Electronic Supplementary Material

Enhancing the aromatic selectivity of cyclohexane aromatization by CO_2 coupling

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1. Materials

Cyclohexane (CYH, AR, Sinopharm Chemical Reagent Co., Ltd.), hexachloroethane(C_2Cl_6, AR, Shanghai Aladdin Biochemical Technology Co., Ltd.), dichloromethane(CH_2Cl_2, AR, Shanghai Aladdin Biochemical Technology Co., Ltd.), hydrofluoric acid (HF, AR, Tianjin Damao Chemical Reagent Co., Ltd), Carbon dioxide (89.9%, containing 10.1% N_2 as an internal standard) was purchased from Dalian Special Gases Co., Ltd., deionized (DI) water and quartz sand (60 mesh)were purchased from Dalian Bono Biochemical Reagent Factory.

2. Catalyst characterization

2.1 X-ray fluorescence analysis (XRF)

The contents of Si and Al in the HZSM-5 zeolite were determined by an X-ray fluorescence spectrometer (Magix-601, Philips Company). Test conditions: the diameter of the test window is 32 mm, the working voltage is 40 kV, and the working current is 40 mA.

2.2 X-ray powder diffraction (XRD)

The phase identification of HZSM-5 zeolite samples was collected by the X'PertPRO X-ray powder diffractometer of Panaco, the Netherlands. Test conditions: Cu target, Kα light source ($\lambda = 1.5418$), working voltage 40 kV, working current 40 mA, scanning range 5-60^{o}, scanning speed 5^{o}/min.

2.3 Ammonia temperature-programmed desorption (NH_3-TPD)

The ammonia temperature programmed desorption (NH_3-TPD) experiment of the HZSM-5 zeolite was carried out on a Micromeritics AutoChem2920 instrument. First, 0.20 g of HZSM-5 zeolite sample was put into a quartz tube, and pretreated in He atmosphere at 500 ^{o}C for 30 minutes. Then, the sample was cooled down to 100 ^{o}C for saturation adsorption in NH_3. The physically adsorbed ammonia of the sample was removed by He. Finally, the sample was treated for ammonia desorption at 100~600 ^{o}C in He atmosphere at a heating rate of 10 ^{o}C/min. The signal of ammonia desorption was detected by the TCD detector.

2.4 Solid-state magic-angle spinning nuclear magnetic resonance spectra of ^{27}Al (^{27}Al MAS NMR)

Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of ^{27}Al were performed on a Bruker AVANCE III NMR spectrometer at a magnetic field of 11.7 T. The ^{27}Al MAS NMR spectra were recorded at a resonance frequency of 130.3 MHz, spinning rate of 12 kHz, and flip angle of 15^{o}. The pulse width was 0.4 μs, which corresponded to $\pi/12$, and the recycle delay was 2 s. Aqueous solutions of $Al(NO_3)_3$ (0 ppm) was used as standard references for chemical shifts of ^{27}Al.

2.5 Pyridine-adsorbed FTIR (py-IR)

Pyridine-adsorbed FTIR (py-IR) is performed using a Nicolet IS50 spectrometer equipped with an MCT detector. Firstly, 5 mg sample was tableted into a small round (i.d. = ~ 5 mm) and put into a heating pool at 300 ^{o}C in vacuum for 1 h. Then, the sample was cooled down to room temperature and saturated with pyridine. Afterwards, the sample was heated to desired temperature (i.e., 100, 200, and 300 ^{o}C) for 30 min and then measured at these temperatures. All the spectra were tested at 32 scans and a resolution of 4 cm^{-1}.

3. Catalytic tests

3.1 Reaction

Catalytic reaction evaluation process: 0.5 g of the HZSM-5 zeolite particles were added into a stainless-steel tube with an inner diameter of 10 mm. The dead volume in the tube is filled with 40-60 mesh quartz sand. The HZSM-5 zeolite was activated in the Ar atmosphere at 550 ^{o}C for 1 h and then cooled down to the reaction temperature. The cyclohexane is fed by a high-pressure liquid phase pump. CO_2 (containing N_2 as an internal standard) is fed through a gas flowmeter. The reaction products were analyzed by an online chromatography (Agilent 7890B) equipped with two detectors, an HP-PONA capillary column connected to an FID detector, and a TDX-01 packed column connected to a TCD detector.

Using N_2 as the internal standard, the conversion rate of CO_2 was calculated through equation 1. Where $n_{CO2\ inlet}$, and $n_{CO2\ outlet}$ respectively represent the amount of imported and exported CO_2 material.

$$X_{CO2}: \frac{n_{CO_2\ inlet} - n_{CO_2\ outlet}}{n_{CO_2\ inlet}} \times 100\% \qquad (1)$$

According to the conservation of the number of carbon atoms, the conversion of cyclohexane and the selectivity of hydrocarbon products can be calculated (equations 2 and 3). CYH_{inlet} and CYH_{outlet} respectively represent the carbon mole fraction of imported cyclohexane and exported cyclohexane, $C_nH_{m\ \mathrm{outlet}}$ represents the carbon mole fraction of export product C_nH_m, and $\Sigma_1^n C_nH_{m\ outlet}$ represents the total carbon mole number of all hydrocarbon products.

$$X_{CYH}: \frac{CYH_{inlet} - CYH_{outlet}}{CYH_{inlet}} \times 100\% \qquad (2)$$

$$S_{CnHm}: \frac{C_nH_{m\ outlet}}{\Sigma_1^n C_nH_{m\ outlet}} \times 100\% \qquad (3)$$

3.2 Analysis of retained species

Organic residues on the HZSM-5 zeolite were detected and analyzed. 0.05g of the HZSM-5 zeolite after the reaction was put into a 5 mL centrifuge tube, and then 1 mL 40% HF solution was added for dissolution. After all HZSM-5 zeolite particles were dissolved, add 1 mL dichloromethane (containing 10 ppm hexachloroethane as the internal standard) for extraction. The extracted organic matter was analyzed by an Agilent 7890A/5975C GC/MSD spectrometer equipped with an HP-5 chromatographic column (60 m×250 μm×0.25 μm), and the identification of the organic was conducted using the NIST database.

4. *In situ* transmission FTIR spectroscopy

In situ transmission FTIR experiment was carried out on the infrared spectrometer (VERTEX70v). Firstly, 20 mg of HZSM-5 zeolite powder was pressed on a 769YP-15A manual powder press with a pressure of 10 MPa. The catalyst sheet was loaded into the *in situ* cell, and then the sample was treated at 500 ^{o}C in a 20 ml/min Air atmosphere for 0.5 h. Next, the sample was cooled down to the reaction temperature in the Ar atmosphere and then exposed to the flow of 12 mL/min CO_2 and cyclohexane steam (saturated at 25 °C) for the reaction test. All the spectra were tested at 64 scans and a resolution of 4 cm^{-1}. The infrared difference spectrum was obtained by subtracting the infrared spectrum of the zeolite framework at the corresponding temperature from the obtained spectrum.

5. Isotope tracing experiments

A certain amount of HZSM-5 zeolite was put into a stainless-steel reactor, then activated at 500 °C for 0.5 h under the atmosphere of Ar. Then $^{13}CO_2$ was introduced into a stainless-steel saturation tube filled with cyclohexane, which carried cyclohexane into the catalyst bed, and then analyzed by online chromatography-mass spectrometry analysis through a 200 °C constant temperature pipeline. ^{13}C content distribution was calculated according to the method reported in the literature [1]. It was necessary to consider the 1.1% natural abundance of ^{13}C in ^{12}C standard substance in comparing the ion fragment of isotope-labeled substance with the mass spectrum fragment of ^{12}C standard substance to calculate the ^{13}C content distribution.

6. Supplemental Figures

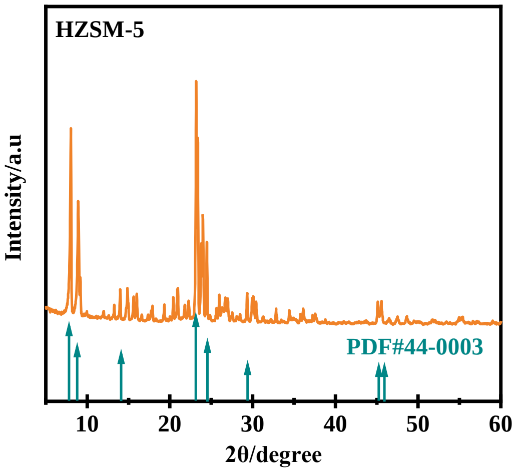

Fig. S1 XRD pattern of HZSM-5.

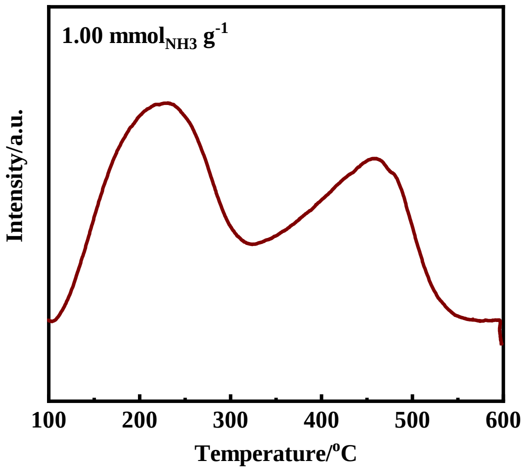

Fig. S2 NH$_3$-TPD profile of HZSM-5.

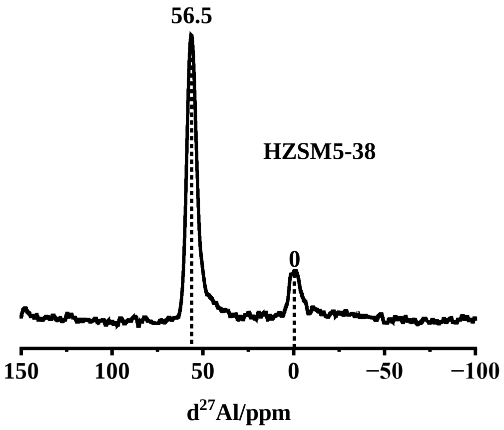

Fig. S3 The ^{27}Al MAS NMR spectrum of HZSM-5.

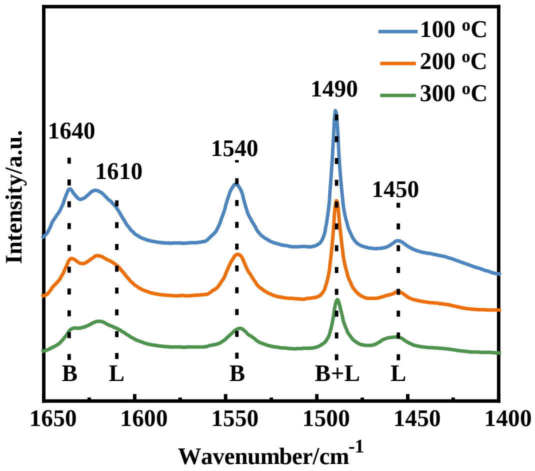

Fig. S4 FTIR spectra of HZSM-5 after pyridine desorption at different temperatures (100, 200, and 300 °C).

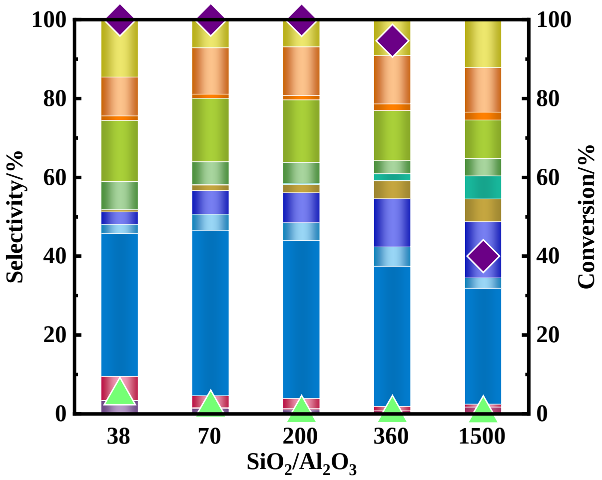

Fig. S5 The CO_2 conversion, cyclohexane conversion and product selectivity at the SiO_2/Al_2O_3 ratios of 38, 70, 200, 360 and 1,500.

Reaction conditions: P_{system} = 3.0 MPa, P_{CO2} = 2.7 MPa, T = 450 °C, WHSV = 1.7 h^{-1}, TOS = 1.0 h, $(CO_2 + N_2)$/cyclohexane = 13.

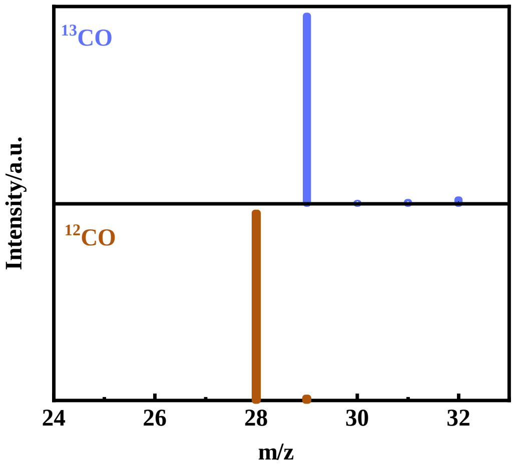

Fig. S6 The contrast of MS spectra of CO of the effluent products in $^{12}CO_2$ (bottom) and $^{13}CO_2$ (top) atmosphere for the coupling reaction process.

7. Supplemental Tables

Table S1 The results of catalytic performance under different reaction conditions. [a)]

			Selectivity/%	
T/°C	P_{CO2}/MPa	WHSV/h^{-1}	Alkanes [c)]	Aromatics [d)]
450	0.09 [b)]	1.7	61.1	38.9
	2.7		51.8	48.2
	0.0		56.8	43.2
	1.0		56.3	43.7
	2.0		54.5	45.5
300	2.7	1.7	55.4	44.6
350			61.0	39.0
400			61.2	38.8
450	2.7	0.5	53.8	46.2
		5.0	63.1	36.9

a) All the reactions were performed by feeding the mixture of cycloalkane and CO_2 with a total flow rate of 50 mL min^{-1} with Ar diluent over 0.5 g of HZSM-5 zeolite (SiO_2/Al_2O_3 = 38, 40−60 mesh). b) This experimental condition was P_{system} = 0.101 MPa, and the other experiments were all P_{system} = 3.0 MPa. Results are obtained at 1 h time-on-stream. c) Alkanes Include CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, C_4H_{10}, C_5H_{12}, C_6H_{14}. d) Aromatics include C_6H_6, C_7H_8, C_8H_{10}-E(ethylbenzene), C_8H_{10}-D(dimethylbenzene), C_{9+}.

Table S2 Conversion and product selectivity from coupling reactions at different system pressures.

	P_{system} = 0.101 MPa	P_{system} = 3.0 MPa
raw materials	Conversion/%	
CYH	75.8	99.9
CO_2	0.85	4.67
Products	Selectivity/%	
CH_4	0.247	3.36
C_2H_4	6.82	0.12
C_2H_6	0.63	6.06
C_3H_8	35.1	36.3
i-C_4H_{10}	3.18	2.28
C_4H_{10}	10.8	3.14
C_5H_{12}	2.79	0.562
C_6H_{14}	1.45	0.094
C_6H_6	4.32	7.02
C_7H_8	14.9	15.6
C_8H_{10}-E (ethylbenzene)	1.02	1.04
C_8H_{10}-D (dimethylbenzene)	13.9	9.91
C_{9+}	4.82	14.6

Table S3 Conversion and product selectivity from coupling reactions at different reaction temperatures.

	T = 300 °C	*T* = 350 °C	*T* = 400 °C	*T* = 450 °C
raw materials	Conversion/%			
CYH	19.4	88.2	99.9	99.9
CO_2	0.57	1.11	2.78	4.67
Products	Selectivity/%			
CH_4	0.012	0.068	0.515	3.36
C_2H_4	0.128	0.070	0.066	0.12
C_2H_6	0.677	0.675	1.69	6.06
C_3H_8	15.1	36.5	44.3	36.3
i-C_4H_{10}	1.74	4.81	4.85	2.28
C_4H_{10}	7.41	11.9	7.46	3.14
C_5H_{12}	4.41	4.19	2.02	0.562
C_6H_{14}	25.9	2.8	0.37	0.094
C_6H_6	1.01	2.33	4.17	7.02
C_7H_8	6.51	11.4	14.1	15.6
C_8H_{10}-E	2.18	1.91	1.04	1.04
C_8H_{10}-D	8.7	14.5	13	9.91
C_{9+}	26.2	8.91	6.51	14.6

Table S4 Conversion and product selectivity from coupling reactions at the different CO_2 pressures.

	P_{CO2} = 0 MPa	P_{CO2} = 1 MPa	P_{CO2} = 2.0 MPa	P_{CO2} = 2.7 MPa
raw materials	Conversion/%			
CYH	99.9	99.9	99.9	99.9
CO_2	–	1.67	1.68	4.67
Products	Selectivity/%			
CH_4	3.9	3.48	3.33	3.36
C_2H_4	0.165	0.172	0.111	0.12
C_2H_6	6.83	6.32	6.1	6.06
C_3H_8	39	39.5	38.3	36.3
i-C_4H_{10}	2.59	2.58	2.52	2.28
C_4H_{10}	3.54	3.52	3.43	3.14
C_5H_{12}	0.662	0.639	0.634	0.562
C_6H_{14}	0.113	0.105	0.114	0.094
C_6H_6	7.82	7.59	7.05	7.02
C_7H_8	16.9	16.6	16	15.6
C_8H_{10}-E	1.13	1.07	1.1	1.04
C_8H_{10}-D	10.7	10.4	10.4	9.91
C_{9+}	6.62	8.04	10.9	14.6

Table S5 Conversion and product selectivity from coupling reactions at different WHSV of cyclohexane.

	WHSV = 0.5 h^{-1}	WHSV = 1.7 h^{-1}	WHSV = 5.0 h^{-1}
raw materials		Conversion/%	
CYH	99.9	99.9	96.4
CO_2	2.49	4.67	0.03
Products		Selectivity/%	
CH_4	6.79	3.36	1.19
C_2H_4	0.284	0.12	0.248
C_2H_6	8.45	6.06	3.15
C_3H_8	35.4	36.3	41.7
i-C_4H_{10}	1.05	2.28	4.48
C_4H_{10}	1.54	3.14	8.67
C_5H_{12}	0.223	0.562	2.74
C_6H_{14}	0.023	0.094	0.88
C_6H_6	7.64	7.02	3.60
C_7H_8	14.9	15.6	11.2
C_8H_{10}-E	0.817	1.04	1.09
C_8H_{10}-D	8.75	9.91	10.7
C_{9+}	14.1	14.6	10.3

Table S6 Conversion and product selectivity from coupling reactions at different SiO_2/Al_2O_3 ratios of HZSM-5

	SiO_2/Al_2O_3 = 38	SiO_2/Al_2O_3 = 70	SiO_2/Al_2O_3 = 200	SiO_2/Al_2O_3 = 360	SiO_2/Al_2O_3 = 1500
raw materials	Conversion/%				
CYH	99.99	99.97	99.92	94.65	40.19
CO_2	4.64	1.03	1.14	1.11	0.44
Products	Selectivity/%				
CH_4	3.36	1.34	1.01	0.263	0.159
C_2H_4	0.120	0.243	0.312	0.529	1.60
C_2H_6	6.06	3.09	2.56	1.17	0.751
C_3H_8	36.3	41.9	40.1	35.5	29.4
i-C_4H_{10}	2.28	4.13	4.67	4.89	2.64
C_4H_{10}	3.14	5.96	7.56	12.3	14.2
C_5H_{12}	0.562	1.35	1.98	4.41	5.79
C_6H_{14}	0.0937	0.220	0.394	1.77	5.87
C_6H_6	7.02	5.71	5.25	3.4	4.38
C_7H_8	15.6	16.1	15.8	12.6	9.76
C_8H_{10}-E	1.04	1.01	1.13	1.69	2.00
C_8H_{10}-D	9.91	11.8	12.3	12.2	11.3
C_{9+}	14.6	7.10	6.92	9.17	12.2

References

1. Price G L, Iglesia E. Matrix method for correction of mass spectra in deuterium-exchange applications. Industrial & Engineering Chemistry Research, 1989, 28(6):839-844