

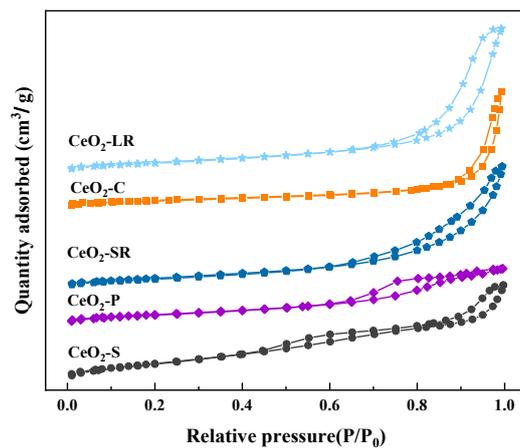
## Supporting Information

### **Nanostructured CeO<sub>2</sub> with different morphologies for methoxycarbonylation of 2,4-toluene diamine with dimethyl carbonate**

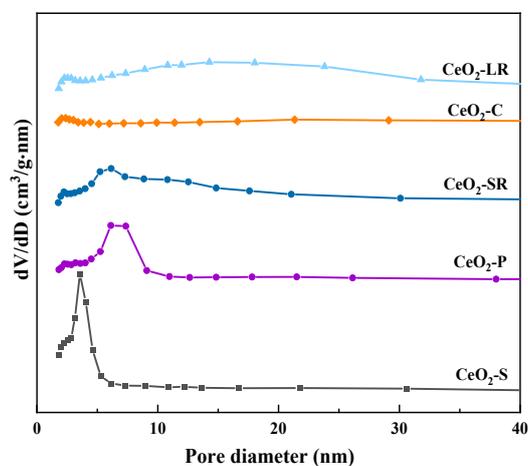
*Mengli Dong, Han Yu, Xinqiang Zhao, Yao Lu<sup>\*</sup>, Hualiang An<sup>\*</sup>, Yanji Wang*

Hebei Provincial Key Laboratory of Green Chemical Technology and Efficient Energy Saving, Tianjin Key Laboratory of Chemical Process Safety, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

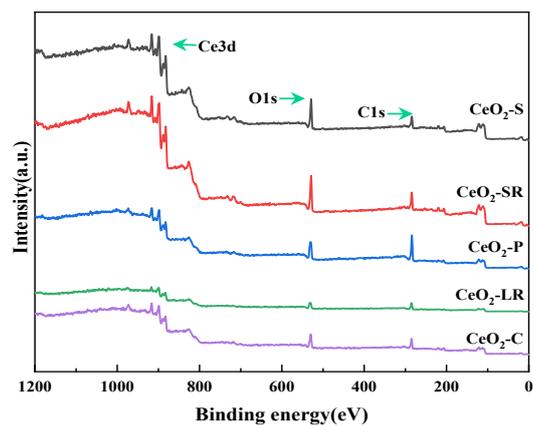
\* Corresponding authors: Yao Lu (ylu@hebut.edu.cn), Hualiang An (anhl@hebut.edu.cn)



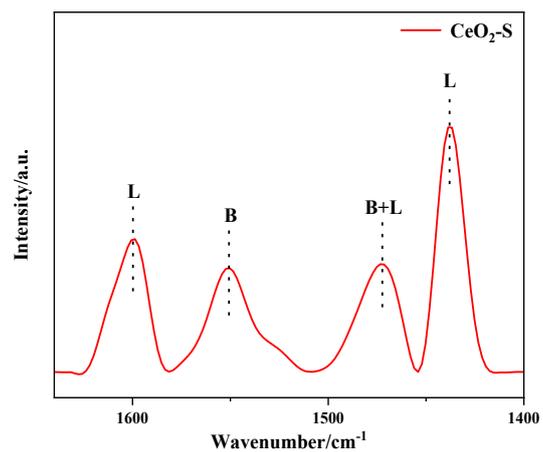
**Figure S1.** N<sub>2</sub> adsorption-desorption isotherms of CeO<sub>2</sub> with different morphologies



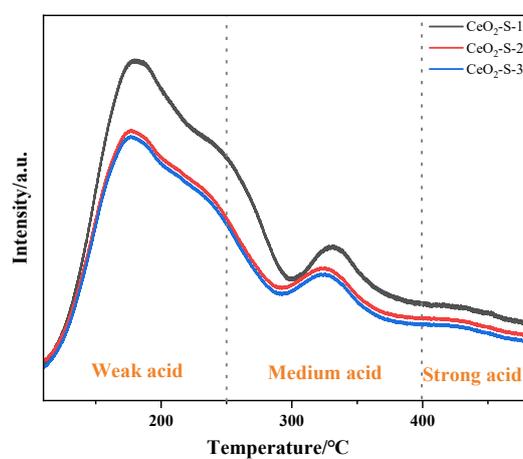
**Figure S2.** Pore size distribution of CeO<sub>2</sub> with different morphologies



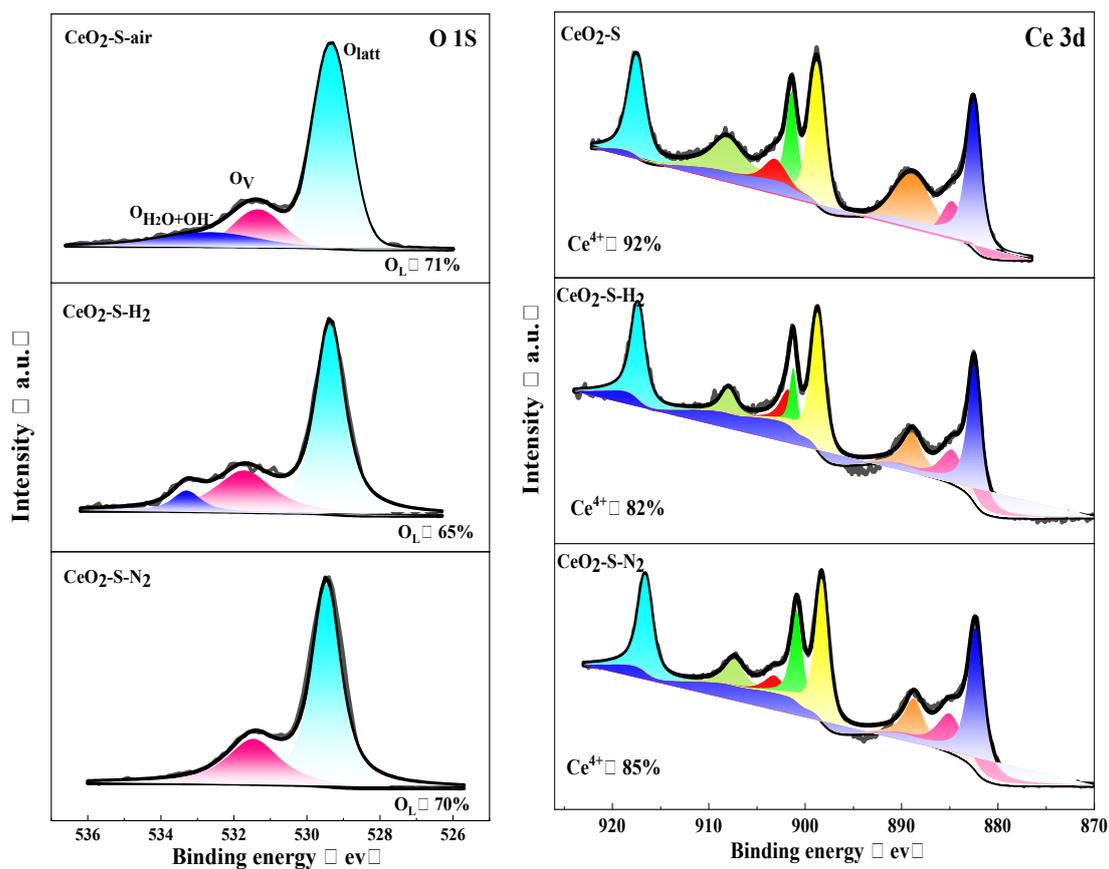
**Figure S3.** XPS spectra of CeO<sub>2</sub> catalysts with different morphologies



**Figure S4.** Py-FTIR spectrum of CeO<sub>2</sub>-S



**Figure S5.** NH<sub>3</sub>-TPD curves of the recycled CeO<sub>2</sub>-S catalyst



**Figure S6.** XPS spectra of CeO<sub>2</sub>-S calcined at different atmospheres

**Table S1.** Acid-base amount of CeO<sub>2</sub> catalysts with different morphologies

| Catalyst             | Acid amount/ $\mu\text{mol}\cdot\text{g}^{-1}$ |        |        |            | Base amount/ $\mu\text{mol}\cdot\text{g}^{-1}$ |        |        |            |
|----------------------|--|--------|--------|------------|--|--------|--------|------------|
|                      | Weak   | Medium | Strong | Total acid | Weak   | Medium | Strong | Total base |
| CeO <sub>2</sub> -S  | 35.19  | 19.64  | 5.78   | 60.60      | 49.54  | 23.61  | 6.60   | 79.76      |
| CeO <sub>2</sub> -SR | 19.01  | 12.04  | 3.98   | 35.04      | 61.29  | 34.45  | 6.86   | 102.6      |
| CeO <sub>2</sub> -LR | 19.26  | 10.20  | 2.85   | 32.31      | 20.36  | 14.96  | 6.62   | 41.95      |
| CeO <sub>2</sub> -P  | 23.40  | 6.48   | 0.05   | 29.93      | 22.88  | 9.94   | 1.92   | 34.74      |
| CeO <sub>2</sub> -C  | 3.81   | 4.07   | 0.00   | 7.88       | 8.48   | 1.37   | 0.16   | 10.01      |

**Table S2.** Effects of calcination atmosphere on CeO<sub>2</sub>-S catalytic performance and XPS analysis

| Catalyst                           | X <sub>TDA</sub> /% | S <sub>2-TMC</sub> /% | S <sub>4-TMC</sub> /% | S <sub>TDC</sub> /% | S <sub>total</sub> /% | O <sub>L</sub> /O <sub>total</sub> | Ce <sup>4+</sup> /Ce <sub>total</sub> |
|------------------------------------|---------------------|-----------------------|-----------------------|---------------------|-----------------------|------------------------------------|---------------------------------------|
| CeO <sub>2</sub> -S-air            | 100.0               | 2.8                   | 6.9                   | 86.8                | 96.5                  | 0.71                               | 0.92                                  |
| CeO <sub>2</sub> -S-N <sub>2</sub> | 100.0               | 2.5                   | 10.6                  | 73.2                | 86.3                  | 0.70                               | 0.85                                  |
| CeO <sub>2</sub> -S-H <sub>2</sub> | 100.0               | 2.5                   | 6.4                   | 72.2                | 81.1                  | 0.65                               | 0.82                                  |

Reaction conditions: TDA=0.25 g, DMC=6 mL, CeO<sub>2</sub>-S=0.25 g, 170 °C, 10 h; P<sub>N<sub>2</sub></sub>=1.5 MPa; S<sub>total</sub>=S<sub>2-TMC</sub>+S<sub>4-TMC</sub>+S<sub>TDC</sub>. O<sub>total</sub>=O<sub>latt</sub>+O<sub>v</sub>+O<sub>H<sub>2</sub>O</sub>+OH<sup>-</sup>. Ce<sub>total</sub>=Ce<sup>3+</sup>+Ce<sup>4+</sup>.