

Supporting Information for

## Hierarchically porous $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ prepared by solvent volatilization for high-efficient synthesis of DMC from $\text{CO}_2$ and methanol

Guanling Yang<sup>1</sup>, Haobo Wang<sup>1</sup>, Aizhong Jia<sup>1,2\*</sup>, Jingde Li<sup>1,2</sup> and Yanji Wang<sup>1,2</sup>

<sup>1</sup>Hebei Provincial Key Laboratory of Green Chemical Technology & High Efficient Energy Saving, Hebei University of Technology, Tianjin, P. R. China.

<sup>2</sup>Tianjin Key Laboratory of Chemical Process Safety, Tianjin, P. R. China.

\*Corresponding E-mail: azhjia@hebut.edu.cn

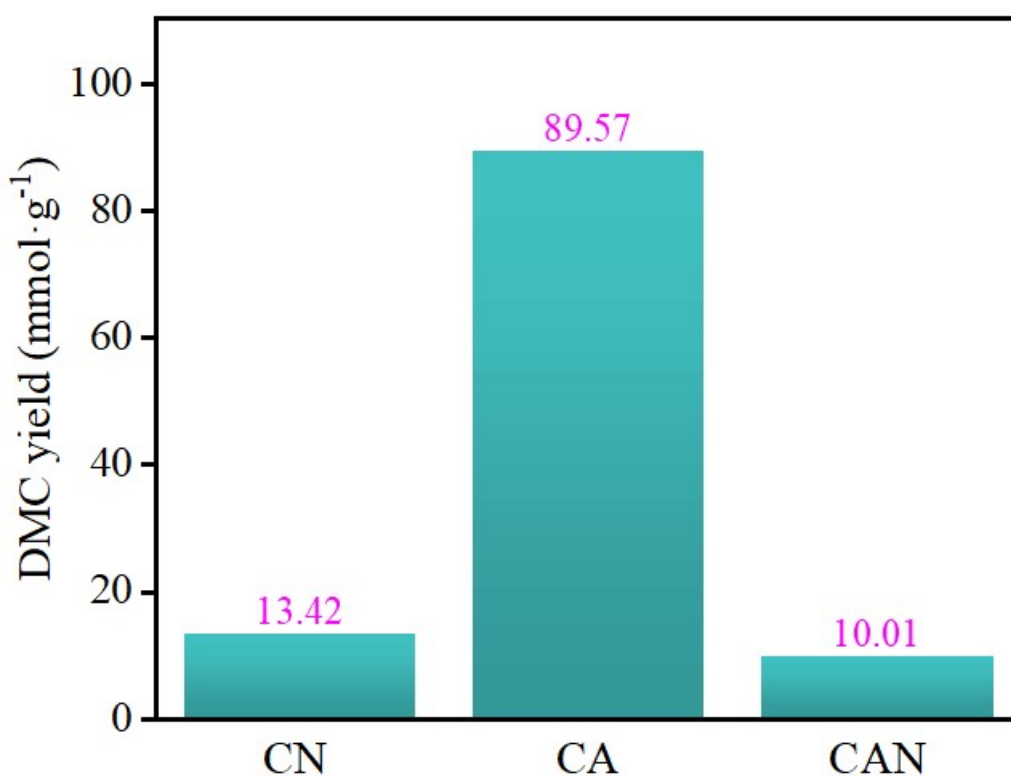


Fig. S1 Catalytic performance of CeO<sub>2</sub> catalysts prepared from different metal salts. (CN: cerium nitrate, CAN: cerium ammonium nitrate, CA: cerium acetate)

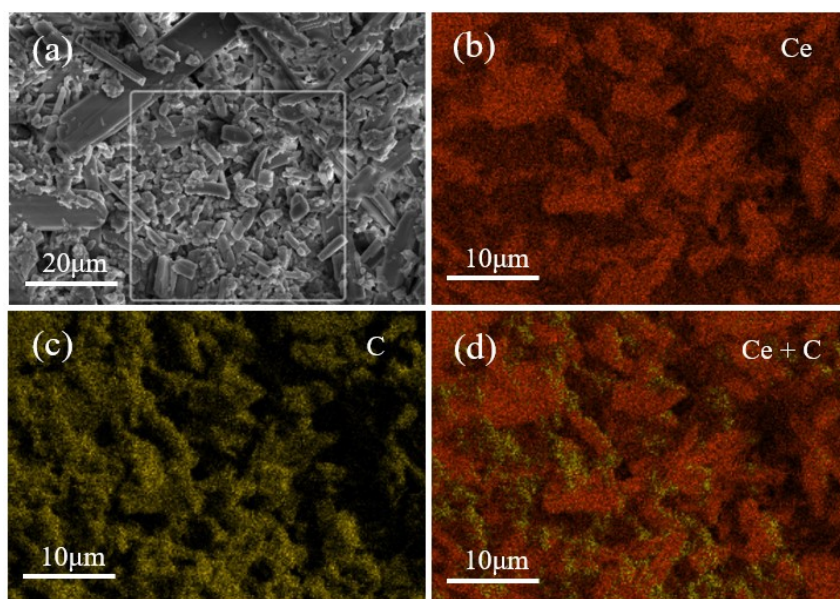


Fig. S2 The SEM mapping of the precursor of sample  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  prepared with cerium acetate as cerium source.

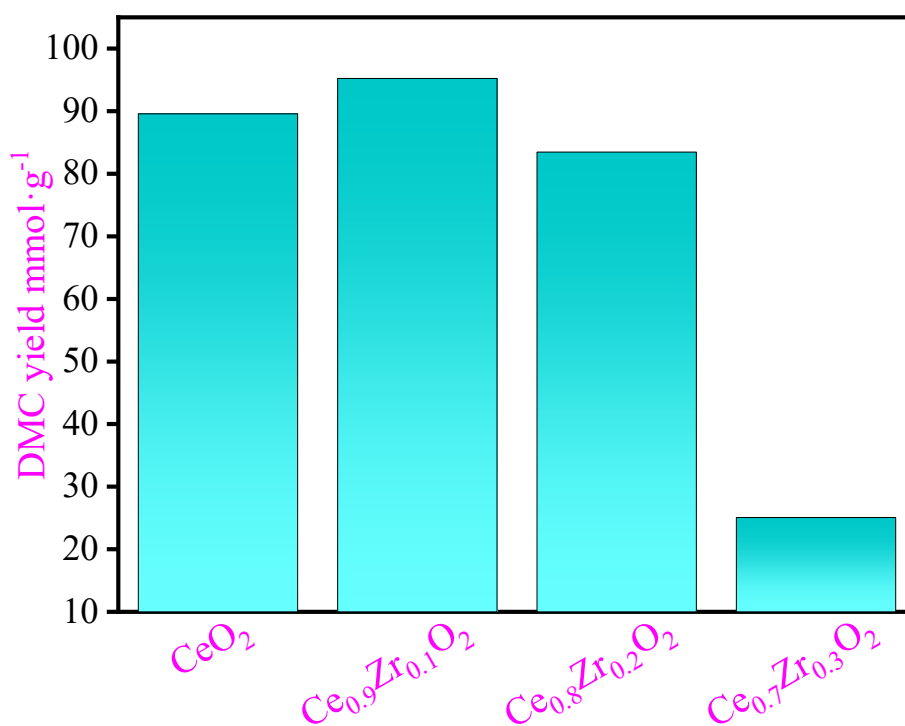


Fig. S3 Catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  samples. Reaction conditions: catalyst 0.1 g,  $\text{CH}_3\text{OH}$  15mL, 2-CP 3g, 5h.

Tab. S1 The acid-basic properties of synthesized  $Ce_xZr_{1-x}O_2$  catalysts.

Catalyst	Basicity <sup>a</sup> ( $\mu\text{mol/g}$ )				Acidity <sup>b</sup> ( $\mu\text{mol/g}$ )			
	$B_W$ ( $<200^\circ$ )	$B_M$ (200~400)	$B_S$ ( $>400$ )	$B_T$	$A_W$ ( $<200$ )	$A_M$ (200~400)	$A_S$ ( $>400$ )	Total
$CeO_2$	192.04	64.28	13.66	269.98	54.24	40.39	15.83	110.47
$Ce_{0.9}Zr_{0.1}O_2$	235.85	80.87	5.63	322.35	63.3	40.69	17.84	113.03
$Ce_{0.8}Zr_{0.2}O_2$	196.37	32.1	5.82	234.28	42.21	26.81	11.95	80.96
$Ce_{0.7}Zr_{0.3}O_2$	190.86	24.06	6.42	221.33	27.12	18.01	8.01	53.14

<sup>a</sup> Calculated by  $CO_2$ -TPD; <sup>b</sup> Calculated by  $NH_3$ -TPD; <sup>c</sup> The unit of temperature is  $^\circ C$ .



Fig. S4 The digital photographs of samples: (a<sub>1</sub>-a<sub>4</sub>)  $Ce_xZr_{1-x}O_2$  precursors and (b<sub>1</sub>-b<sub>4</sub>)  $Ce_xZr_{1-x}O_2$  materials (x=1-0.7, for the sample number from 1 to 4).

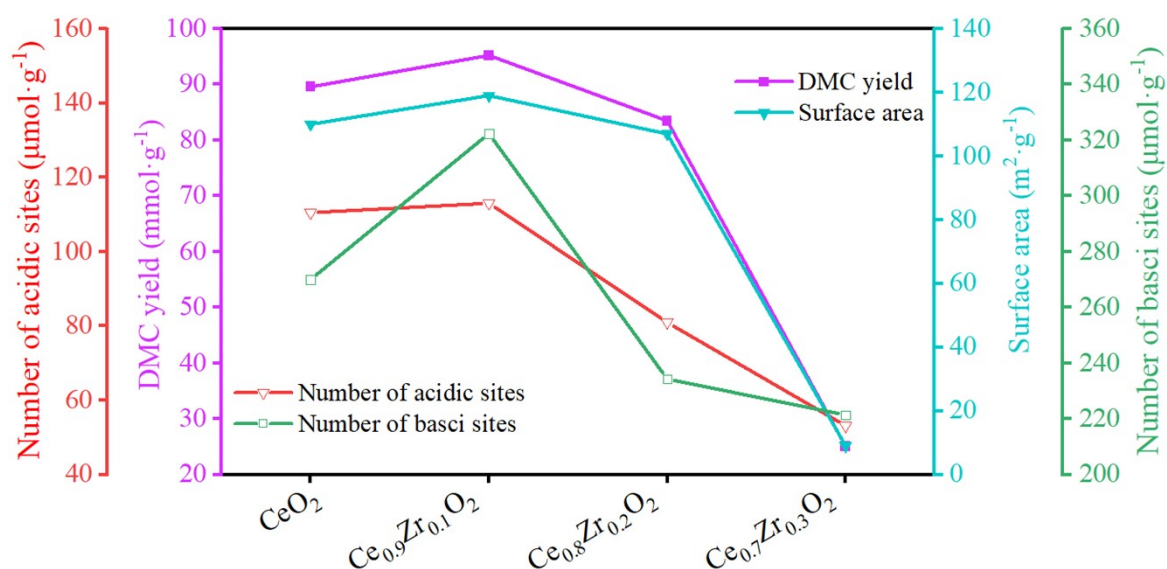


Fig. S5 The relationship between catalytic performance and acid-base site content of  $Ce_xZr_{1-x}O_2$ .

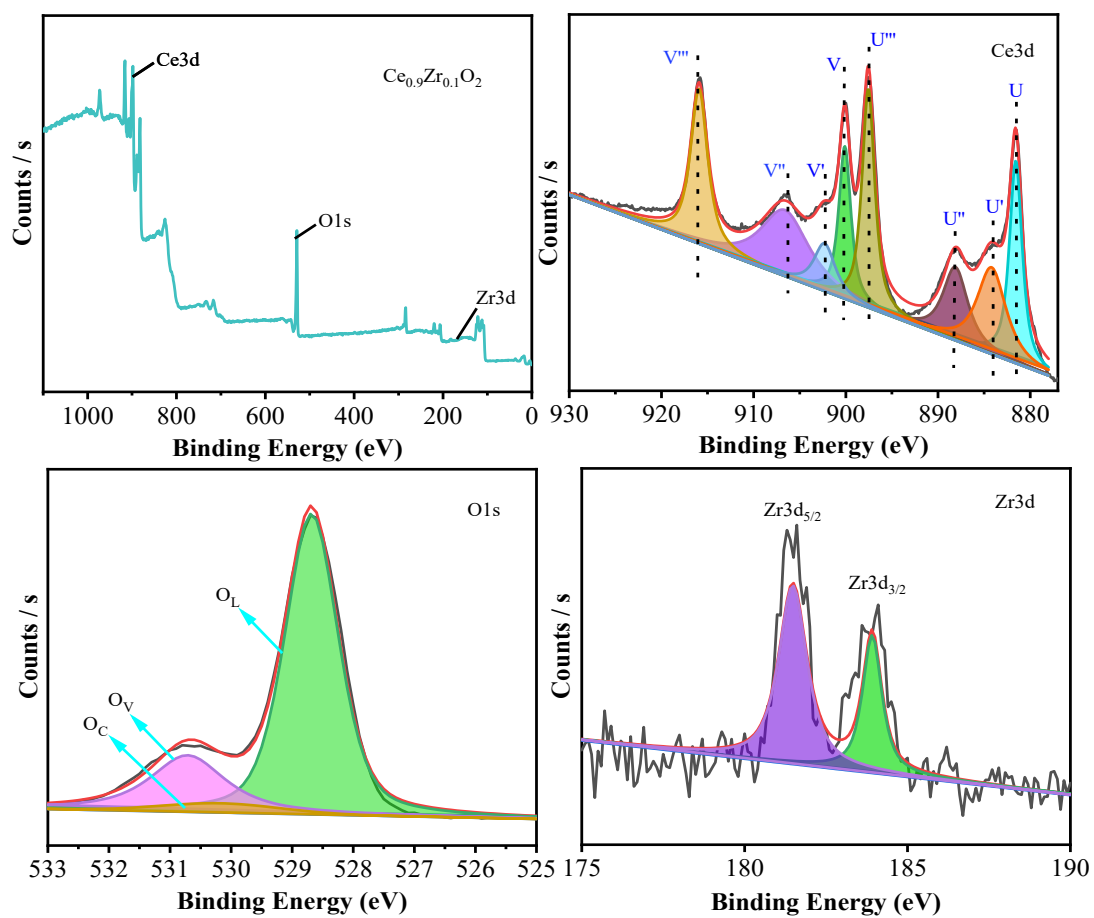


Fig. S6 XPS spectras of (a) full spectra; (b) Ce3d; (c) O1s and (d) Zr3d of  $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ .