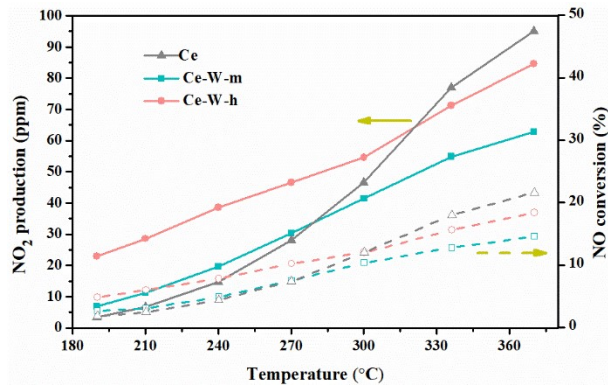


Fig. S6 The conversion of NO oxidation and the concentration of NO₂ generation over the catalysts. Reaction conditions: 500 ppm NO, 5 vol.% O₂, balance gas N₂, GHSV: 30,000 h⁻¹.

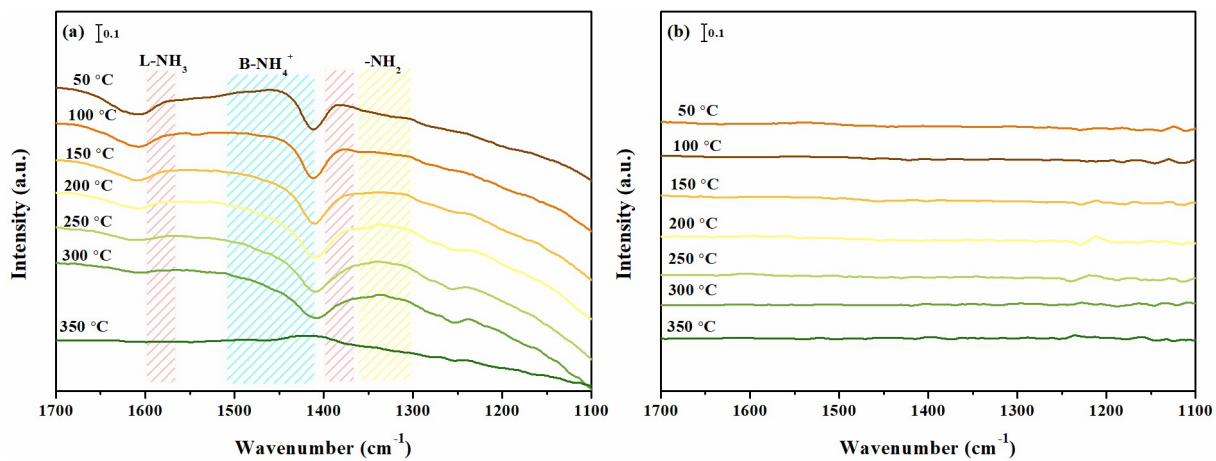


Fig. S7 DRIFTS spectra of NH_3 adsorption over W-h (a) and W-m (b) catalysts.

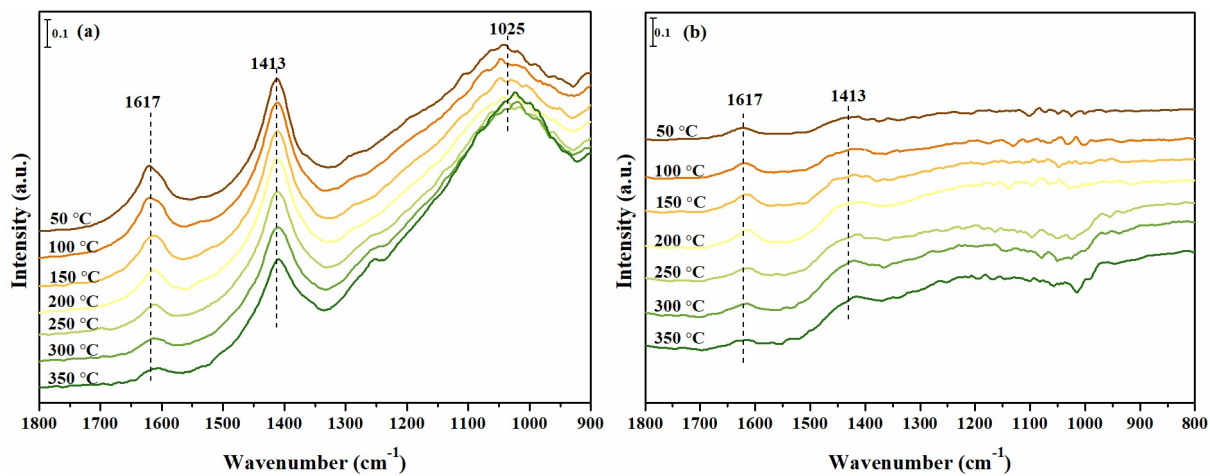


Fig. S8 DRIFTS spectra of NO+O₂ adsorption over W-h (a) and W-m (b) catalysts.

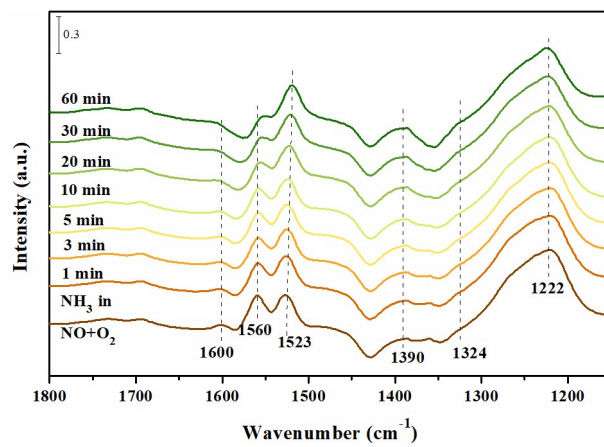


Fig. S9 *In situ* DRIFTS reaction of NH₃ with pre-adsorbed NO + O₂ over Ce at 300 °C.