

Supporting information for

Highly selective conversion of CO₂ to *para*-xylene over tandem catalysts

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Catalyst preparation

The 20% ZnZrO catalyst was prepared by the co-precipitation method. 298.2 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1720.0 g $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and 8 L deionized water were added to the reaction kettle, and the temperature was increased to 70°C while stirring. The prepared solution containing 865.8 g $(\text{NH}_4)_2\text{CO}_3$ and 3 L deionized water was added by a peristaltic pump at a rate of 15-20 mL/min to the Zn, Zr nitrate aqueous solution with stirring during the process. After the addition of $(\text{NH}_4)_2\text{CO}_3$, the mixed solution continued to be aged at 70°C with constant stirring for 4 h. The sample was cooled to room temperature and then filtered and washed thoroughly with deionized water. The washed sample was dried at 110°C and then calcinated at 500°C in static air for 4h, with a calcination temperature increase rate of 5°C/min.

ZSM-5 use a commercial catalyst with a Si/Al ratio of 27. nT-ZSM-5 was prepared by silylation reaction. Raw zeolite, tetraethyl orthosilicate (TEOS), and hexane were mixed in the ratio of 1 g: 2.2 mL: 10 mL, and then the mixture was stirred at room temperature for 4 h. After stirring, the samples were filtered without washing. The filtered samples were dried at 110°C and then calcinated at 500°C in static air for 4h, with a calcination temperature increase rate of 5°C/min. Mg-modified 3T-ZSM-5 was prepared using the impregnation method. 0.053, 0.105, and 0.211 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed with 2 mL of deionized water and 1 g of 3T-ZSM-5 uniformly by grinding and ultrasonication, respectively. The sample was then dried at 110°C and then calcinated at 500°C in static air for 4h, with a calcination temperature increase rate of 5°C/min. The samples were 0.5 wt% Mg-3T-ZSM-5, 1 wt% Mg-3T-ZSM-5 and 2 wt% Mg-3T-ZSM-5, respectively.

The modified zeolites in the experiment to investigate the effect of modified elements on the catalytic performance of zeolites were prepared by impregnation on zeolites with a Si/Al ratio of 40. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_3PO_4 (85%), or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in an appropriate amount of deionized water and then ZSM-5 was added. The sample was stirred at 80°C for 3 h, dried at 110°C, warmed at 10°C/min, and calcinated at 550°C for 4 h. The loading of Zn, Mg, P or Co were 1 , 3 and 5 wt%, respectively.

Catalyst evaluation

The CO₂ hydrogenation to aromatics reaction was carried out in a tubular fixed bed continuous flow reactor and the catalyst activity was tested by gas chromatography attached to the fixed bed. Before activity testing, all catalysts were sieved into 40-80 mesh particles by grinding, mixing, compacting, and crushing. The reactions were carried out at 1.0~3.0 MPa, 300~360°C, V(H₂)/V(CO₂)/V(Ar) = 72/24/4, m(ZZO): m(ZSM-5) = 1:1~3:1, and GHSV = 2400 ~ 7200 mL g⁻¹ h⁻¹. When there is no special indication, the mass ratio of ZZO to ZSM-5 is 2:1. The reacted gases were held at 180°C and analyzed directly in a gas chromatograph (Agilent GC-7890B). CO₂, CO, and Ar were separated by a TDX-01 packed column and analyzed by a TCD detector. Hydrocarbon species were separated by a PONA capillary column and analyzed by an FID detector.

The activity of the *m*-xylene isomerization reaction was tested using the same reactor and gas chromatography. The reaction was conducted at atmospheric pressure and a temperature of 320°C. *m*-xylene was bubbled in a bubbler cooled with an ice-water bath and carried into the reactor by Ar. The Ar carrier gas flow rate was set at 6000 mL g⁻¹ h⁻¹.

The activity of the *p*-xylene isomerization reaction was tested using the same reactor and gas chromatography. The reaction was carried out under the following conditions: pressure of 0.1~1.0 MPa, temperature of 320°C, and Ar or CO₂ and H₂ mixture as the carrier gas with a GHSV of 14400~24000 mL g⁻¹ h⁻¹. *p*-Xylene was bubbled at room temperature in a bubbler using Ar or CO₂ and H₂ mixture as the carrier gas and then carried into the reactor for the reaction.

The CO₂ conversion (denoted as X(CO₂)), the carbon-based selectivity of the hydrocarbon species (denoted as S(product)), the proportion of *p*-xylene in xylene (denoted as P(PX)), and the conversion of *m*-xylene and *p*-xylene (denoted as X(PX) and X(MX)) were calculated using the normalization method. The calculation equations are as follows.

$$X(\text{CO}_2) = \frac{f_{\text{CO}}A_{\text{CO}} + i \sum n f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}}{f_{\text{CO}_2}A_{\text{CO}_2} + f_{\text{CO}}A_{\text{CO}} + i \sum n f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}} \times 100\%$$

f : relative mole correction factor

A : peak area on chromatographic spectra

$$i = \frac{f_{\text{CH}_4\text{-TCD}} A_{\text{CH}_4\text{-TCD}}}{f_{\text{CH}_4\text{-FID}} A_{\text{CH}_4\text{-FID}}}$$

i : internal normalization conversion coefficient

$$S(\text{C}_n\text{H}_m) = \frac{n f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}}{\sum n f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}} \times 100\%$$

$$S(\text{CO}) = \frac{f_{\text{CO}} A_{\text{CO}}}{f_{\text{CO}} A_{\text{CO}} + i \sum n f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}} \times 100\%$$

$$P(\text{PX}) = \frac{f_{\text{p-xylene}} A_{\text{p-xylene}}}{f_{\text{p-xylene}} A_{\text{p-xylene}} + f_{\text{m-xylene}} A_{\text{m-xylene}} + f_{\text{o-xylene}} A_{\text{o-xylene}}} \times 100\%$$

$$X(\text{PX}) = \frac{\sum f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m} - f_{\text{p-xylene}} A_{\text{p-xylene}}}{\sum f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}} \times 100\%$$

$$X(\text{MX}) = \frac{\sum f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m} - f_{\text{m-xylene}} A_{\text{m-xylene}}}{\sum f_{\text{C}_n\text{H}_m} A_{\text{C}_n\text{H}_m}} \times 100\%$$

Catalyst characterization

The powder X-ray diffraction was performed to analyze the crystal structure of the samples on a Rigaku Smartlab diffractometer. Diffractometer with $\text{CuK}\alpha$ radiation source worked at 40kV and 200 mA at room temperature. The scan rate was $10^\circ/\text{min}$.

Scanning electron microscopy was used to characterize the morphology of the catalyst on a JSM-7800F microscope.

Ar adsorption was performed on Autosorb iQ (Quantachrome Instruments) at -186°C to measure the pore size distribution of the catalysts. The NL-DFT method was used to determine the pore volume.

The acid amount and strength of zeolites were tested by temperature-programmed desorption of ammonia (NH_3 -TPD) on a chemisorption analyzer (Micromeritics Autochem II 2920) coupled with a HIDEN mass spectrometer. Typically, 100 mg zeolite was pretreated at 450°C for 120 minutes with a heating rate of $10^\circ\text{C}/\text{min}$ and a pretreatment gas of helium gas flow rate of 30 mL/min. The catalyst was then cooled to 100°C and the

gas was switched to 10 V% NH₃/He at 30 mL/min to adsorb NH₃ for 30 min. After the NH₃ adsorption was completed, the gas was switched to He for 60 min at a flow rate of 30 mL/min to remove the physically adsorbed NH₃. After the desorption was completed, the zeolite was heated to 800 °C at a rate of 10 °C/min, and the signal was recorded by mass spectrometry.

The external surface acid amount of the zeolite was determined by 2,6-di-tert-butylpyridine (DTBPy) adsorbed Fourier transform infrared spectroscopy. IR was performed using a TENSOR27 spectrometer. The samples were pressed into a wafer and then processed at 450 °C (10 °C/min ramp-up) for 1 h at 10⁻² Pa. The samples were then cooled to 150 °C and allowed to adsorb DTBPy for 15 min. The samples were then processed under a high vacuum for 1 h to remove the physically adsorbed DTBPy and the samples were scanned for IR spectra.

The solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were measured on a Bruker AVANCE NEO 400 MHz equipped with a 4.0 mm probe. For ²⁹Si MAS NMR, the spinning rate is 8 kHz with a recycle delay of 5 s. For ¹H MAS NMR, the spinning rate is 14 kHz.

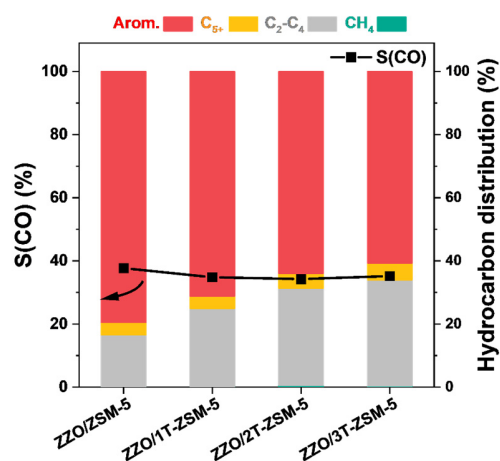


Figure S1. CO selectivity and hydrocarbon distribution of CO₂ hydrogenation on ZZO/nT-ZSM-5 corresponding to Figure 1a in the main text. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

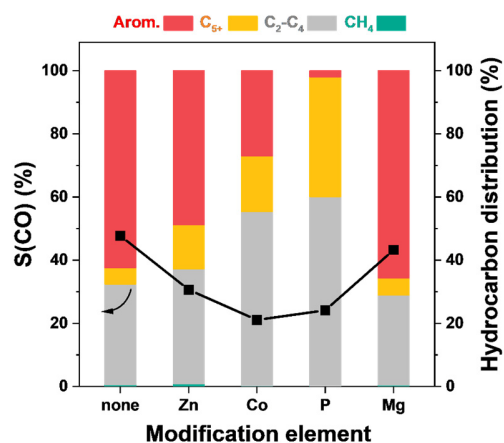


Figure S2. CO selectivity and hydrocarbon distribution of CO₂ hydrogenation on ZZO/Modified-ZSM-5 corresponding to Figure 1b in the main text. Reaction conditions: 320°C, 4.0 MPa, CO₂: H₂ of 1:3, GHSV of 7200 mL g⁻¹ h⁻¹. The contents of modified elements are 5 wt% Zn, 3 wt% Co, 5 wt% P and 3 wt% Mg, respectively.

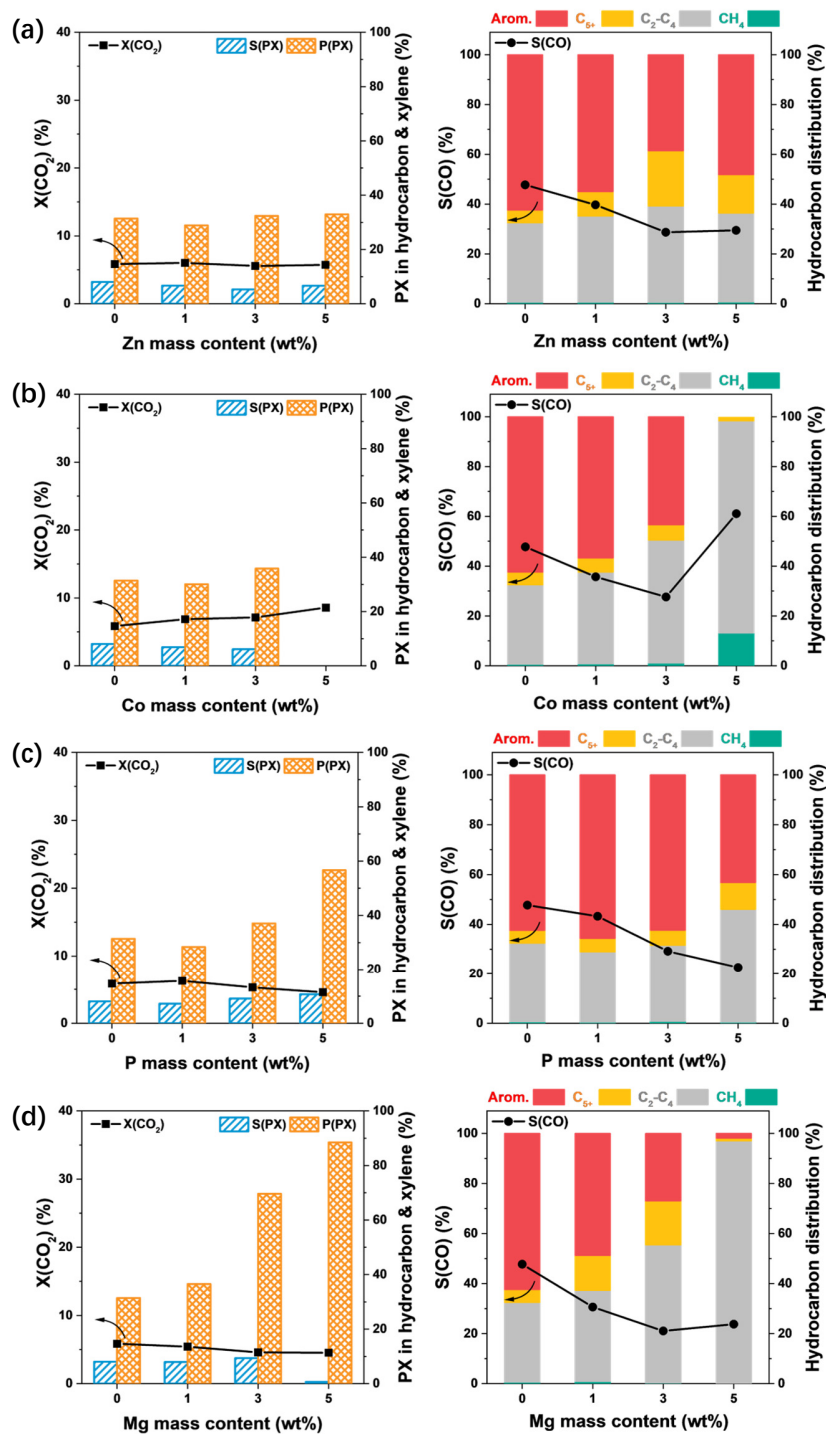


Figure S3. CO₂ conversion, PX selectivity, CO selectivity, and hydrocarbon distribution of CO₂ hydrogenation on ZZO/Modified-ZSM-5 with different element content, (a) Zn, (b) Co, (c) P and (d) Mg. Reaction conditions: 320°C, 4.0 MPa, CO₂: H₂ of 1:3, GHSV of 7200 mL g⁻¹ h⁻¹.

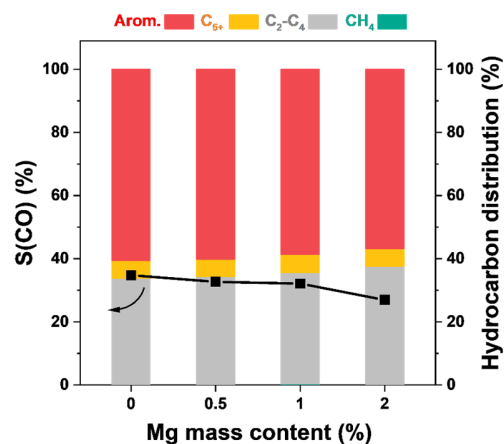


Figure S4. CO selectivity and hydrocarbon distribution of CO₂ hydrogenation on ZZO/x%Mg-nT-ZSM-5 corresponding to Figure 1c in the main text. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, 4800 mL g⁻¹ h⁻¹.

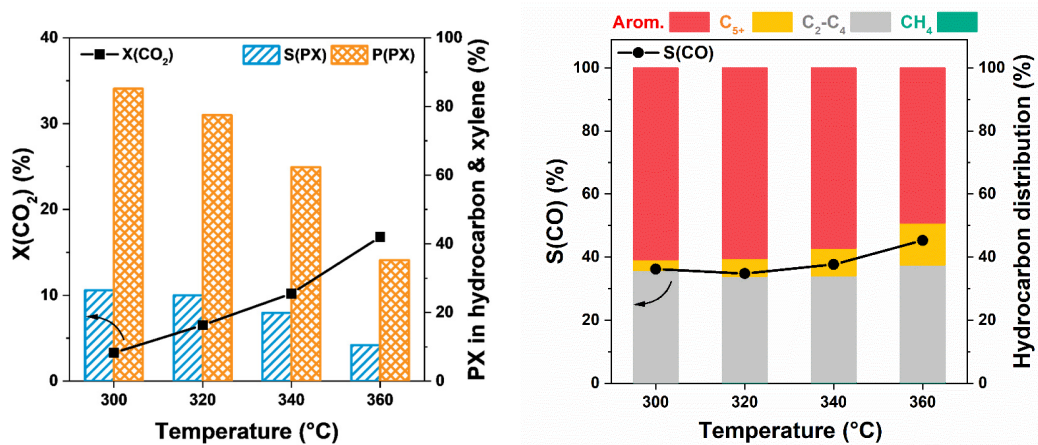


Figure S5. CO₂ conversion, PX selectivity, CO selectivity, and hydrocarbon distribution of CO₂ hydrogenation on ZZO/3T-ZSM-5 with different temperature. Reaction conditions: 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

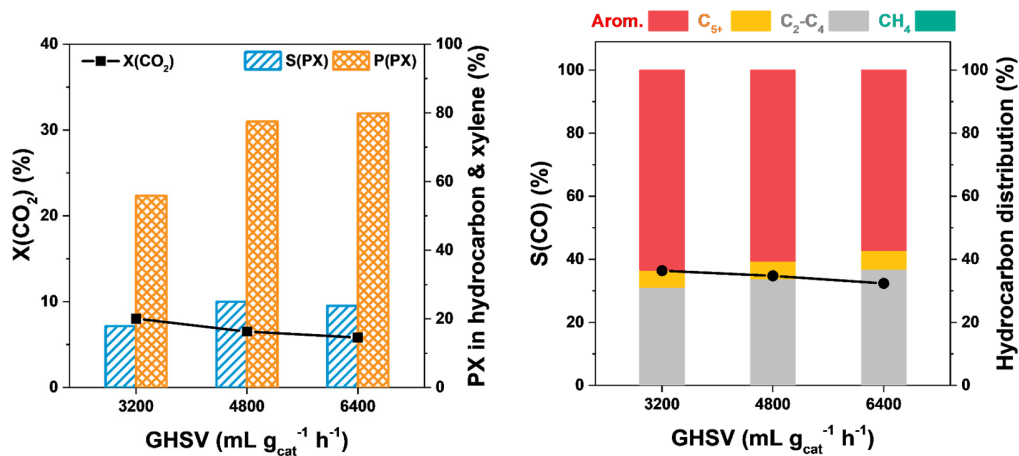


Figure S6. CO₂ conversion, PX selectivity, CO selectivity, and hydrocarbon distribution of CO₂ hydrogenation on ZZO/3T-ZSM-5 with different GHSV. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3.

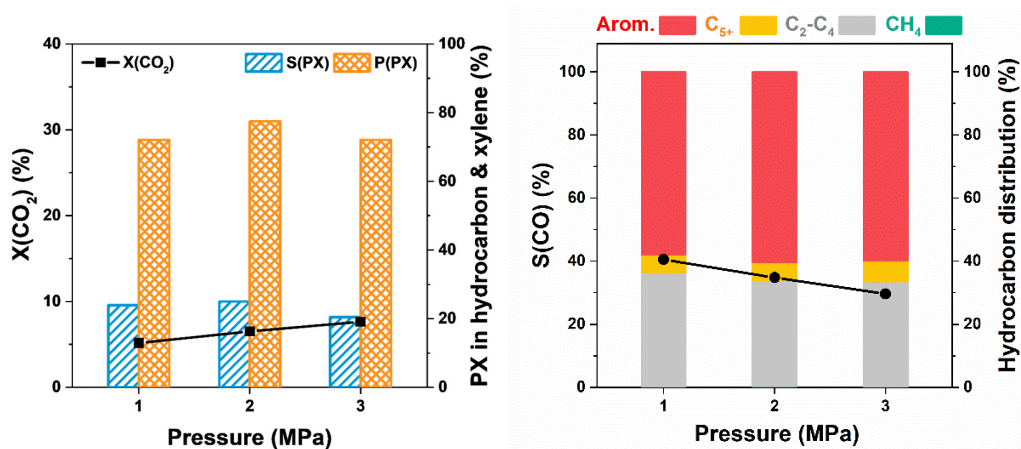


Figure S7. CO₂ conversion, PX selectivity, CO selectivity, and hydrocarbon distribution of CO₂ hydrogenation on ZZO/3T-ZSM-5 with different pressure. Reaction conditions: 320°C, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

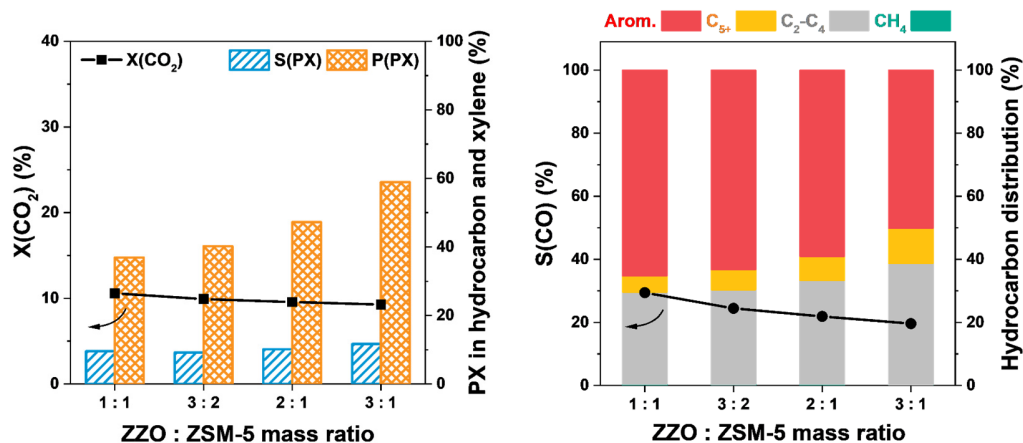


Figure S8. CO₂ conversion, PX selectivity, CO selectivity, and hydrocarbon distribution of CO₂ hydrogenation on ZZO/2T-ZSM-5 with different ZZO: ZSM-5 ratio. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹ (calculated by ZZO), ZSM-5 with Si/Al ratio of 40.

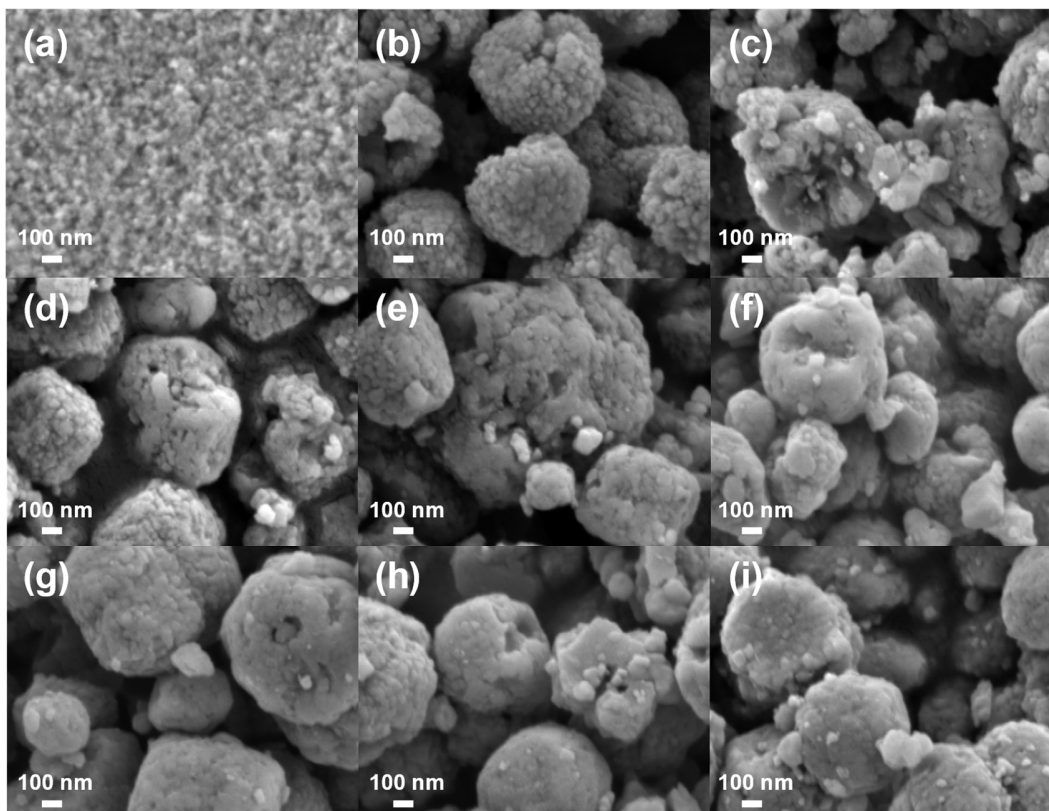


Figure S9. SEM images of ZnZrO (a), ZSM-5 (b), ZZO/ZSM-5 (c), 1T-ZSM-5 (d), 2T-ZSM-5 (e), 3T-ZSM-5 (f), 0.5Mg-3T-ZSM-5 (g), 1Mg-3T-ZSM-5 (h), and 2Mg-3T-ZSM-5(i).

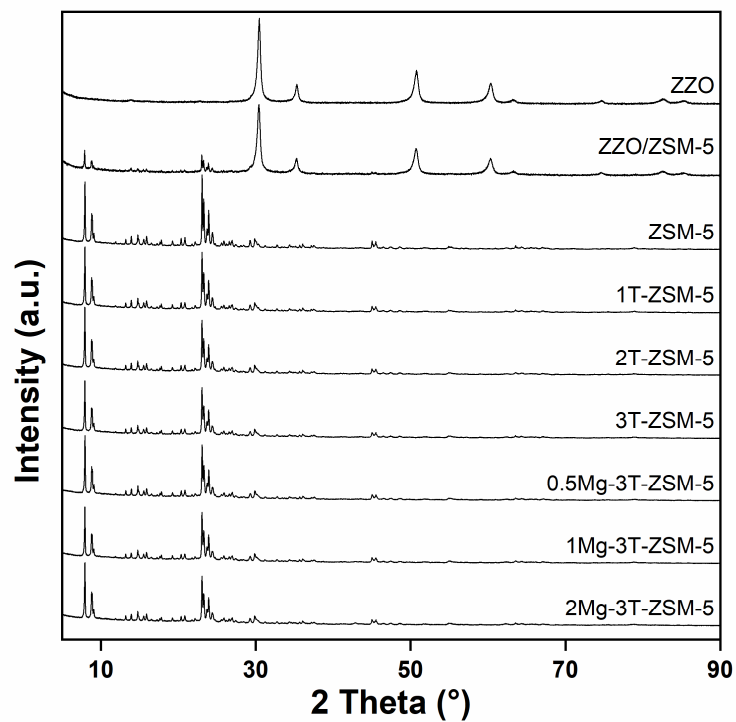


Figure S10. XRD patterns of ZZO, ZZO/ZSM-5, ZSM-5, nT-ZSM-5, and xMg-3T-ZSM-5.

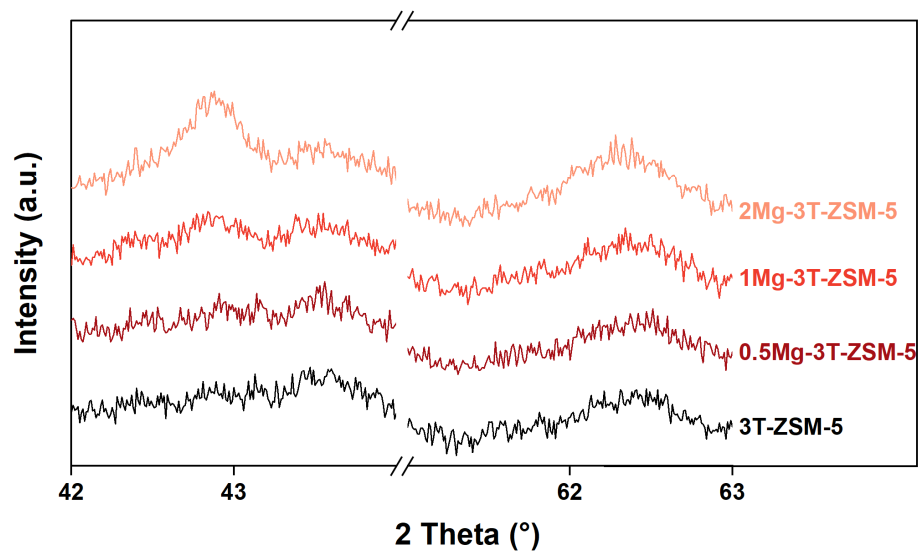


Figure S11. Detailed XRD patterns of 3T-ZSM-5 and Mg modified 3T-ZSM-5.

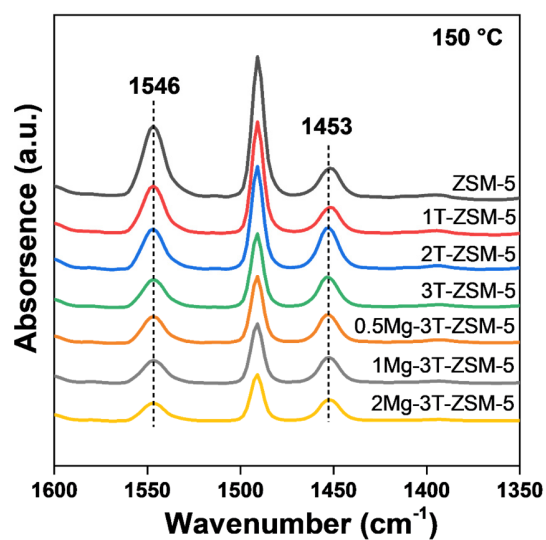


Figure S12. Pyridine FTIR of ZSM-5, nT-ZSM-5 and xMg-nT-ZSM-5.

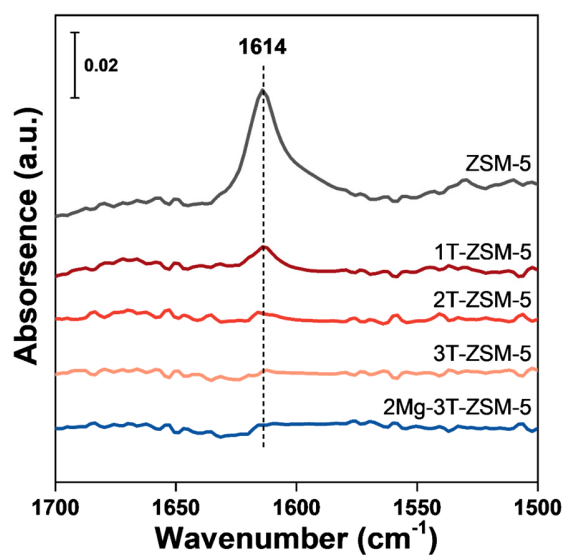


Figure S13. 2,6-di-tert-butylpyridine FTIR of ZSM-5, nT-ZSM-5, and 2Mg-3T-ZSM-5.

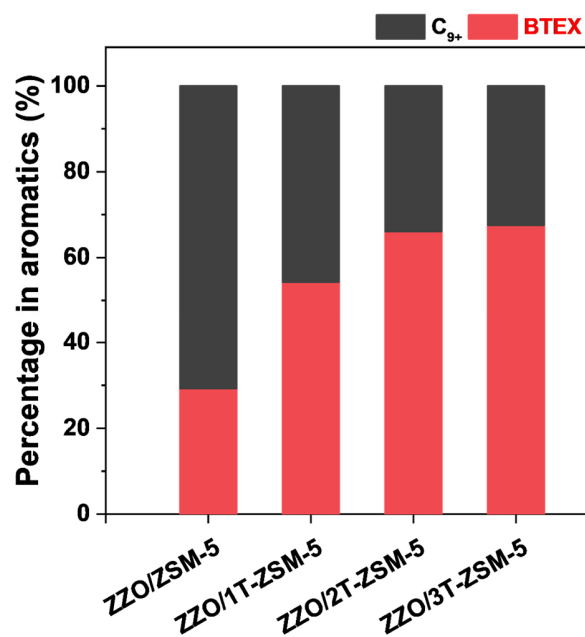


Figure S14. Benzene, toluene, ethylbenzene, xylene, (BTEX) and C₉₊ aromatics percentage in all aromatics of CO₂ hydrogenation on ZZO/nT-ZSM-5. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

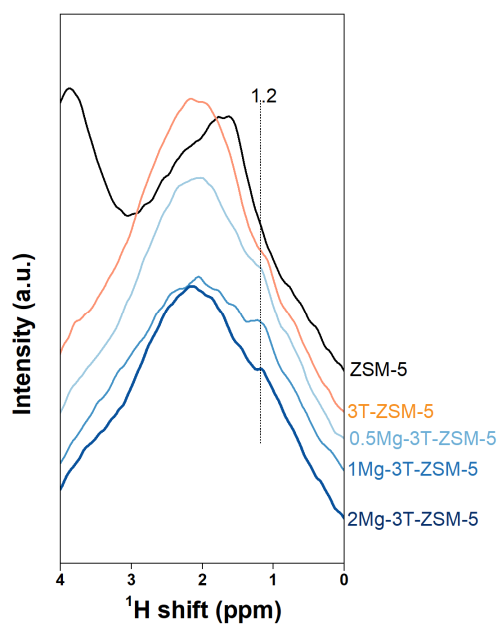


Figure S15. ¹H NMR of ZSM-5 series in detail.

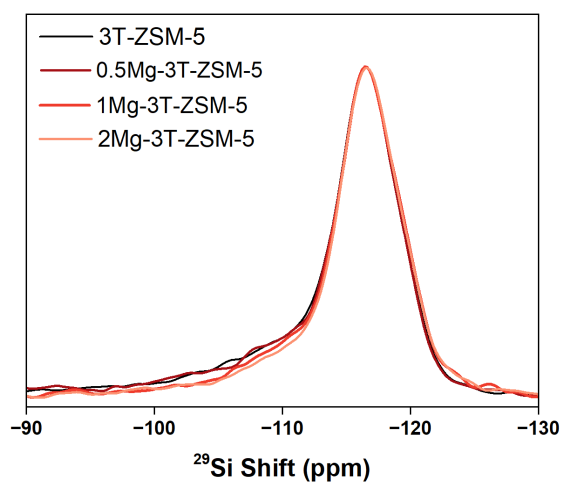


Figure S16. ^{29}Si NMR of 3T-ZSM-5 and xMg-3T-ZSM-5 after normalization.

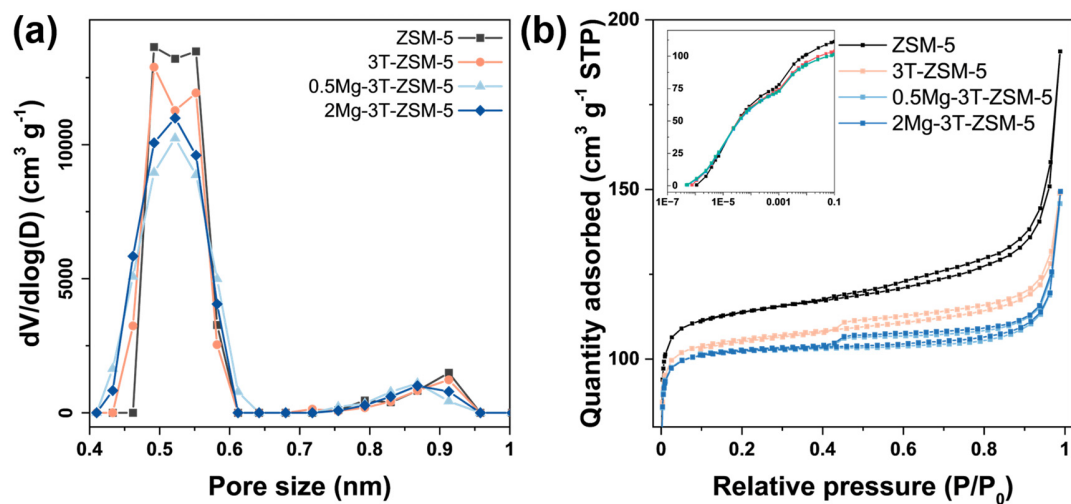


Figure S17. NL-DFT calculation based on Ar adsorption-desorption isotherms (a) and Ar adsorption-desorption isotherms (b) of different catalysts.

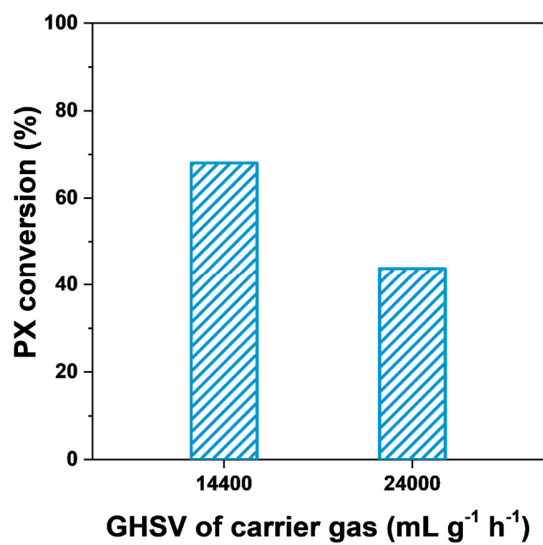


Figure S18. PX isomerization conversion on 3T-ZSM-5 with different GHSV. Reaction conditions: 320°C, 1.0 MPa.

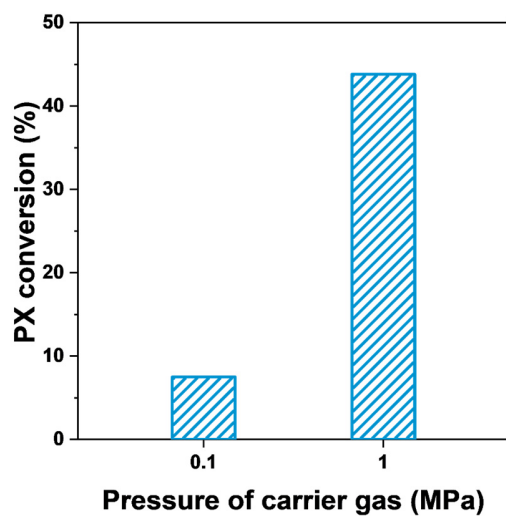


Figure S19. PX isomerization conversion on 3T-ZSM-5 with different GHSV. Reaction conditions: 320°C, Ar of 24000 mL g⁻¹ h⁻¹

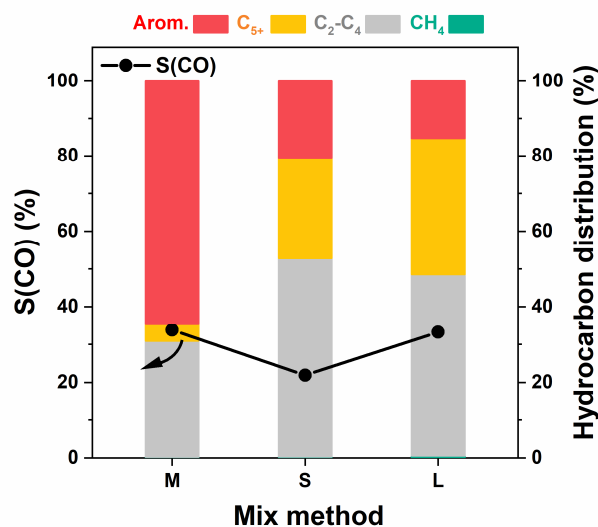


Figure S20. CO selectivity and hydrocarbon distribution of CO₂ hydrogenation on catalysts with different mixing method corresponding to Figure 3c in the main text. Reaction conditions: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

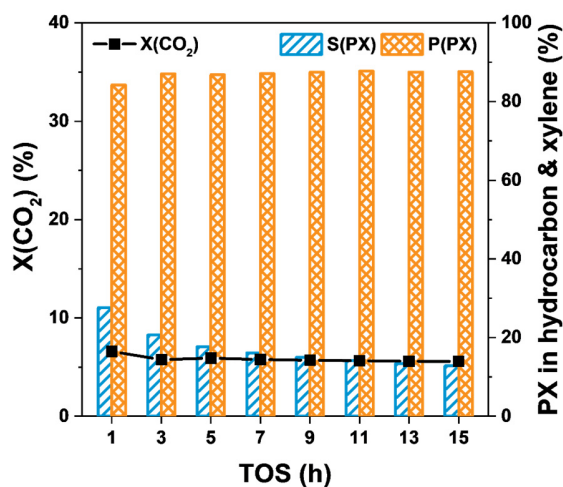


Figure S21. Stability test of ZZO/1%Mg-3T-ZSM-5 catalyst. Reaction condition: 320°C, 2.0 MPa, CO₂: H₂ of 1:3, GHSV of 4800 mL g⁻¹ h⁻¹.

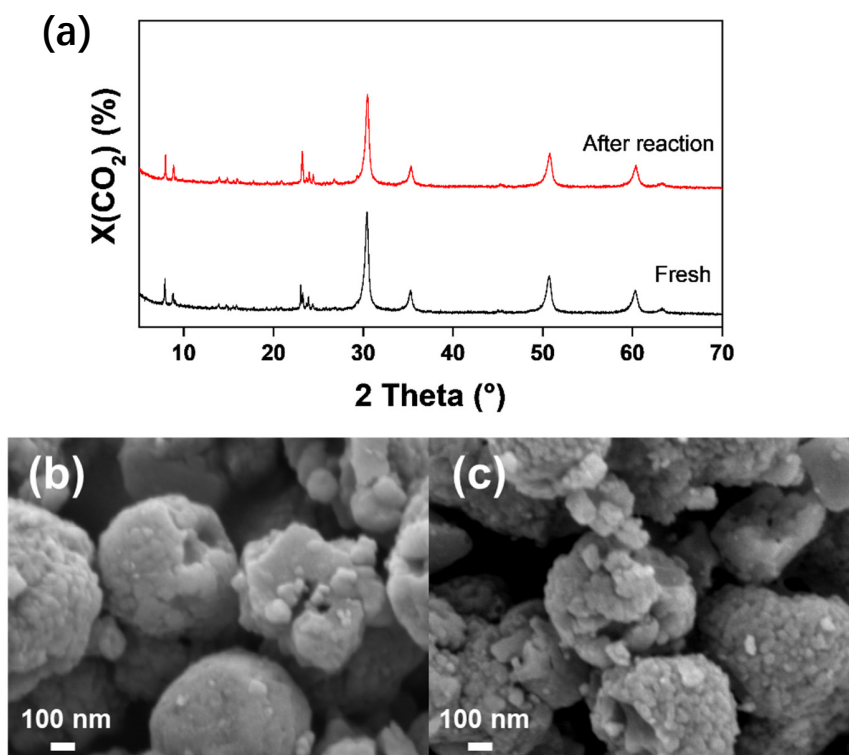


Figure S22. XRD patterns of fresh ZZO/3T-ZSM-5 and used ZZO/1%Mg-3T-ZSM-5 (a). SEM images of fresh 1%Mg-3T-ZSM-5 (b) and used ZZO/1%Mg-3T-ZSM-5 (c).

Table S1. ICP results of 3T-ZSM-5 and xMg-3T-ZSM-5

Catalyst	Weight (g)	Mass concentration (mg/L)			Mg mass content (%)
		Mg	Al	Si	
3T-ZSM-5 #1	0.023	134.8	14310	475700	0.01
3T-ZSM-5 #2	0.0237	128.7	13600	451900	0.01
0.5Mg-3T-ZSM-5 #1	0.0242	5804	14320	487200	0.54
0.5Mg-3T-ZSM-5 #2	0.0266	5294	13190	446000	0.54
1Mg-3T-ZSM-5 #1	0.0223	10340	12450	440900	1.07
1Mg-3T-ZSM-5 #2	0.0222	10540	12740	448300	1.07
2Mg-3T-ZSM-5 #1	0.0218	19370	11960	422700	2.09
2Mg-3T-ZSM-5 #2	0.0263	20120	12450	430900	2.13

Table S2. Content of Si(3Si,1Al) and Si(4Si) calculated from the ²⁹Si-NMR.

Zeolites	Si(3Si, 1Al) (%)	Si(4Si) (%)
3T-ZSM-5	23.4	76.6
0.5Mg-3T-ZSM-5	22.2	77.8
1Mg-3T-ZSM-5	14.7	85.3
2Mg-3T-ZSM-5	14.1	85.9

Table S3. Pore size calculates by NL-DFT.

Zeolites	Pore size (nm)
ZSM-5	0.552
3T-ZSM-5	0.552
0.5Mg-3T-ZSM-5	0.522
2Mg-3T-ZSM-5	0.522

Table S4. Catalytic performance and STY of PX of ZZO/ZSM-5 series.

ZZO/zeolites	X(CO ₂) (%)	S(CO) (%)	S(PX) (%)	P(PX) (%)	STY(PX) mg/g _{cat} /h
ZSM-5	7.6	37.7	4.7	23.5	1.5
1T-ZSM-5	7.3	34.8	13.3	42.5	4.3
2T-ZSM-5	6.7	34.2	22.0	65.3	6.6
3T-ZSM-5	7.0	35.2	25.0	76.3	7.7
0.5Mg-3T-ZSM-5	6.5	32.7	27.0	81.4	8.1
1Mg-3T-ZSM-5	6.6	32.1	27.6	84.2	8.4
2Mg-3T-ZSM-5	5.6	27.0	27.2	85.7	7.7

Reaction condition: 320 °C, 2 MPa, 4800 mL/g_{cat}/h

Equation S1.

$$T_R = \frac{H}{v} = \frac{\frac{V_c}{\pi(l/2)^2}}{\frac{p_0}{p_r} \cdot \frac{V_{in}}{\pi(l/2)^2}} = \frac{p_r \cdot V_c}{p_0 \cdot V_{in}} = \frac{1}{p_0 \cdot \rho_c} \cdot \frac{p_r}{GHSV}$$

T_R - Residence time

H - Height of catalyst bed

V - Velocity of carrier gas through the catalyst bed

V_c - Volume of catalyst

L - Inner diameter of the reaction tube

p_r - Pressure

p_0 - Atmospheric pressure

V_{in} - Inlet gas flow rate

P_c - Density of catalyst

$GHSV$ - Gas hourly space velocity

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