

Supporting Information

Probing the role of surface activated oxygen species of CeO₂ nanocatalyst during the redox cycle in CO oxidation

Ruishi Zhang^{a,#}, Xiaoyuan Liu^{b,#}, Hai Liang^a, Xijun Yang^a, Jing Li^{c,d}, Wenfeng Ye^e, Xiaomin Wang^{a,} and Baodan Liu^{c,d,*}*

^aLiaoning Key Laboratory of Chemical Additive Synthesis and Separation, Yingkou Institute of Technology, Bowen Road, Yingkou, 115014 China

^bShenyang National Laboratory of Material Science, Institute of Metal Research, Chinese Academy of Sciences, No. 72, Wenhua Road, Shenyang, 110016, China

^cSchool of Material Science and Engineering, Northeastern University, No.11 Wenhua Road, Shenyang 110819, China

^dFoshan Graduate School of Innovation, Northeastern University, No. 2 Zhihui Road, Foshan 528311, China

^eFoshan Dongfo Surface Technology Co. Ltd. No. 99, Taoyuan East Road, Foshan, 528200, China

* Corresponding Author: baodanliu@hotmail.com

Figures and tables

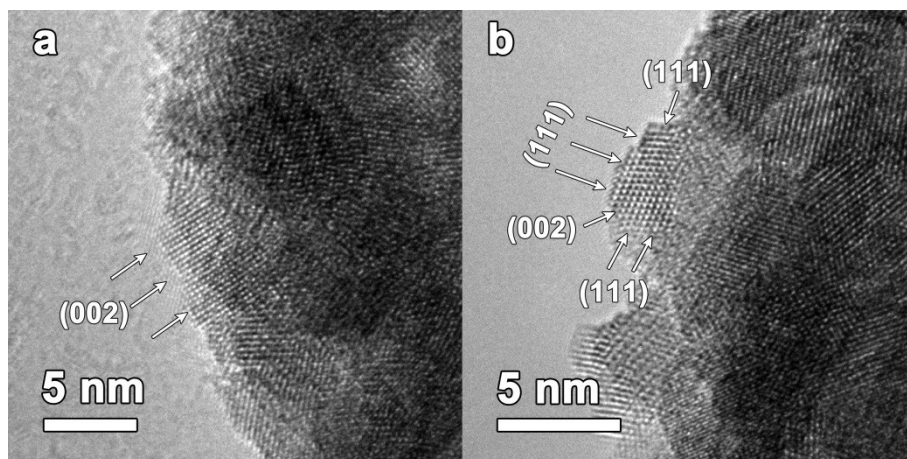


Figure S1. (a, b) HRTEM images of HT-CeO₂;

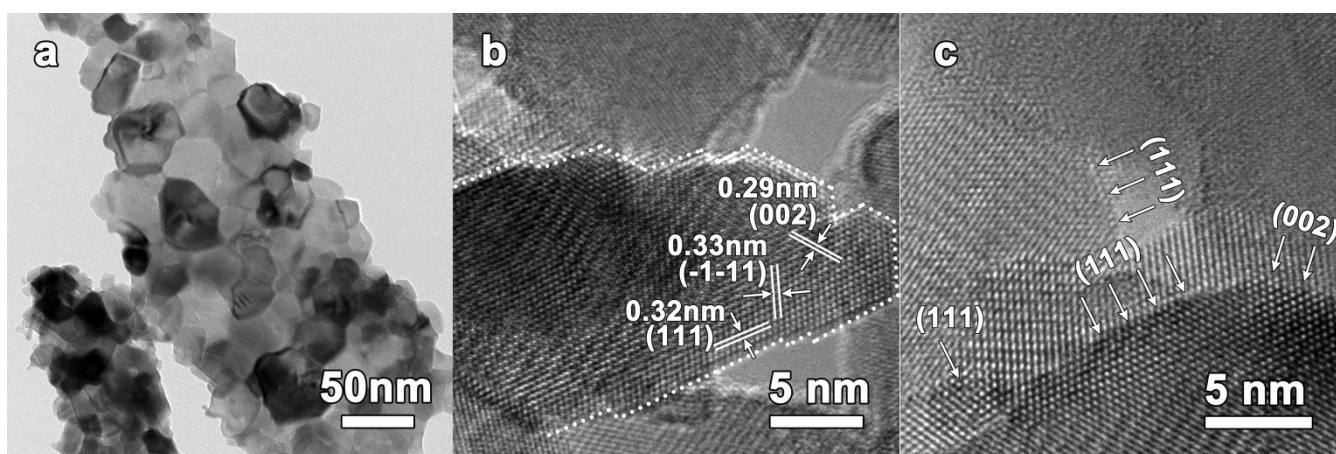


Figure S2. (a) Bright field TEM image of HT-CeO₂ after 650°C annealing; (b, c) HRTEM images of HT-CeO₂ after 650°C annealing;

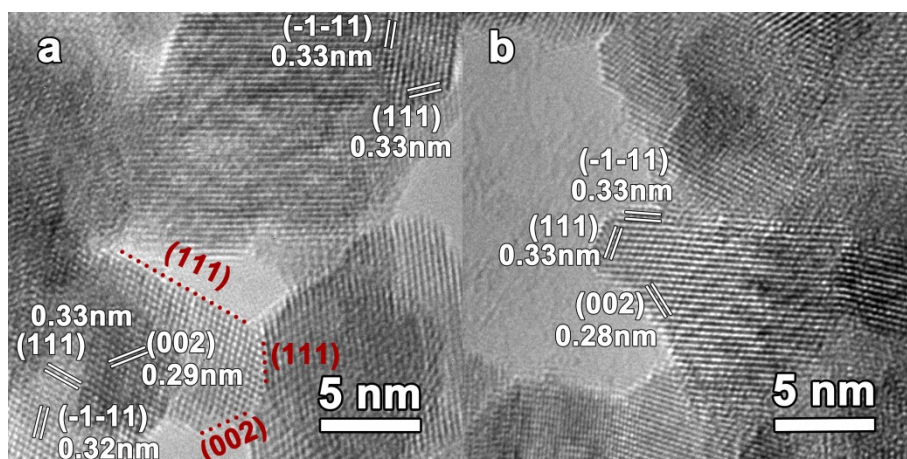


Figure S3. (a, b) HRTEM images of P-CeO₂;

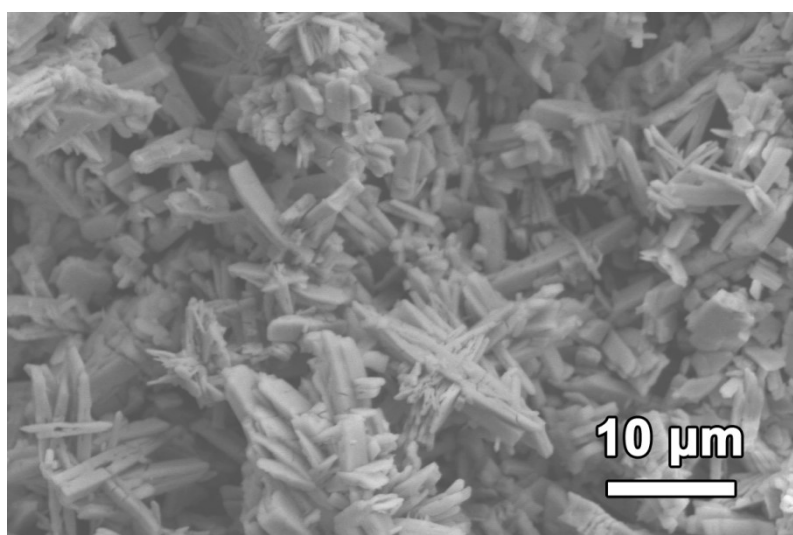


Figure S4. SEM image of C-CeO₂

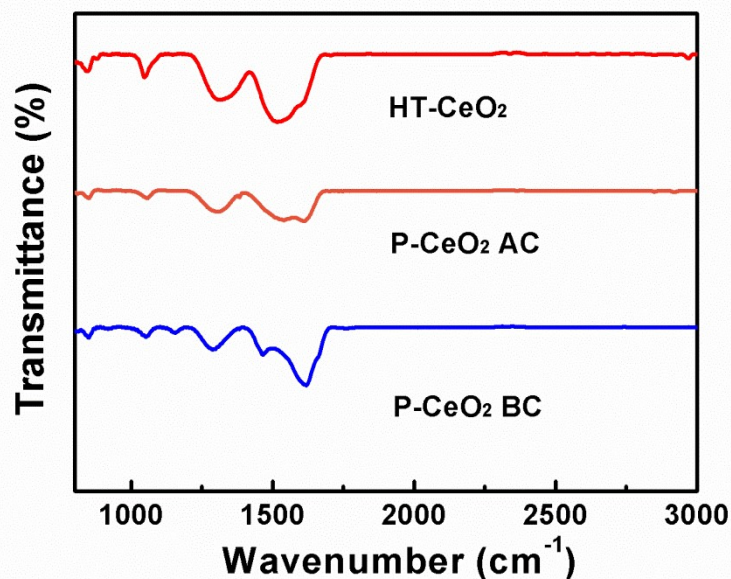


Figure S5. IR spectra of P-CeO₂ before catalytic test (P-CeO₂ BC), after catalytic test (P-CeO₂ AC) and HT-CeO₂ in the carbonate region;

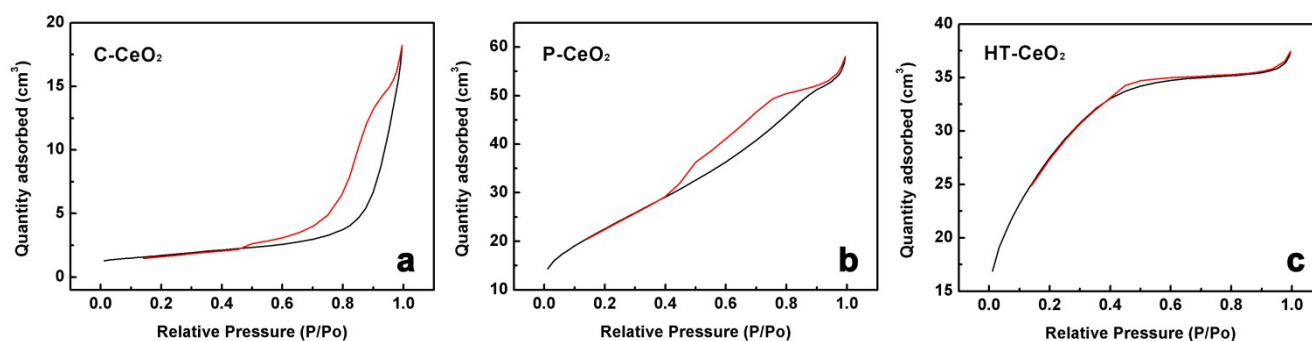


Figure S6. Isothermal adsorption-desorption curves of (a) C-CeO₂; (b) P-CeO₂ and (c) HT-CeO₂. The curves of C-CeO₂ show a type IV characteristic, the hysteresis loop is caused by the sheet-like pores of C-CeO₂ which matches well with the SEM morphology of C-CeO₂ (Figure S4);

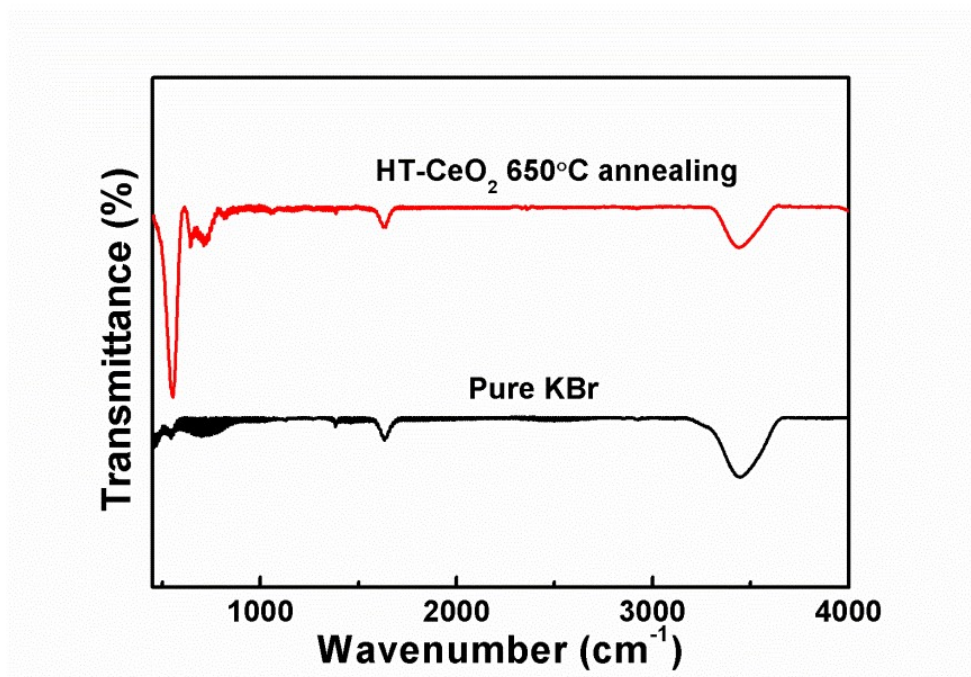


Figure S7. IR spectra of HT-CeO₂ after annealing in Ar at 650°C for 2 h;

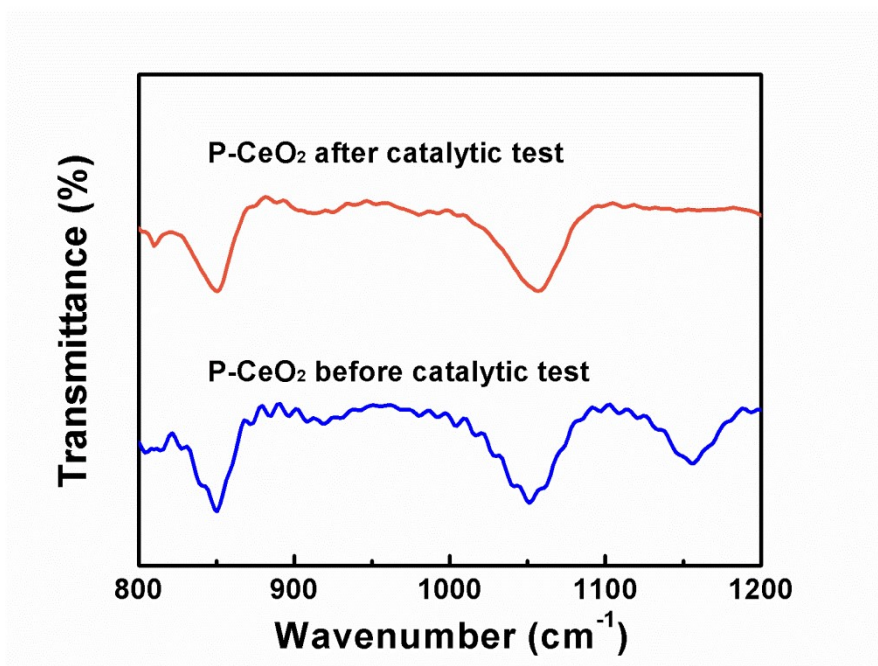


Figure S8. IR spectra of P-CeO₂ before & after CO catalytic test in the O- 2 region;

Table S1. Binding energies of Ce 3d and Ce³⁺/Ce ratios of HT-CeO₂, P-CeO₂ and C-CeO₂;

Sample	u ⁰ (eV)	v ⁰ (eV)	u'(eV)	v'(eV)	u(eV)	v(eV)	u''(eV)	v''(eV)	u'''(eV)	v'''(eV)	Ce ³⁺ /Ce
HT-CeO ₂	899.3	881.4	903.2	885.0	901.1	882.7	907.3	888.5	916.9	898.3	28.15%
P-CeO ₂	898.6	880.9	902.7	884.7	900.3	882.1	907.0	888.2	916.4	897.9	28.43%
C-CeO ₂	899.1	880.9	903.4	885.2	901.0	882.4	907.3	888.5	916.5	898.1	7.97%

The Ce³⁺/Ce ratios are calculated through the following equation:

$$\frac{\text{Ce}^{3+}}{\text{Ce}} = 100\% \times \frac{A(u^0) + A(v^0) + A(u') + A(v')}{A(u) + A(v) + A(u^0) + A(v^0) + A(u') + A(v') + A(u'') + A(v'') + A(u''') + A(v''')}$$

The fitting details of XPS curves used by “XPSPEAK software” are presented as below. First, the number of average points at end points and the background type are generally set to “ten” and “Shirley” for the fitting of background curves. After that, the characteristic peaks are then added for the fitting of XPS curves. The number and position of characteristic peaks are mainly referred to the data in the XPS database or the references. Generally, in the fitting process, the position of added characteristic peaks is fixed and the FWHM, the area and the percentage of Lorentzian-Gaussian (about 80%) are unfixed. Finally, all the added characteristic curves are simultaneously and repeatedly optimized to get a perfect overall curve, which almost coincides with the original tested curve.

Table S2. T₅₀ and activation energy (E_a) of HT-CeO₂, P-CeO₂ and C-CeO₂;

Sample	T ₅₀ (°C)	E _a (eV)
HT-CeO ₂	273	48.6
P-CeO ₂	287	55.4
C-CeO ₂	404	--