Regulation of Frustrated Lewis Pairs on CeO_2 facilitates tandem transformation of styrene and CO_2

Yong Zou[a#], Zhaoming Xia[b#], You Wang[a], Yuxuan Liu[a], Sai Zhang[a,c]* and Yongquan Qu[a]*

[a] *School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an 710072, China*

[b] *Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China*

[c] *Research & Development Institute of Northwestern Polytechnical University in Shenzhen, 518057 Shenzhen, China*

[#] These authors contributed equally to this work.

Email: zhangsai1112@nwpu.edu.cn and yongquan@nwpu.edu.cn

1. Experimental section

1.1. Materials and reagents

Lanthanum (III) nitrate hexahydrate (Energy Chemical, 99%), Cerium (III) nitrate hexahydrate (Energy Chemical, 99%), styrene (Energy Chemical, 99%), tert-butyl hydroperoxide (Energy Chemical, 99%), DMF (N, N-Dimethylformamide, Sigma-Aldrich, 99.8%), Ethyl acetate (Energy Chemical, 99.5%), tert-Butyl hydroperoxide solution (Shanghai Macklin Biochemical Co.,Ltd,), Tetrabutylammonium bromide(Energy Chemical, 99%), Methanol (Guangdong Guanghua Sci-Tech Co., Ltd, $\geq$ 99.7%), Ethanol (Guangdong Guanghua Sci-Tech Co., Ltd, $\geq$ 99.7%), NaOH (Sinopharm Chemical Reagent Co., Ltd, $\geq$ 98%). All reagents were of analytical grade and used directly without any further purification before the experiments.

1.2. Synthesis of PN-CeO$_2$ and PN-La$_x$Ce$_{1-x}$O$_2$ catalysts

The PN-CeO$_2$ and PN-La$_x$Ce$_{1-x}$O$_2$ catalysts were preparted by the two-step synthesis under hydrothermal conditions, smiliar as our previously reports.[1] Initially, 5 mL of Ce(NO$_3$)$_3$ aqeous solution (0.8 M) was added into 75 mL of NaOH solution (6.4 M) with stirring. After 1 h reaction at room temperature, the mixture was maintained at 100 °C in a Pyrex bottle for 24 h. Subsequently, the obtained solids were collected by centrifugarion, washed with water and ethanol alternatively for three times and dried at 60 °C overnight to yield the Ce(OH)$_3$/CeO$_2$ precursors.   Finally, the precursors were dispersed in H$_2$O with concentration of 2 g L^{-1} under ultrasonication, which were treated by hydrothermal process at 180 °C for 12 h to yiled the PN-CeO$_2$ catalysts.

The PN-La$_x$Ce$_{1-x}$O$_2$ catalsyts were prepared by the same process for synthesis of PN-CeO$_2$, in which Ce(NO$_3$)$_3$·6H$_2$O and La(NO$_3$)$_2$·6H$_2$O were used as the mixed metal precursors.

1.3. Synthesis of La$_2$O$_3$ catalysts

The La$_2$O$_3$ catalysts were prepared by calcining La(NO$_3$)$_3$·6H$_2$O in air at a ramping rate of 5 °C min^{-1} from room temperature to 800 °C for 2 h.

1.4. DFT calculations

All periodic DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP).[2–4] The projector augmented wave (PAW)[5] method was used for the interactions between the core and valence electrons. The valence electron densities were described by plane-wave basis sets with an energy cutoff of 400 eV.[4] The exchange-correlation energies were calculated using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional,[6] and the spin-unrestricted Kohn-Sham scheme[7] was adopted. The 4f orbitals of Ce and La were described by DFT+U with U-J=4.5 eV for Ce from previous report[8,9] and U-J=6 eV for La according to the test in table S1. In all calculations, the energy cutoff of the plane wave basis sets was 400 eV. The thresholds for converging the electronic wavefunctions and atomic structures are 10^{-6} eV for the energy and 0.02 eV/Å for the maximal force, respectively.

The calculated lattice constant (a=5.418 Å) and Ce-O bond length (2.360 Å) of CeO$_2$ bulk are consistent with the experiment results.[10] To simulate the effect of lattice expansion, the lattice constants were set to a×(1+stress) for stresses of 1% and 2%. The CeO$_2$ (110) surface was then modeled by a p(3 × 2) 5-layer supercell with the

bottom 3 layers fixed, and a 15 Å vacuum gap was included to separate the periodic images along the z-axis. A (2 × 2 × 1) Monkhorst-Pack grid was used to sample the Brillouin zone. The dipole correction along the z-axis was applied. The energy of gas phase CO_2 was simulated in a 20 Å × 20 Å × 20 Å unit cell with (1 × 1 × 1) Gamma-only k-point.

The adsorption energy of CO_2 was defined as:

$$E_{ad} = E_{tot} - E_{slab} - E_{CO2}$$

Where E_{tot} is the total energy of the CO_2 adsorption model; E_{slab} is the energy of the clean slab model; E_{CO2} is the energy of a CO_2 molecule.

Table S1. The test of DFT+U parameters for La.

$U - J$ (eV)	ΔE (eV)[a]
9	1.266
7	1.226
6	1.213
5	1.178

Note: The simulated energy for the reaction of $LaCl_3 + H_2O = LaOCl + 2HCl$. The experimental value is 1.21 eV. When $U - J = 6$ eV, the simulated energy is close to the experimental value.

1.5. Characterizations

The structures and compositions of the catalysts were monitored by X-ray diffraction of Shimadzu XRD-6000 with Cu $K\alpha$ radiation. Transmission electron microscopy (TEM, Hitachi HT-7700) with an accelerating voltage of 120 kV and high-

resolution TEM (FEI Talos F200X) with an accelerating voltage of 200 kV were used to studied the morphology and structures of the catalysts. The contents of copper and ceria of all catalysts were detected by an inductively coupled plasma emission spectrometer (ICP-AES) on a Agilent 5110(OES). Gas-chromatography (Techcomp., GC 7980) with a HP-5 capillary column (30 m × 0.32 mm ×0.25 μm) equipped with a flame ionization detector (FID) was used to analyz the yields of phenylethylene carbonates. X-ray photoelectron spectroscopy (XPS) measurements were performed with an Axis Ultra DLD X-ray photoelectron spectroscopy.

1.6. CO_2 temperature-programmed desorption (CO_2-TPD)

The CO_2-TPD tests were carried out on a Micromeritics Autochem II chemisorption analyzer. Generally, 100 mg of catalysts were loaded in a quartz reactor and pretreated with a flow of Ar (50 sccm) at 300 °C for 30 min. After cooling to 50 °C, CO_2 adsorption was performed by switching Ar to a flow of 10%CO_2/Ar (50 sccm), and then maintained for 2 h. Then, the physically adsorbed CO_2 was removed by an Ar purging (50 sccm) for 1 h at the same temperature. Finally, TPD was performed on the chemisorption analyzer in the Ar flow by raising the temperature from 50 °C to 900 °C at a ramping rate of 10 °C min^{-1}.

1.7. The tandem transformation of olefin and CO_2 to phenylethylene carbonates

For a typical catalytic reaction, 5 mmol of styrene, 40 mg of nBu$_4$NBr and 30 mg of catalysts were mixed in 0.65 mL of 70 wt.% TBHP aqueous solution. The reactions were performed in an autoclave charged with 0.5 MPa of CO_2 at 80 °C under stirring. After the desired time, the reaction mixture was cooled naturally. Then, the reaction
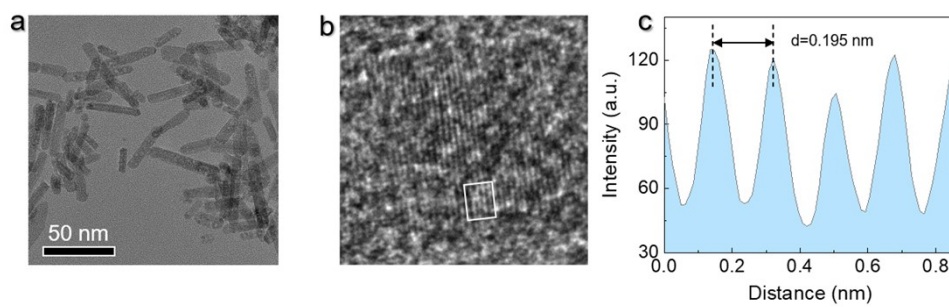
solution was extracted and diluted with ethyl acetate for three times. Finally, the liquid extract was analyzed by the gas chromatography-mass spectrometer (GC-MS) and GC.
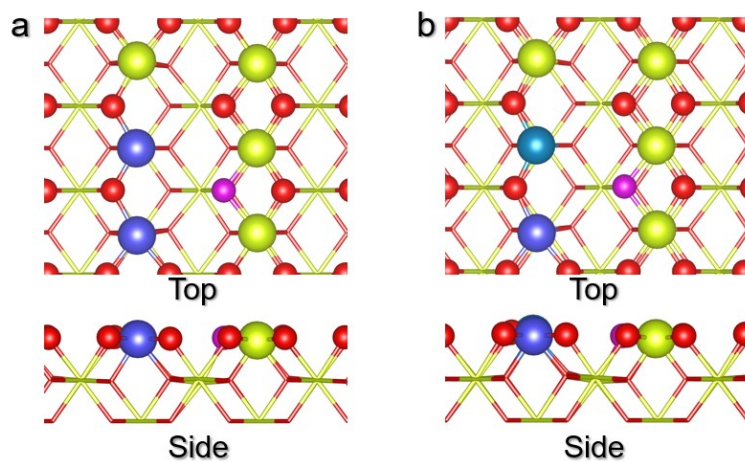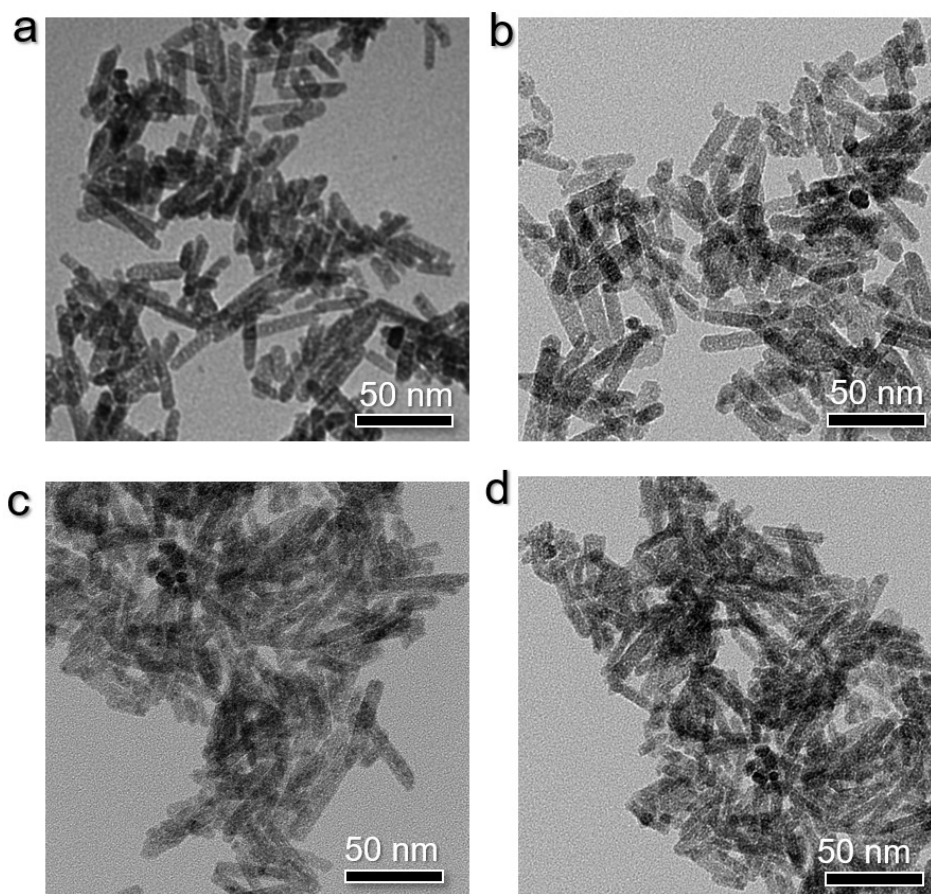

Figure S1. The optimized configuration of (a) (Ce, Ce)-O and (b) (La, Ce)-O FLP sites.
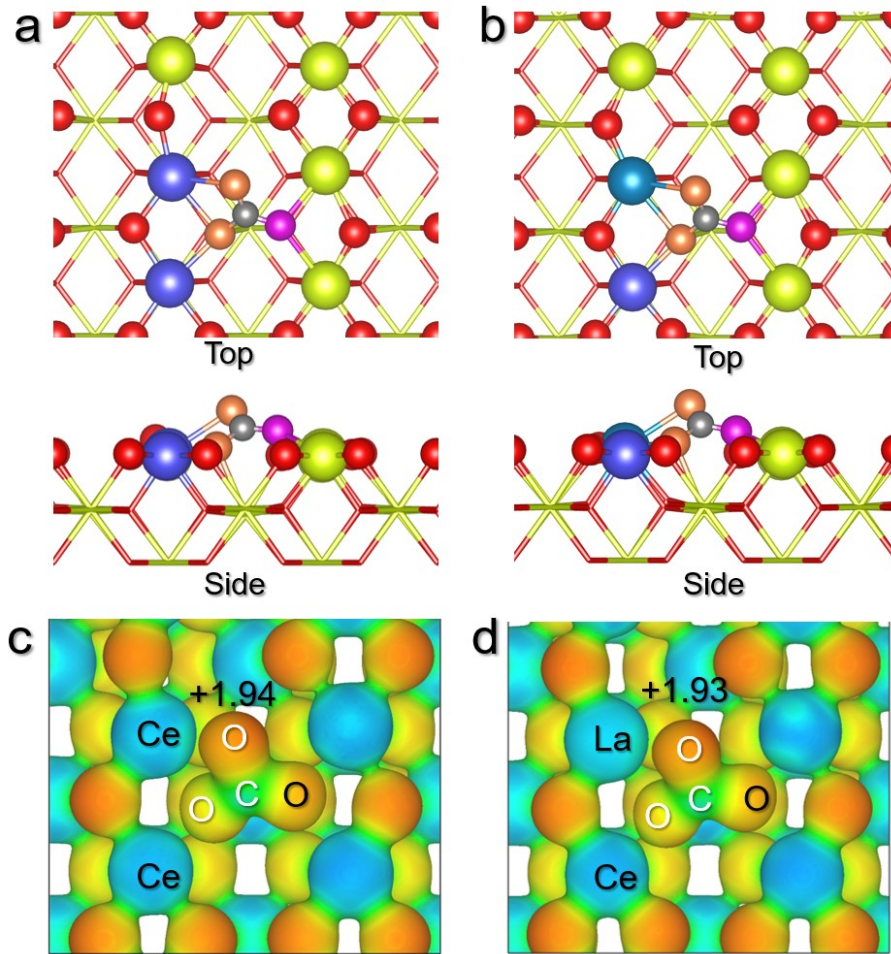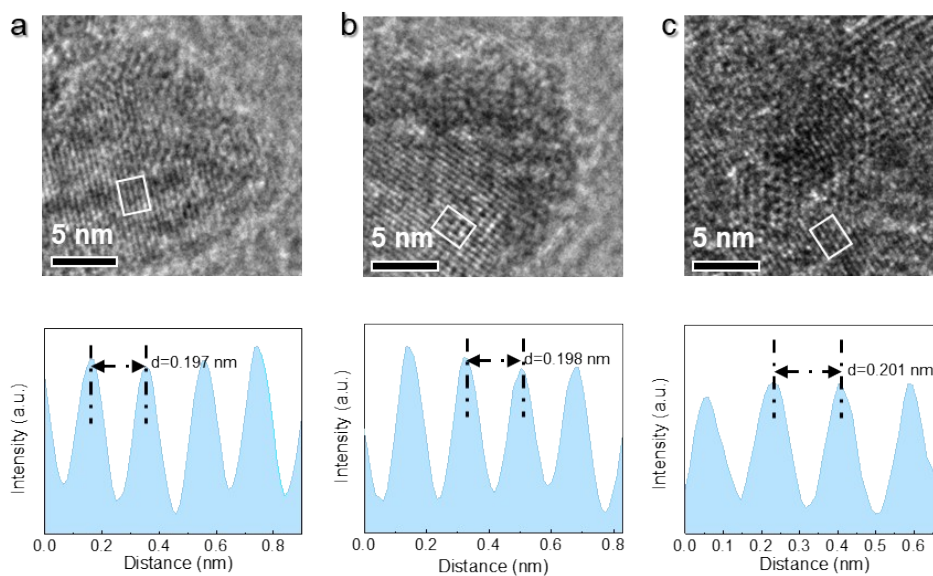
Figure S2. The optimized adsorption configuration of CO_2 on FLP site of (a) (Ce, Ce)-O and (b) (La, Ce)-O.

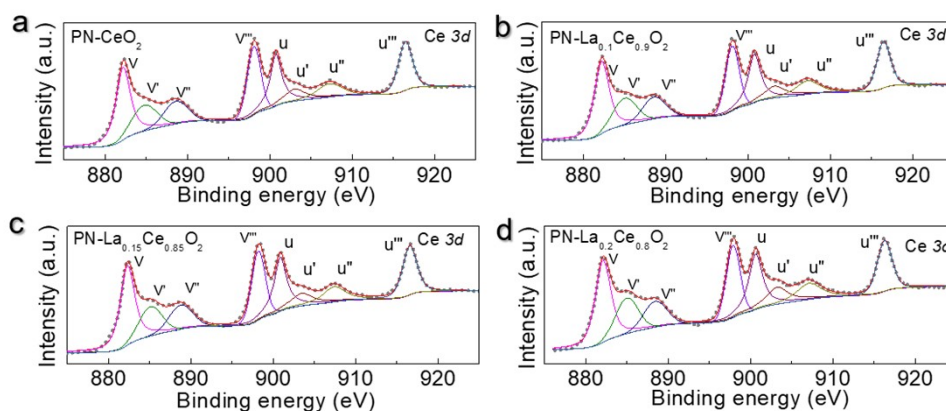**Figure S3.** (a) TEM, (b) HRTEM images and (c) the line profiles of PN-CeO_2.

Figure S4. TEM images for the (a) PN-La$_{0.1}$Ce$_{0.9}$O$_2$, (b) PN-La$_{0.15}$Ce$_{0.85}$O$_2$, (c) PN-La$_{0.2}$Ce$_{0.8}$O$_2$ and (d) PN-La$_{0.25}$Ce$_{0.75}$O$_2$ catalysts, respectively.
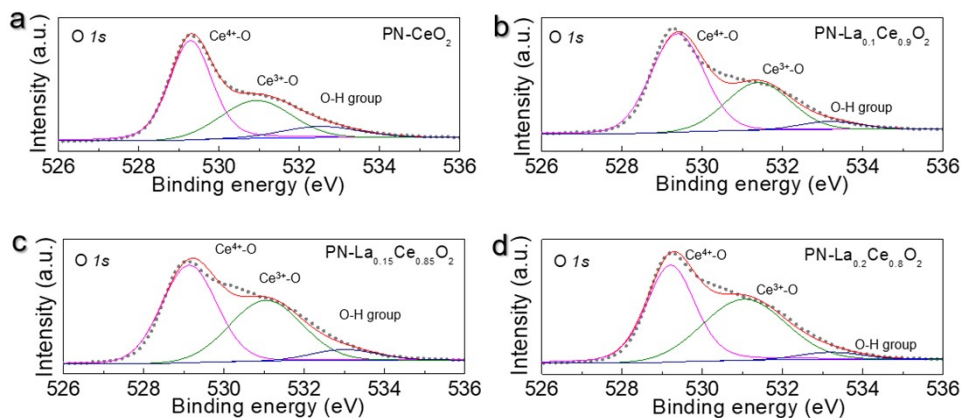
Figure S5. The HRTEM images and lattice fringe spacing of exposed (110) surface for the (a) PN-La$_{0.1}$Ce$_{0.9}$O$_2$, (b) PN-La$_{0.15}$Ce$_{0.85}$O$_2$ and (c) PN-La$_{0.2}$Ce$_{0.8}$O$_2$, respectively.

Figure S6. XPS analysis of Ce *3d* for the (a) PN-CeO$_2$, (b) PN-La$_{0.1}$Ce$_{0.9}$O$_2$, (c) PN-La$_{0.15}$Ce$_{0.85}$O$_2$ and (d) PN-La$_{0.2}$Ce$_{0.8}$O$_2$ catalysts, respectively.

Figure S7. XPS analysis of O *1s* for the (a) PN-CeO$_2$, (b) PN-La$_{0.1}$Ce$_{0.9}$O$_2$, (c) PN-La$_{0.15}$Ce$_{0.85}$O$_2$ and (d) PN-La$_{0.2}$Ce$_{0.8}$O$_2$ catalysts, respectively.
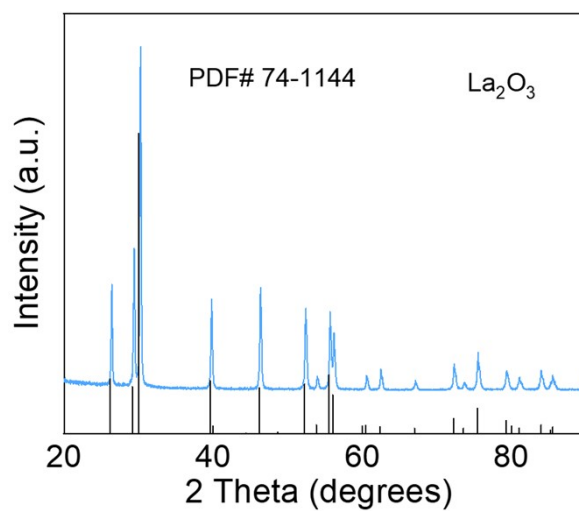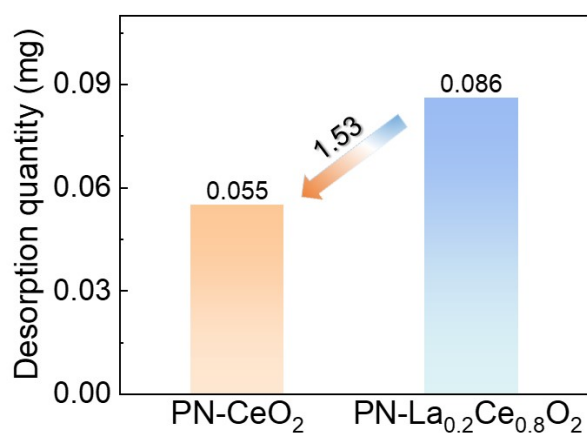
Figure S8. XRD pattern of the La_2O_3 catalysts.
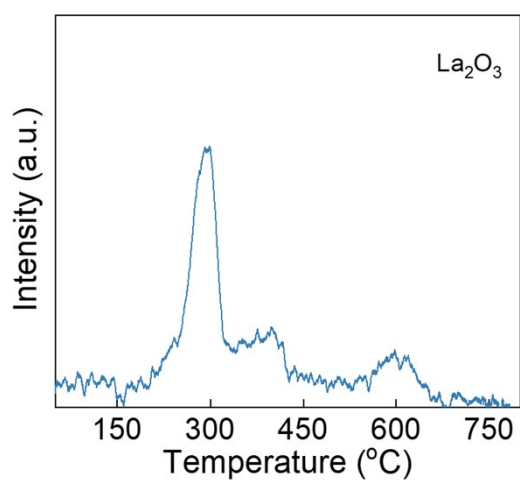
**Figure S9.** CO_2-TPD result for the La_2O_3 catalysts.
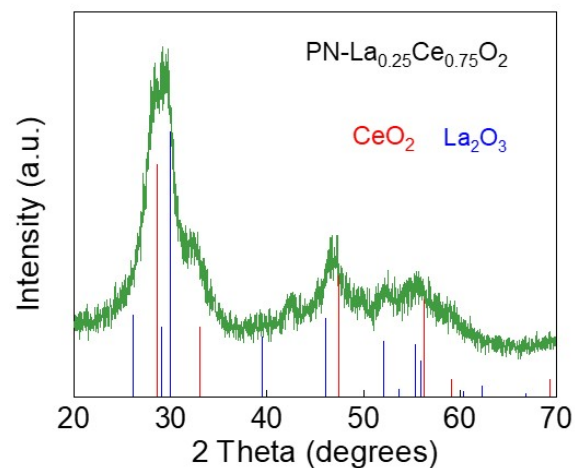
Figure S10. XRD pattern of the PN-La$_{0.25}$Ce$_{0.75}$O$_2$ catalysts.

Figure S11. The desorption quantity of phenylethylene carbonate from the PN-CeO$_2$ and PN-La$_{0.2}$Ce$_{0.8}$O$_2$ catalysts. **Note:** The experimental process was as following: Firstly, phenylethylene carbonate (50 mg) and catalysts (20 mg) were dissolved in dichloromethane (5 mL). The mixture was stirred at room temperature for 10 h to reach the adsorption saturation. After adsorption of phenylethylene, the catalysts were

collected by centrifugal separation and washed with dichloromethane for several times to remove the physically adsorbed phenylethylene molecule. Subsequently, the obtained catalysts were dried in vacuum oven at 80 °C for 24 h. Finally, the catalysts that adsorbs of phenylethylene were dispersed in CDCl$_3$ and sonicated for 10 h to separate the chemisorbed phenylethylene. And, nuclear magnetic resonance was used to measure the content of phenylethylene carbonate, which was desorbed from the catalyst surface.
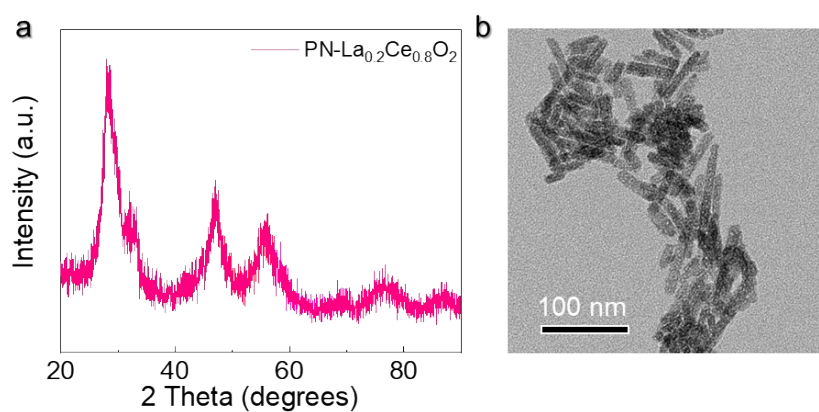
Figure S12. (a) XRD pattern and (b)TEM image of the spent PN-La$_{0.2}$Ce$_{0.8}$O$_2$ catalysts.
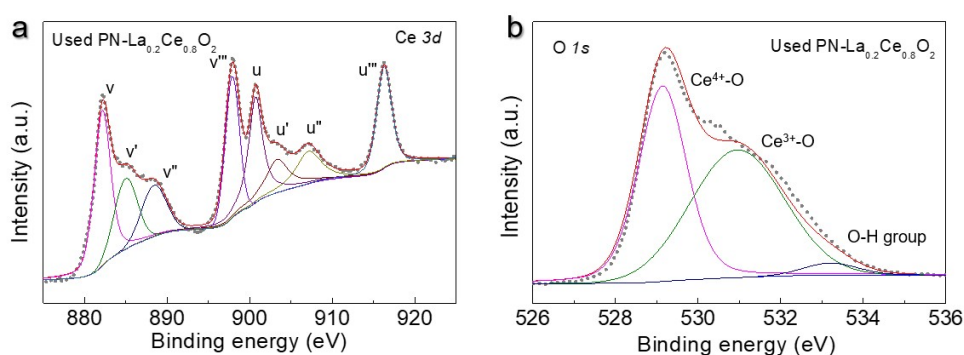
Figure S13. XPS analysis of (a) Ce *3d* and (b) O *1s* of the used PN-La$_{0.2}$Ce$_{0.8}$O$_2$ catalysts, respectively.

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(1) Zhang, S.; Xia, Z.; Zou, Y.; Cao, F.; Liu, Y.; Qu, Y. Interfacial Frustrated Lewis Pairs of CeO_2 Activate CO_2 for Selective Tandem Transformation of Olefins and CO_2 into Cyclic Carbonates. *J. Am. Chem. Soc.* **2019**, *141*, 11353–11357

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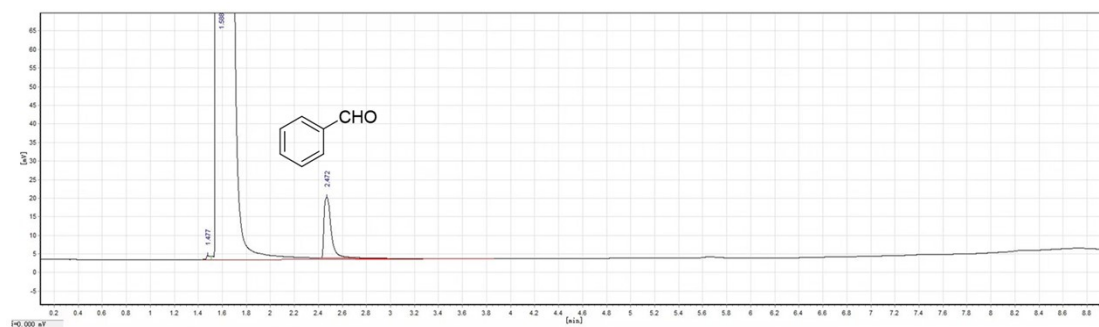
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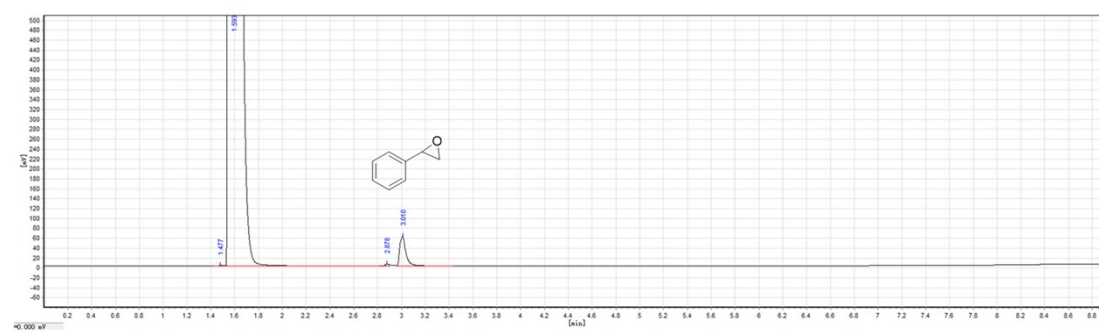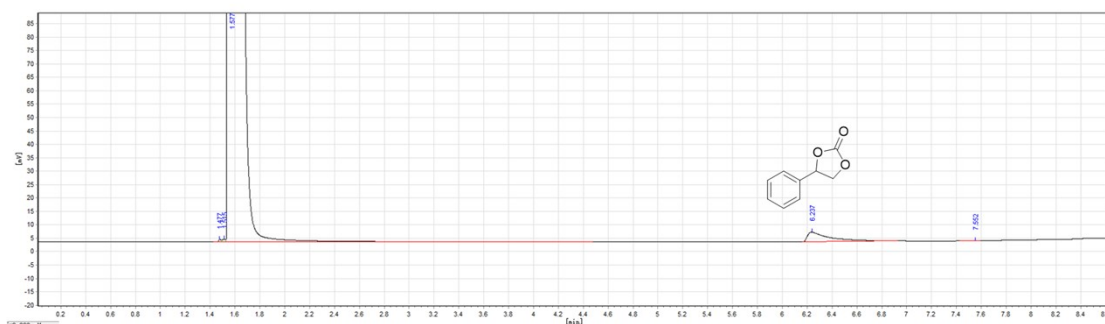
Summary of the relevant GC data.
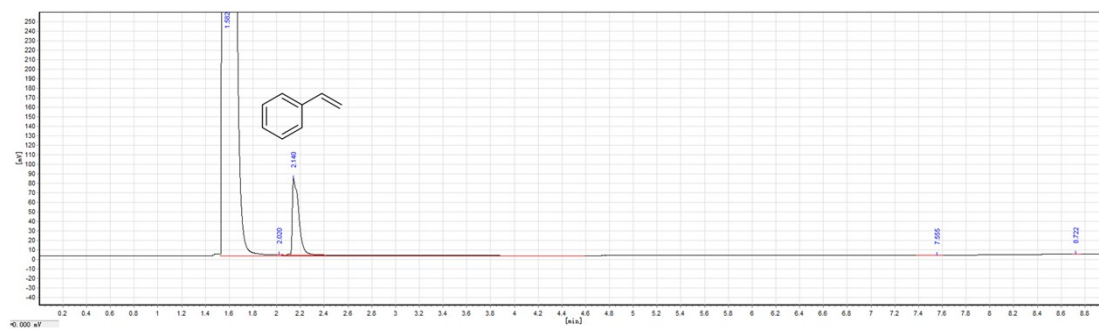
Figure S14. GC spectrum of styrene. (b) benzaldehyde, (c) styrene oxide, (d) phenylethylene carbonate and (e) the reaction mixture.

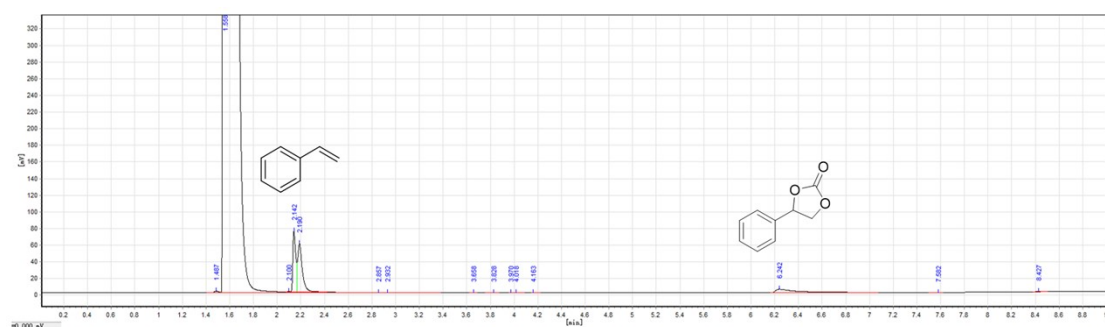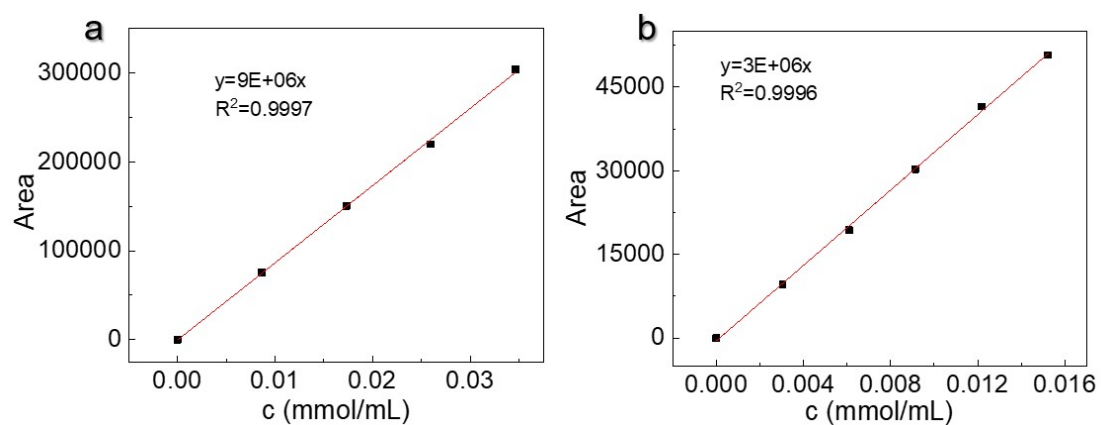**Figure S15.** GC spectrum of benzaldehyde.

Figure S16. GC spectrum of styrene oxide.

Figure S17. GC spectrum of phenylethylene carbonate.

Figure S18. Typical GC spectrum of typical tandem transformation of styrene and CO2 to phenylethylene carbonates.

Figure S19. Standard curve of molar concentration of reactants and integral area. (a) styrene and (b) phenylethylene.

Table S2. Summary of the GC results for the various catalysts*

| Catalysts | Styrene | | Phenylethylene carbonate | | Conv. (%) | Sel. (%) |
	Integral area	Molar mass (mmol)	Integral area	Molar mass (mmol)		
PN-CeO$_2$	266407	2.96	55562	1.852	41	91
PN-La$_{0.1}$Ce$_{0.9}$O$_2$	243903	2.71	63426	2.114	46	92
PN-La$_{0.15}$Ce$_{0.85}$O$_2$	197112	2.19	78331	2.611	56	93
PN-La$_{0.2}$Ce$_{0.8}$O$_2$	66603	0.74	118565	3.952	85	93
PN-La$_{0.25}$Ce$_{0.75}$O$_2$	85506	0.95	110314	3.677	81	91

* Corresponding to the Figure 3c in the main text.

Table S3. Summary of the GC results for PN-La$_{0.2}$Ce$_{0.8}$O$_2$ at various reaction time*

| Times (h) | Styrene | | Phenylethylene carbonate | | Conv. (%) | Sel. (%) |
	Integral area	Molar mass (mmol)	Integral area	Molar mass (mmol)		
2	310526	3.45	45137	1.50	31	97
4	242157	2.69	65123	2.17	46	94
6	187259	2.08	82356	2.75	58	94
8	157542	1.75	92714	3.09	65	95
10	97273	1.08	110422	3.68	78	94
12	53194	0.59	123098	4.10	88	93
14	22561	0.25	132613	4.42	95	93

* Corresponding to the Figure 4a in the main text.

Table S4. Summary of the GC results for PN-La$_{0.2}$Ce$_{0.8}$O$_2$ during recyclability*

Cycles	Styrene		Phenylethylene carbonate		Conv. (%)	Sel. (%)
	Integral area	Molar mass (mmol)	Integral area	Molar mass (mmol)		
1	62142	0.69	120673	4.02	86	93
2	67529	0.75	118547	3.95	85	93
3	70275	0.78	117648	3.92	84	93
4	85514	0.95	114325	3.81	81	94

* Corresponding to the Figure 4b in the main text.