Supporting Information

Synergistic CeO_2-HMOR Bicomponent Catalyst Enables Efficient Coproduction of Dimethyl Carbonate and Methyl Formate via CO_2-Methanol Coupling Assisted by 1,1,1-Trimethoxymethane Hydrolysis

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Experimental

Materials: $Ce(NO_3)_3 \cdot 6\ H_2O$ (99.5 wt.%) and 1,1,1-trimethoxymethane (TMM, 99.56% wt.%, anhydrous) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. Sodium hydroxide (96.0 wt.%, AR), anhydrous methanol (97.0 wt.%, AR) and n-propanol (99.5 wt.%) were obtained from Sinopharm Chemical Reagent Co., Ltd. HZSM-5 and Hβ zeolites were purchased from Tianjin Shenneng Technology Co., Ltd. HY and HMOR zeolites were purchased from Nankai University Catalyst Co., Ltd.

Catalysts preparation:

Nano-rod CeO_2 was prepared by co-precipitation method as previously reported[1]. Typically, 12.42 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 8.44 g of NaOH were dissolved in 20 mL and 15 mL of deionized water, respectively. The precipitate was formed by a full mixing of above two solutions, and added to a 100 mL Teflon-lined stainless steel autoclave and crystallized at 100 ^oC for 24 h. When it cooled down to room temperature, the product was separated by filtration, washed with deionized water and ethanol several times and dried at 100 ^oC for a night. Finally, nano-rod CeO_2 sample was obtained after calcination in the air at 600 ^oC for 4 h.

CeO_2-HMOR, CeO_2-HZSM-5, CeO_2-Hβ and CeO_2-HMOR bifunctional catalysts were prepared by a simple mixing of powder of CeO_2 and zeolites.

For comparison, CeO_2-HMOR bifunctional catalyst were prepared by grinding mixing for 30 minutes, and by incipient wetness impregnation with aqueous of $Ce(NO_3)_3 \cdot 6H_2O$, respectively. In addition, CeO_2-HMOR bifunctional catalyst also was prepared by co-precipitation method that were similar to the method of nano-rod CeO_2, except for the addition of HMOR zeolite to the precipitate before it was added to the Teflon-lined stainless steel autoclave.

Catalysts characterization

HRTEM analysis was obtained with a JEOL JEM-2100 instrument. SEM experiments were carried out on a ZEISS Gemini SEM 300 instrument. XRD patterns were obtained on a Rigaku SmartLab SE with scanning speed of 5^o min^{-1} during 5-80 ^{o}. N_2 adsorption experiments were performed on a Microactive ASAP 2460 apparatus at -196 ^{o}C. Contact angle testings were operated on Chengdedingsheng JY-82C instrument. IR spectra were collected by Thermo Fisher Scientific Nicolet iS20 with KBr matrix after desorption at 100 ^{o}C for 12 h. Py-IR spectra were collected in the range of 1400–1700 cm^{-1} using a Bruker Tensor 27 spectrometer in transmission mode after desorption at 150 ^{o}C and 350 ^{o}C. The amounts of acidic sites were investigated by NH_3 temperature programmed experiment (NH_3-TPD) on a Micromeritics AutoChem II 2920 instrument with a TCD. The100 mg sample was placed in the reaction tube and pretreated in the flow of He for 60 min at 600 ^{o}C with a heating rate of 10 ^{o}C min^{-1}. After the temperature cooled to 100 ^{o}C, the 10% NH_3/He mixed gas

was introduced for 1 hour. Next, the samples were purified with He for 60 min. NH_3 desorption process was carried out in the temperature range of 100 to 600 ^oC at a ramping rate of 10 ^oC min^{-1} in the He atmosphere.

The in-situ IR spectra were obtained using a Thermo Scientific Nicolet iS50 instrument in transmission mode. Prior to the tests, the self-supported wafer samples were treated in N_2 atmosphere at 200 ^oC for 30 min to thoroughly remove adsorbed impurities. After the temperature of in-situ chamber dropped to 50 °C, the mixed gas of CO_2, methanol and TMM was continuously introduced for 30 minutes. During this process, methanol and TMM solution were first pumped into the vaporization furnace to complete vaporization and then introduced into the sample chamber. Afterwards, the inlet and outlet of the chamber were sealed，and then the background spectrum was obtained at 50 °C with 0.1 MPa. The in-situ spectra were collected while the sample temperature was increased from 50 °C to70 °C, 90 °C, 100 °C, 110 °C, 130 °C, 140 °C and maintained 140 °C for 15 min and 30 min.

Computational Models and Methods

In this theoretical study, all geometric and energetic calculations were performed using density functional approximation as implemented in the CP2K package.[1] The exchange-correction energies were calculated using the generalized-gradient approximated Perdew–Burke–Ernzerh functional (GGA-PBE).[2,3] The dispersion interaction was calculated by using the empirical parameterized Grimme (D3) method. [4] The **valence-shell electrons** ($1s^2$ for H, $2s^22p^2$ for C, $2s^22p^4$ for O, and $3s^23p^2$ for Si) are described using hybrid Gaussian and plane-wave (GPW) basis sets[5]. Such basis sets are at level of triple-ζ valence plus polarization function (TZVP) with minimizing basis set superposition errors.[6] The cutoff energy of 600

Rydberg of auxiliary plane wave basis sets were applied. Core-shell electrons of all elements were described using the Norm-conserving and separable Goedecker-Teter-Hutter (GTH) pseudopotentials.[7] Transition states of elementary reaction were computed by using the climbing image nudged-elastic-band method (CI-NEB) with a convergence criterion of 0.05 eV/Å.[8] The cluster model was constructed from MOR zeolite supper cell within a box of sizes of 25x25x25 Angstroms. One proton was introduced into the model and binding on bridge O atom to simulate the real catalyst environment.

Catalytic performance measurement

The catalytic performance measurement was operated using a 50 mL stainless autoclave reactor (Anhui Kemi Instrument Co., Ltd). A certain of methanol, TMM and catalyst were added into reactor. The reactor was purged several times with CO_2 and pressurized up to 3.0 MPa, and then heated at 140 ^oC for 3h. After reaction, the reactor was cooled to room temperature and depressurized. The liquid products were verified by 1H NMR spectroscopy (AVANCE NEO, 400 MHz, using DMSO-d_6) and detected by a gas chromatograph (FULI 9790 II) with RB-INNOWAX capillary column and FID detector. The 1-propanol was used as an internal standard. After the reaction of measurement, the CeO_2-HMOR bicomponent catalyst was recycled by centrifugation followed by absolute methanol washing third times under ultrasound for 10 min.

The product yield and space time yield were calculated as follow:

Based on methanol:

$$\text{DMC yield} = \frac{Amount\ of\ DMC\ formed\ (mmol) \times 2}{Amount\ of\ MeOH\ added\ (mmol)} \times 100\ \% \qquad \text{(Eq. 1)}$$

$$\text{DME yield} = \frac{Amount\ of\ DME\ formed\ (mmol) \times 2}{Amount\ of\ MeOH\ added\ (mmol)} \times 100\ \% \quad \text{(Eq. 2)}$$

Based on TMM:

$$\text{DMC yield} = \frac{Amount\ of\ DMC\ formed\ (mmol)}{Amount\ of\ TMM\ added\ (mmol)} \times 100\ \% \quad \text{(Eq. 3)}$$

$$\text{DME yield} = \frac{Amount\ of\ DME\ formed\ (mmol)}{Amount\ of\ TMM\ added\ (mmol)} \times 100\ \% \quad \text{(Eq. 4)}$$

$$\text{MF yield} = \frac{Amount\ of\ MF\ formed\ (mmol)}{Amount\ of\ TMM\ added\ (mmol)} \times 100\ \% \quad \text{(Eq. 5)}$$

$$\text{DMC formation rate} = \frac{Amount\ of\ DMC\ formed\ (mmol)}{Amount\ of\ CeO_2\ added\ (g)} \quad \text{(Eq.6)}$$

Supplementary Figures and Tables

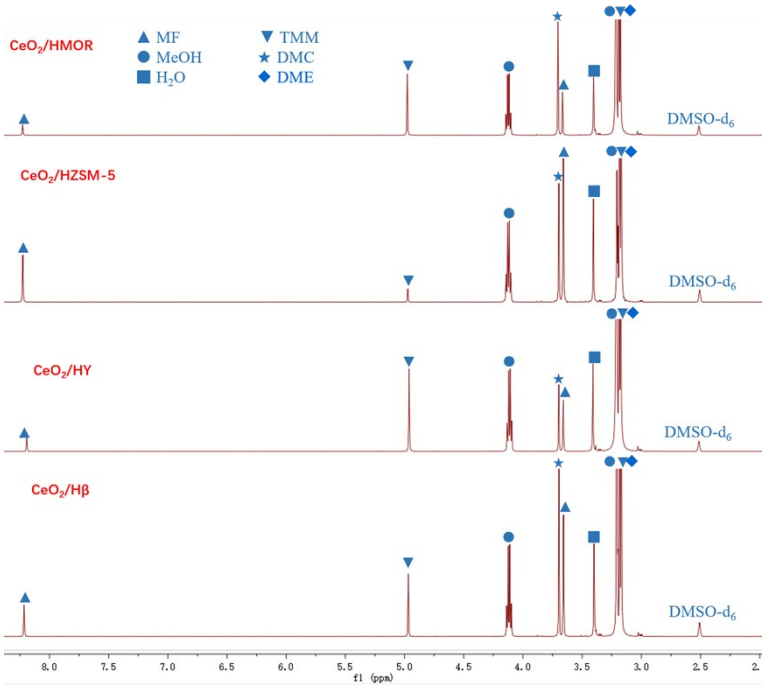

Figure S1 ^{1}H NMR spectra of reaction products over CeO_2-HMOR, CeO_2-HZSM-5, CeO_2-HY and CeO_2-Hβ.

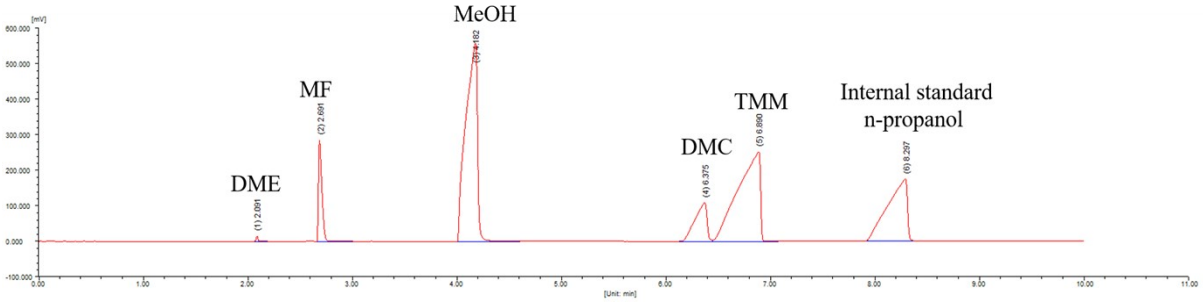

Figure S2 The gas phase chromatography signal of coproduction of dimethyl carbonate and methyl formate via CeO_2-methanol coupling assisted by 1,1,1-trimethoxymethane hydrolysis over the CeO_2-HMOR bicomponent catalyst

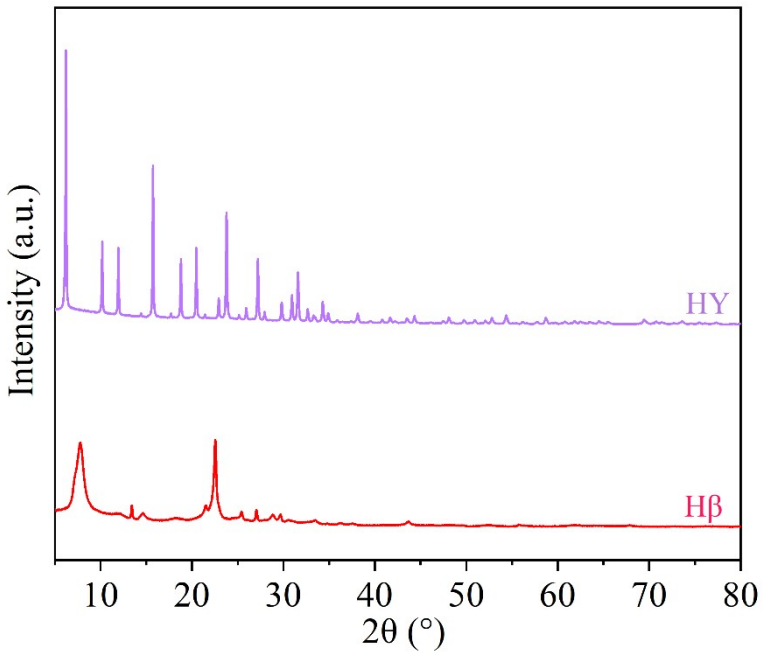

Figure S3 XRD patterns of HY and Hβ zeolites.

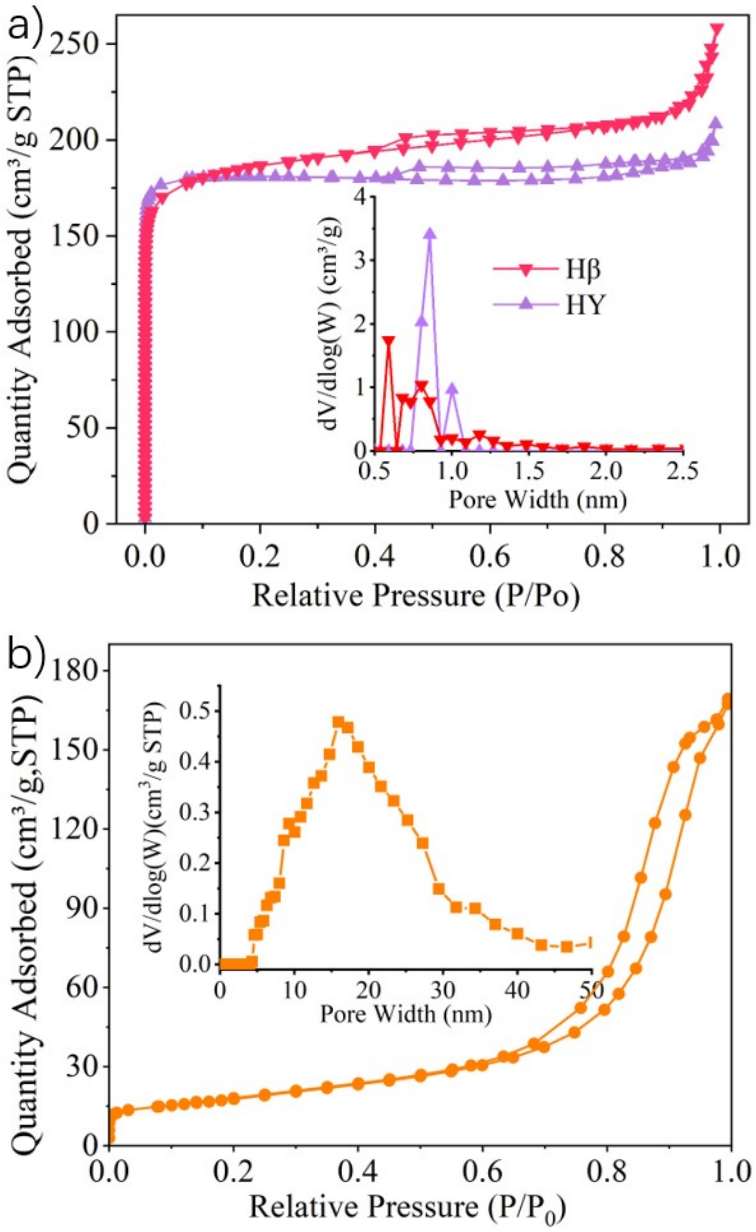

Figure S4 N_2 adsorption isotherms and pore size distributions of a) HY and Hβ zeolites, and b) CeO_2.

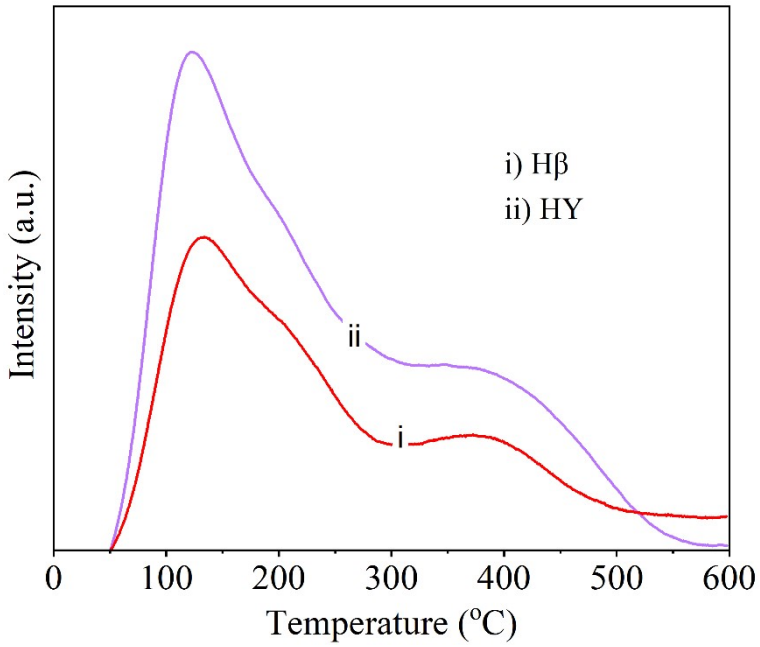

Figure S5 NH_3-TPD profiles of HY and Hβ.

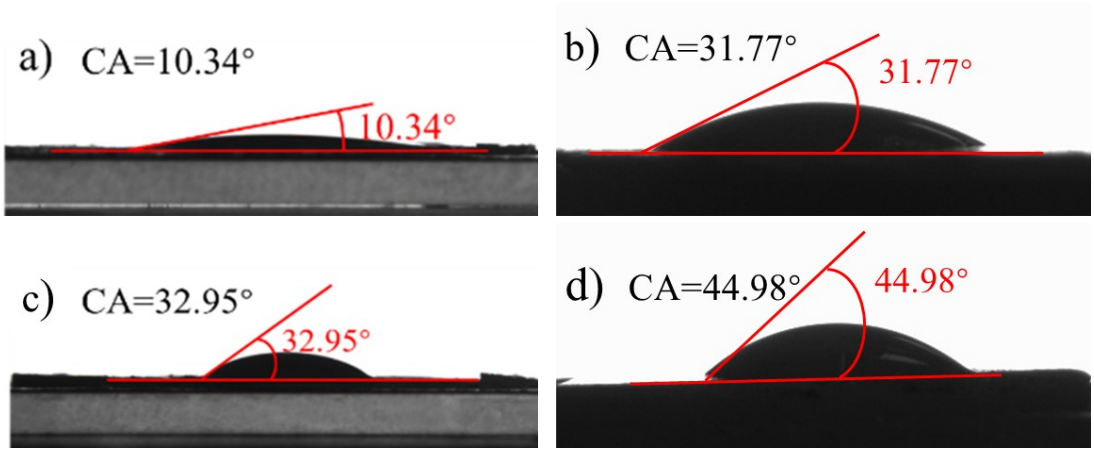

Figure S6 Contact angle of a) HMOR, b) Hβ, c) HZSM-5 and d) HY.

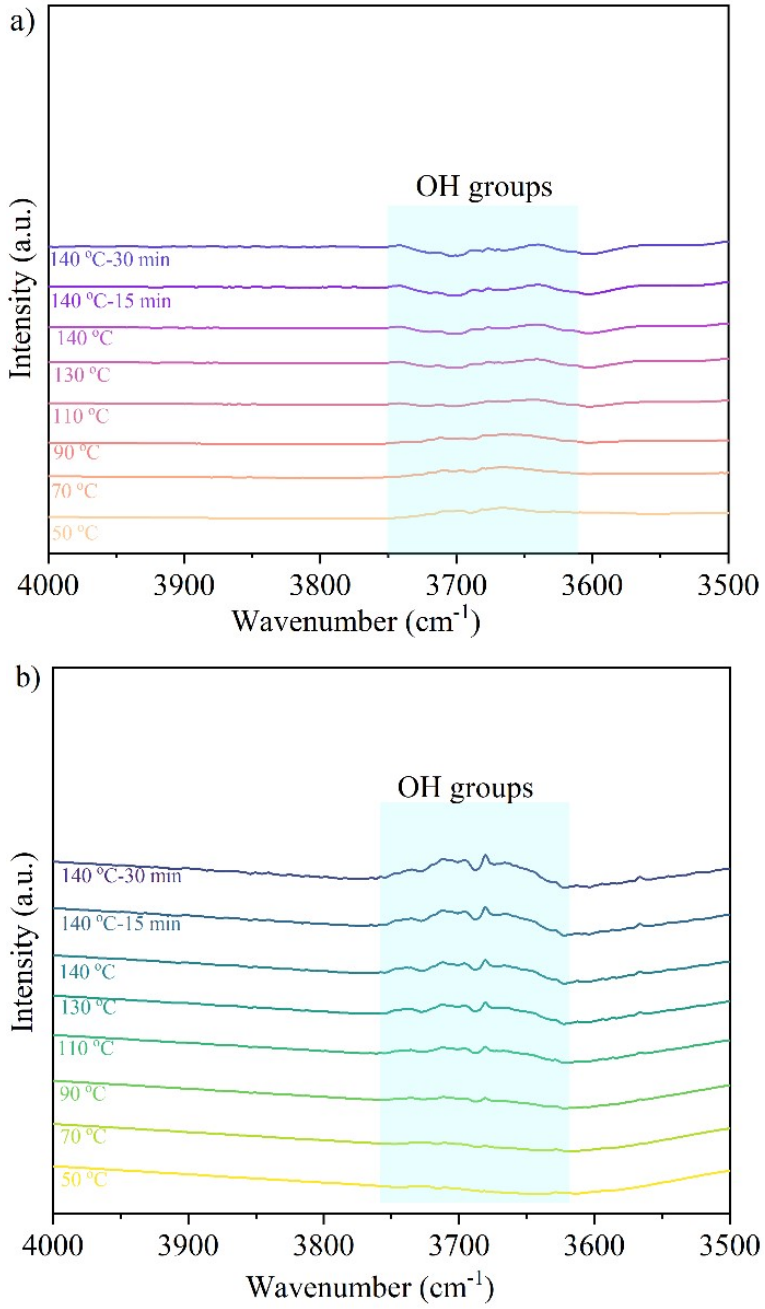

Figure S7 In-situ IR spectra in the region of 3620 – 3700 cm^{-1} wavenumber for a) CeO_2-HMOR and b) CeO_2 after adsorption of the mixture of methanol, TMM and CO_2.

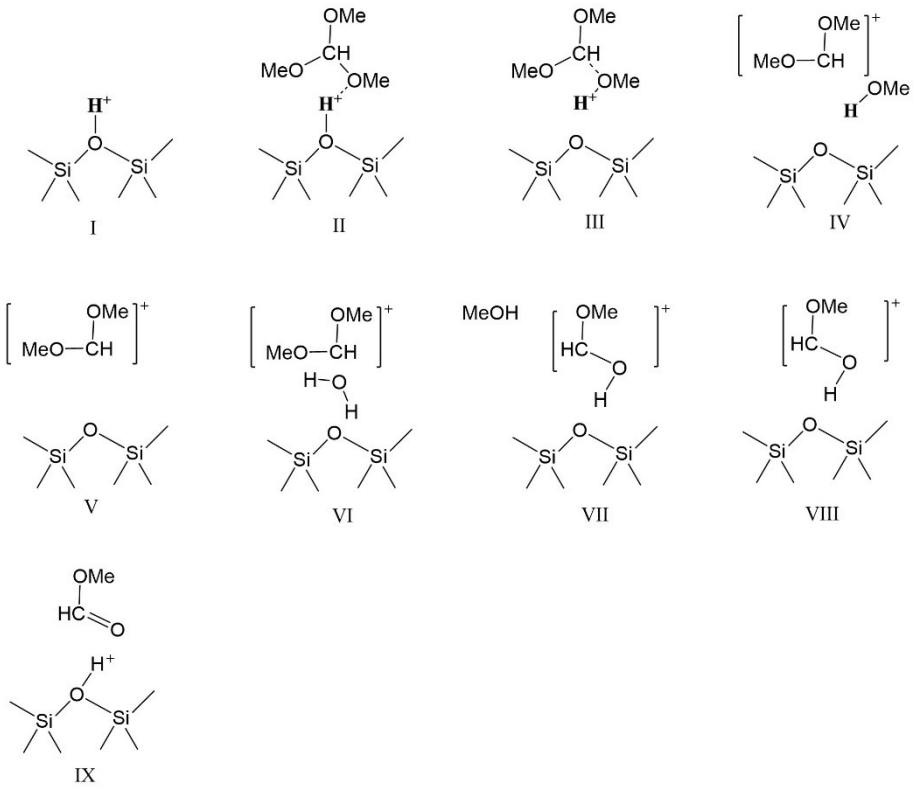

Figure S8 The detailed structure of intermediates in TMM hydrolysis reaction.

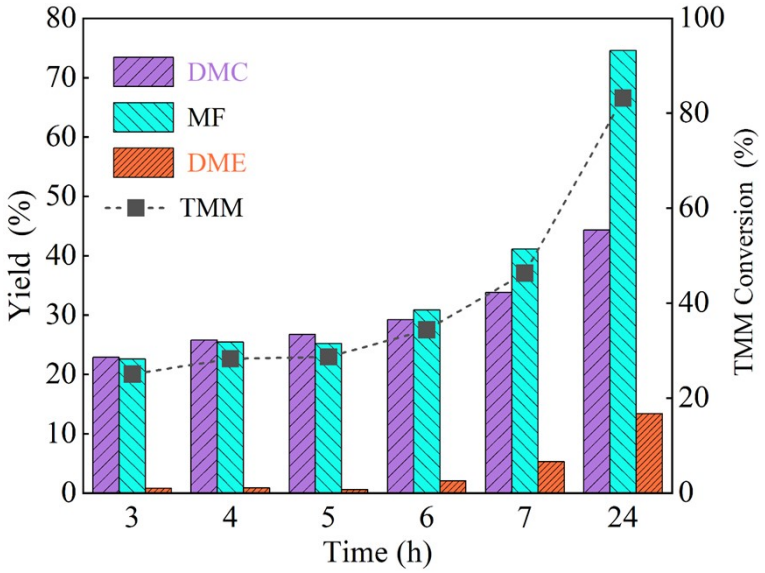

Figure S9 Effect of reaction time on catalytic performance of CeO_2-HMOR bicomponent catalyst under identical reaction conditions: n_{MeOH}=372 mmol, n_{TMM}=186 mmol, m_{CeO2} = 0.1 g, $m_{zeolites}$ = 0.4 g, P_{CO2} = 4.0 MPa, Tr = 140 °C.

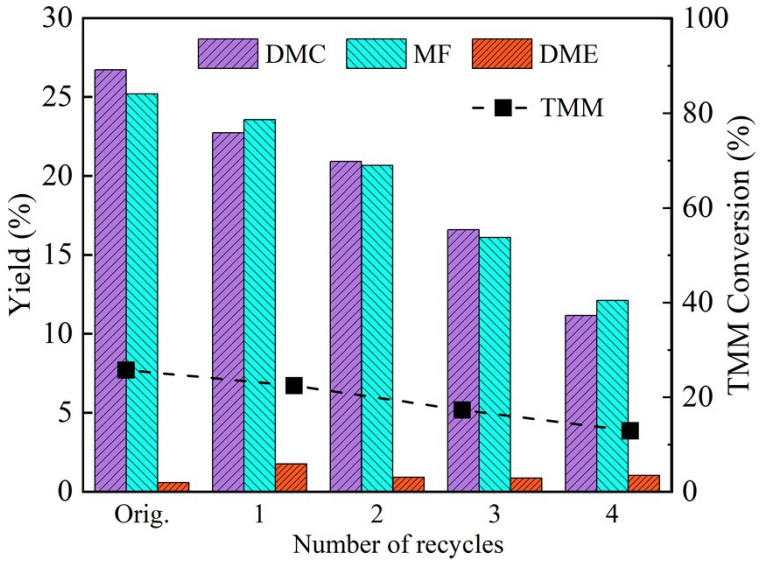

Figure S10 Recyclability tests of the CeO_2-HMOR bicomponent catalyst under identical reaction conditions. n_{MeOH}=372 mmol, n_{TMM}=186 mmol, m_{CeO2} = 0.1 g, m_{HMOR} = 0.4 g, P_{CO2} = 4.0 MPa, Tr = 140 °C, t=5 h.

Table S1. Catalytic performance for TMM hydrolysis reaction over zeolites catalysts.

Zeolites	TMM Conversion (%)	Yield (%)		
		DMC	MF	DME
HMOR	100	0	78.0	1.4
Hβ	100	0	74.3	0.4
HZSM-5	100	0	85.9	3.2
HY	100	0	77.3	0.3

Reaction conditions: n_{TMM} =186 mmol, n_{H2O} =186 mmol, m_{zeolites} = 0.2 g, P_{CO2} = 3.0 MPa, T_r = 140 °C, t_r = 5 h

Table S2. Characterization data of the CeO_2, HMOR, HZSM-5, Hβ and HY.

Catalyst	S_{BET}[a] ($m^2\ g^{-1}$)	$S_{t\text{-}plot}$[b] ($m^2\ g^{-1}$)	V_{total}[c] ($mL\ g^{-1}$)	$V_{t\text{-}plot}$[d] ($mL\ g^{-1}$)	SiO_2/Al_2O_3[e]
CeO_2	63	9	0.25	0	/
HMOR	401	381	0.24	0.19	25
HZSM-5	303	244	0.16	0.12	27
Hβ	602	465	0.40	0.23	27
HY	568	557	0.32	0.28	5

[a]BET surface area, [b]*t*-plot surface area, [c]Total volume of pores at P/Po=0.99, [d]*t*-plot micropore volume,[e]molar ratio of SiO_2/Al_2O_3.

Table S3. Acid amounts determined by NH_3-TPD of the CeO_2, HMOR, HZSM-5, Hβ and HY zeolites.

Catalyst	Weak acid (mmol g^{-1})	Moderate acid (mmol g^{-1})	Strong acid (mmol g^{-1})	Total acid (mmol g^{-1})
CeO_2	0.18	0.19	0.15	0.52
HMOR	0.98	0.66	0.58	2.23
HZSM-5	0.84	0.86	0.55	2.25
HY	1.51	1.27	0.42	3.20
Hβ	0.94	0.79	0.32	2.05

Table S4. Amounts of Lewis acid and Brønsted acid determined by *py*-IR of the HMOR and HZSM-5 zeolites.

Catalyst	Temperature (°C)	Amounts (μmol g^{-1})		
		Lewis acid	Brønsted acid	Total acid
HMOR	150	45.9	183.3	229.2
	350	33.6	150.6	184.2
HZSM-5	150	103.1	218.2	321.3
	350	27.9	188.1	216.0

Table S5. Effect of mole ratio of MeOH/TMM on catalytic performance over CeO_2-HMOR catalysts.

Mole ratio of MeOH/TMM	TMM Conversion (%)	Yield based on MeOH (%)		Yield based on TMM (%)			DMC formation rate (mmol g_{CeO2}^{-1})
		DMC	DME	DMC	MF	DME	
1	28.7	41.2	4.8	20.6	25.2	2.4	381.5
2	27.0	21.4	2.3	21.4	24.7	2.3	395.8
4	22.2	9.2	0.8	18.4	20.3	1.5	342.2

Reaction conditions: m_{CeO2} = 0.1 g, $m_{zeolites}$ = 0.4 g, P_{CO2} = 3.0 MPa, T_r = 140 °C, t_r = 5 h

Table S6. Catalytic performance for CO_2 and H_2O coupled with TMM over the CeO_2-HMOR catalyst

Catalyst	Reactant (mmol)		TMM Conversion (%)	Yield based on TMM (%)		
	TMM	H_2O		DMC	MF	DME
CeO_2-HMOR	186	186	99.9	0.1	77.3	Trace
CeO_2-HMOR	186	141	87.7	9.6	64.5	0.3
CeO_2-HMOR	186	56	62.1	24.0	52.3	2.7
CeO_2-HMOR	186	0	58.2	1.1	72.7	5.8

Reaction conditions: m_{CeO2} = 0.1 g, m_{HMOR} = 0.4 g, P_{CO2} = 4.0 MPa, *Tr* = 140 °C, *tr* = 5 h

Table S7. DMC formation rate over CeO_2-HMOR compared to the excellent catalysts reported in the literature in DMC synthesis from CO_2 and methanol.

Sample	MeOH [mL]	TMM [mL]	T_r [°C]	P_{CO2} [Mpa]	t_r [h]	DMC formantion rate		Reference
						[mmol g_{CeO2}^{-1}]	[mmol g_{CeO2}^{-1} h^{-1}]	
CeO_2-HMOR	15.1	20.3	140	4	5	465.1	93.0	This work
CeO_2-HMOR	15.1	20.3	140	4	24	821.2	34.2	This work
ZrO_2-13X	1	1.3	130	2	48	61.0	1.3	[10]
CeO_2	60	78	130	2	48	199.5	4.2	[11]
Ce_3-NPs/Co_7- NSs	3.5	5.5	120	5	12	34.8	2.9	[12]
[EMIM]Br/$Ce_{0.5}Zr_{0.5}O_2$	5	4	100	12	48	13.0	0.3	[13]
HPW@MOF-808	8	10	140	12	4	9.4	2.4	[14]
MOF-808-X	8	10	140	12	4	6.4	1.6	[15]

Table S8. Acid and base amountsof the fresh and spent CeO_2-HMOR bicomponent catalyst.

Catalyst	Total acid [a] (mmol/g)	Total base [b] (mmol/g)
Fresh CeO_2-HMOR	1.47	0.29
Spent CeO_2-HMOR	0.74	0.20

[a] determined by NH_3-TPD, [b] determined by CO_2-TPD,

References

[1] Li, L.;, Liu, W. X.; Chen, R. H.; et al.; Atom-economical synthesis of dimethyl carbonate from CO_2: Engineering reactive frustrated Lewis pairs on ceria with vacancy clusters. *Angewandte Chemie International Edition* **2022**, *61*(51), e202214490.

[2] VandeVondele, J.; Krack, M.; Mohamed, F.; et al.; Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* **2005**, *167*(2), 103-128.

[3] Perdew, J.P.; Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986**, *33*, 8822-8824.

[4] Perdew, J.P.; Burke, K.; Ernzerhof, M.; Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

[5] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H.; A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* **2010**, *132*, 154104.

[6] Lippert, G.; Michele, P.; Jurg, H.; A hybrid Gaussian and plane wave density functional scheme. *Mol. Phys.* **1997**, *92*, 477-488.

[7] VandeVondele, J.; Hutter,J.; Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J Chem Phys* **2007**, *127*, 114105.

[8] Goedecker, S.; Teter,M.; Hutter, J.; Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703.

[9] Henkelman,G.; Jónsson,H.; Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J Chem Phys* 2000, *113*, 9978-9985.

[10] Shi, D.; Heyte, S.; Capron, M.; and Paul, S.; Direct synthesis of dimethyl carbonate from methanol and CO_2 over ZrO_2 catalysts combined with a dehydrating agent and a cocatalyst. *Catalysts* **2024**, *14*, 657.

[11] Shi, D.; Heyte, S.; Capron, M.; and Paul, S.; Ceria-catalysed production of dimethyl carbonate from methanol and CO_2: effect of using a dehydrating agent combined with a solid cocatalyst. *Molecules* **2024**, *29*, 5663.

[12] He, Z.-H.; Sun Y. -C.; Wei, Y.-Y.; et al.; Synthesis of dimethyl carbonate from CO_2 and methanol over CeO_2 nanoparticles/Co_3O_4 nanosheets. *Fuel* **2022**, *325*, 124945.

[13] Zhang, Z.-F.; Liu, Z.-W.; Lu, J.; and Liu Z.-T.; Synthesis of dimethyl carbonate from carbon dioxide and methanol over $Ce_xZr_{1-x}O_2$ and [EMIM]Br/$Ce_{0.5}Zr_{0.5}O_2$. *Ind. Eng. Chem. Res.* **2011**, *50*, 1981–1988.

[14] Xuan, K.; Chen, S.; Pu Y.; et al.; Encapsulating phosphotungstic acid within metal-organic framework for direct synthesis of dimethyl carbonate from CO_2 and methanol. *Journal of CO_2 Utilization* **2022**, *59*, 101960.

[15] Xuan, K.; Pu, Y.; Li, F.; et al.; Metal-organic frameworks MOF-808-X as highly efficient catalysts for direct synthesis of dimethyl carbonate from CO_2 and methanol. *Chinese Journal of Catalysis* **2019**, *40*, 553–566.