Supporting Information

Zeolitic Imidazolate Framework-67 Derived CeO_2@Co_3O_4 Core-shell Microspheres with Enhanced Catalytic Activity towards Toluene Oxidation

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Contents

Preparation of the CoCe-P catalyst

The CoCe-P catalyst was synthesized with a modified co-precipitation method. [1] Firstly, 667.6 mg $Co(NO_3)_2 \cdot 6H_2O$ and 306.4 mg $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in 40 ml ethanol and water mixed solution (v/v=1:1). Then, 10 vol.% aqueous ammonia solution was added dropwise to the above solution with continuous stirring until the pH was 9.30 ± 0.02. Subsequently, the precipitants were collected by centrifugation, washed for at least 3 times and dried at 80 °C overnight. Finally, the product was calcined at 400 °C for 2 h and marked as CoCe-P.

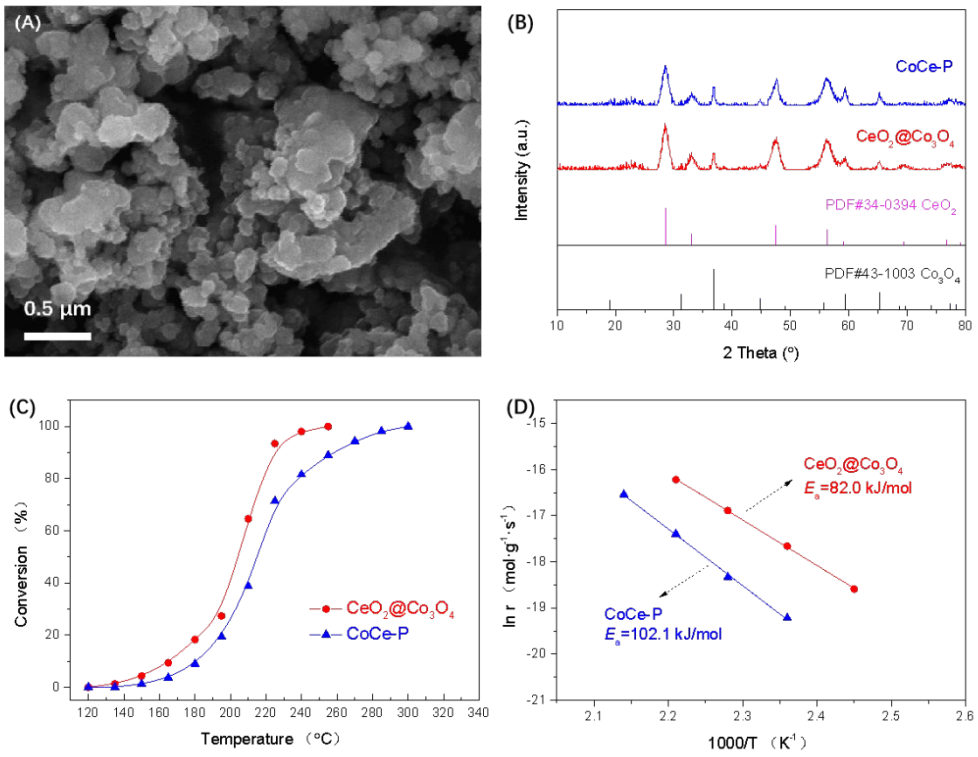

Figure S1. SEM image (A) of CeCe-P; XRD pattern (B), Toluene conversion (C) and Arrhenius plots (D) of $CeO_2@Co_3O_4$ and CoCe-P.

As shown in Figure S1A, the SEM image of CoCe-P exhibited clusters of irregular particles,

which was similar with the previous work. [2] From Figure S1B, the XRD pattern of CoCe-P could be ascribed to CeO_2 and Co_3O_4. No other phases were detected.

Furthermore, the catalytic activity towards toluene oxidation (C) and Arrhenius plots (D) of CoCe-P were also given in Figure 1, and the results were summarized in Table 1. From Figure 1C-D and Table 1, the $CeO_2@Co_3O_4$ sample showed better activity than CoCe-P. Additionally, the E_a of the core-shell catalyst was lower than that of the CoCe-P sample, which further verified that core-shell $CeO_2@Co_3O_4$ was superior to the CeCo catalyst prepared by the co-precipitation method.

Table S1： The catalytic activity results of $CeO_2@Co_3O_4$ and CoCe-P for toluene

Sample	T_{50} (℃)	T_{90} (℃)	E_a [a] (kJ/mol)
$CeO_2@Co_3O_4$	204	225	82.0
CoCe-P	215	259	102.1

[a] Apparent activation energy for toluene oxidation obtained from the Arrhenius plot.

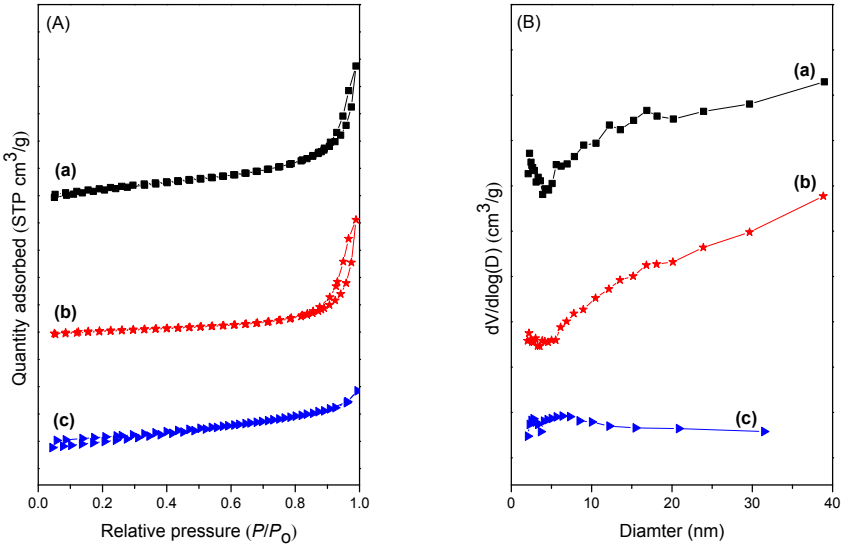

Figure S2. N_2 adsorption/desorption isotherms (A) and pore size distributions (B) of (a) Co_3O_4, (b) CeO_2@Co_3O_4 and (c) CeO_2.

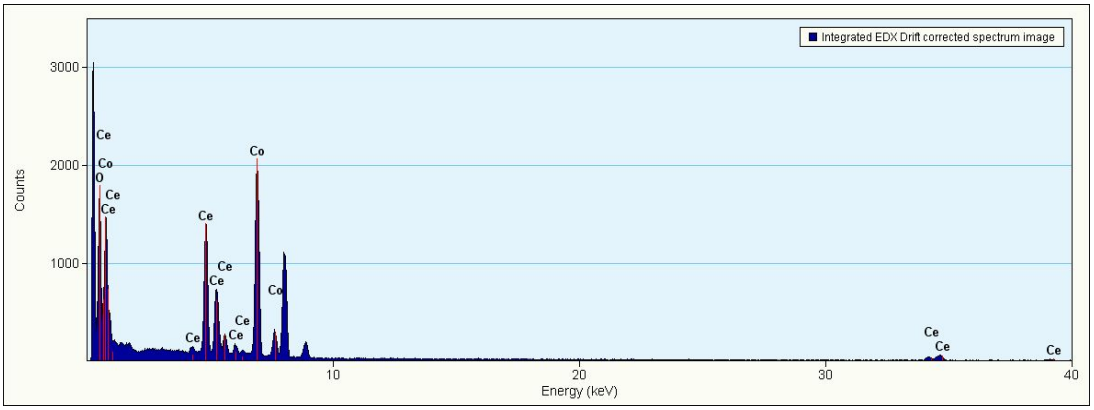

Figure S3. EDX image of the CeO_2@Co_3O_4 sample.

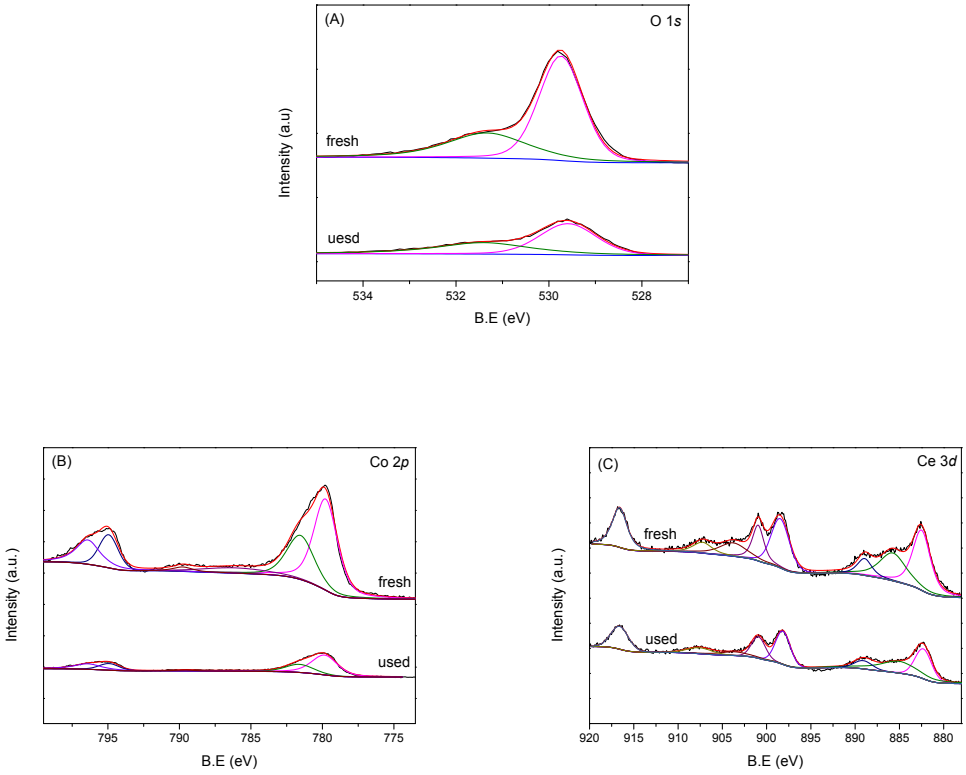

Figure S4. XPS spectra of CeO_2@Co_3O_4 before and after reaction.

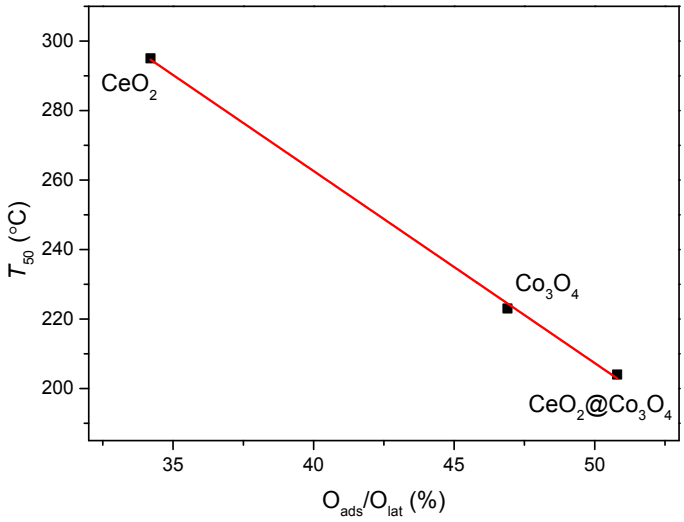

Figure S5. Correlations between the O_{ads}/O_{lat} ratios and the catalytic activity at 50% conversion of the three catalysts.

References

(1) Chen, J.; Zhang, X.; Arandiyan, H.; Peng, Y.; Chang, H.; Li, J., Low temperature complete combustion of methane over cobalt chromium oxides catalysts. *Catal. Today* **2013**, *201*, 12-18.

(2) Liotta, L. F.; Ousmane, M.; Di Carlo, G.; Pantaleo, G.; Deganello, G.; Marcì, G.; Retailleau, L.; Giroir-Fendler, A., Total oxidation of propane at low temperature over Co_3O_4–CeO_2 mixed oxides: Role of surface oxygen vacancies and bulk oxygen mobility in the catalytic activity. *App. Catal., A* **2008**, *347* (1), 81-88.