Supplementary Information

Synthesis of dimethyl carbonate from CO_2 and methanol over

hydrophobic Ce/SBA-15 catalyst

Yanfeng Pu^a, Keng Xuan^{a,b}, Feng Wang^a, Aixue Li^{a,b}, Ning Zhao^{a,*}, Fukui Xiao^{a,*}

^aState Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
^bUniversity of Chinese Academy of Sciences, Beijing 100049, PR China
*Corresponding authors.
E-mail addresses: zhaoning@sxicc.ac.cn (N. Zhao), xiaofk@sxicc.ac.cn (F. Xiao)

Table of contents:

- Fig.S1. TEM images of catalysts for SBA-15 (a); Ce/SBA-15 (b1, b2); Ce/SBA-15-6 (c1, c2). Scale bars are 2 nm.
- Fig.S2. Ce 3d XPS spectra of the catalysts: (a) Ce/SBA-15; (b) Ce/SBA-15-3; (c) Ce/SBA-15-6; (d) Ce/SBA-15-9.
- Fig.S3. O1s spectra of SBA-15, Ce/SBA-15 and Ce/SBA-15-X (X=3, 6, 9) catalysts.
- Fig.S4. CO₂-TPD profiles of CeO₂, SBA-15, Ce/SBA-15 and Ce/SBA-15-X (X=3, 6, 9) catalysts.
- Fig.S5. Effects of the reaction time on DMC yield over Ce/SBA-15-6 and Ce/SBA-15-9 catalysts.
- Fig.S6. DMC yield over Ce/SBA-15-6 catalyst with the different catalyst amount.
- Fig.S7. DMC yield during recycling of Ce/SBA-15-6 as a catalyst.



Fig. S1. TEM images of catalysts for SBA-15 (a); Ce/SBA-15 (b1, b2); Ce/SBA-15-6 (c1, c2). Scale bars are 2 nm.



Fig. S2. Ce 3d XPS spectra of the catalysts: Ce/SBA-15 (a); Ce/SBA-15-3 (b); Ce/SBA-15-6 (c); Ce/SBA-15-9 (d).



Fig. S3. O1s spectra of SBA-15, Ce/SBA-15 and Ce/SBA-15-X (X=3, 6, 9) catalysts.



Fig. S4. CO_2 -TPD profiles of CeO₂, SBA-15, Ce/SBA-15 and Ce/SBA-15-X (X=3, 6, 9) catalysts. Adsorption amount of CO₂ was measured by the volumetric methods, the unit "mmol·gcat⁻¹"

In order to evaluate the desorbed CO_2 amount excluding CO_2 derived from the organic species on SBA-15, the samples were desorpted directly without CO_2 adsorption after the Ar purification, and then the obtained value was used as curve(i).

The detailed procedure was as follows: Temperature programmed desorption of CO_2 (CO₂-TPD) were carried out on the GAM 200 Mass Spectrometer for the measurement of the acidity- basicity of the catalysts. Each sample (50 mg) was placed in the quartz reactor and pretreated in an Ar flow (40 mL min⁻¹) at 500 °C for 1 h. the purified samples was then cooled to 50 °C, followed by an Ar purge for 1 h to remove the physisorbed CO₂. The desorption process was performed at a heating rate of 10 °C min⁻¹ from 50 °C to 500 °C and the evolved CO₂ was monitored with a thermal conductivity detector (TCD), and quantitatively analyzed by the external standard method.

Furthermore, the samples with CO₂ adsorption were desorpted (the detailed procedure was as the "**2.2 Physical Characterization**") were used as the curve(ii). Then, curve(ii) subtracted curve(i) equaled to the results curve and shown in the **Fig. S4.**



Fig. S5. Effects of the reaction time on DMC yield over Ce/SBA-15-6 and Ce/SBA-15-9 catalysts. Reaction conditions: 130 °C; CH₃OH weight, 6.4 g; CO₂, 100 mmol; reaction pressure (P) = 10 MPa; catalyst weight, 0.5 g.



Fig. S6. DMC yield over Ce/SBA-15-6 catalyst with the different catalyst amount (0.5 g; 1.0 g). Reaction conditions: 130 °C; 12 h; CH₃OH, 6.4 g; CO₂, 100 mmol; reaction pressure (P) = 10 MPa;.



Fig. S7. DMC yield during recycling of Ce/SBA-15-6 as a catalyst, 12 h for each cycle. Reaction conditions: 130 °C; CH₃OH weight, 6.4 g; CO₂, 100 mmol; reaction pressure (P) = 10 MPa; catalyst weight, 0.5 g.