

Supporting Information

Selective synthesis of *para*-xylene and light olefins from CO₂/H₂ in the presence of toluene

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Experimental Section

Catalyst Preparation

ZnCr metal oxide with a Zn/Cr molar ratio of 2/1 (named as ZnCr) was prepared using a co-precipitation method.¹ Briefly, certain amounts of $\text{Zn}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3$ were dissolved in distilled water, and then $(\text{NH}_4)_2\text{CO}_3$ aqueous solution was added to form precipitate. After being aged at 70 °C for 3 h, the precipitate was centrifuged and washed with distilled water. After being dried at 110 °C for 12 h, the precipitate was finally calcined at 500 °C for 4 h.

H-ZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio were purchased from Nankai University Catalyst Co.. Phosphorus modification ZSM-5 was carried out by impregnating the pristine ZSM-5 powder (Z5-pristine, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 146) with H_3PO_4 aqueous solution. After stayed at room temperature for 12 h, the sample was dried at 110 °C for 12 h and calcined at 550 °C for 4 h. The obtained samples were denoted as $x\text{P}/\text{Z5}$, where x represented the content of P (wt%).

Silica modification on Z5-pristine or 3P/Z5 was carried out by a chemical liquid deposition method using polysiloxane (Dow Corning-550) as the silica source, a molecule larger than the pore size of H-ZSM-5.² In detail, 8g Dow Corning-550 was dissolved in 40 ml n-hexane and 6 g ZSM-5 was introduced into the solution. After the solvent was evaporated at room temperature, the solid was dried at 110 °C for 5 h and calcined at 600 °C for 4 h. The obtained samples were denoted as $(3\text{P})/\text{Z5-Siy}$, where y represented the cycle of silica deposition.

The ZnCr-ZSM-5 composite catalyst was obtained by mixing well the metal oxides and zeolites with a granule size 40-60 mesh (equivalent to 250-380 μm) with a mass ratio of 1/1 unless otherwise stated.

Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytic X'Pert Pro-1 instrument at 40 mA and 40 kV using Cu K α as the radiation source ($\lambda = 0.1541$ nm). The specific surface area was analyzed by N $_2$ adsorption at -196 °C over QuadraSorb SI instrument (Quantachrome). All samples were evacuated at 300 °C for 6 h prior to measurements. SEM and EDS mapping were carried out on a JEOL JSM-7900F. The samples were ultrasonically suspended in ethanol and placed onto a carbon film supported over a Cu grid. The acidity of ZSM-5 was characterized by NH $_3$ temperature-programmed desorption (NH $_3$ -TPD) on a Micromeritics AutoChem 2910 instrument, following the previously reported procedure.²

The external acid sites were characterized by adsorption of 2,6-di-tert-butyl-pyridine (2,6-DTBPY).² The self-supported samples were first evacuated at 450 °C for 1.5 h and cooled down to 150 °C inside the *in situ* IR cell. 2,6-DTBPY was then introduced into the cell. After adsorption for 10 min, the cell was evacuated for 1 h before IR spectra were recorded. Single-pulse ^{27}Al MAS experiments were carried out with a $\pi/8$ pulse length of 0.5 μs and a recycle delay of 0.5 s at 14.1 T and 12 kHz MAS. The chemical shifts were referenced to 1 M Al(NO $_3$) $_3$ aqueous solution.

Catalytic reaction

300 mg ZnCr-ZSM-5 was loaded in a fixed-bed reactor and heated to the desired temperature under H $_2$. A mixture of CO $_2$ and H $_2$ containing 5% Ar as the internal standard for GC analysis was introduced using a mass flow controller and toluene was injected with a pump (Elite P230). The reaction was operated at H $_2$ /CO $_2$ = 3, 4 MPa and 390 °C, and a gas hourly space velocity of H $_2$ /CO $_2$ /Ar (GHSV $_{\text{CO}_2/\text{H}_2}$) = 15,000 ml/g/h, a weight hourly space velocity of toluene (WHSV $_{\text{toluene}}$) = 0.87 h $^{-1}$ unless otherwise stated.

The products were analyzed by an on-line GC Agilent 7890 B equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Hydrocarbons were separated in a HP-FFAP column and a HP-AL/S capillary column and analyzed by FID, while Ar, CO, CO₂, C₂H₄ and C₂H₆ were separated in a Porapak Q column and a 5A molecular sieve column and analyzed by TCD.

CO₂ conversion, X_{CO_2} , was calculated according to

$$X_{CO_2} = \frac{CO_{2\text{inlet}} - CO_{2\text{outlet}}}{CO_{2\text{inlet}}} \times 100\% \quad (1)$$

where $CO_{2\text{inlet}}$ and $CO_{2\text{outlet}}$ were the moles of CO₂ at the inlet and outlet of the reactor, respectively.

Toluene conversion, X_T , was obtained according to

$$X_T = \left(1 - \frac{7 \times C_{7H_8\text{outlet}}}{\sum_6^n (nC_nH_m\text{outlet})}\right) \times 100\% \quad (2)$$

where $C_nH_m\text{outlet}$ represented moles of aromatics at the outlet.

CO selectivity, S_{CO} , was obtained according to

$$S_{CO} = \frac{CO_{\text{outlet}}}{CO_{2\text{inlet}} - CO_{2\text{outlet}}} \times 100\% \quad (3)$$

where CO_{outlet} was the mole of CO at the outlet.

The selectivity of hydrocarbon C_nH_m ($S_{C_nH_m}$) was calculated according to:

$$S_{C_nH_m} = \frac{nC_nH_m\text{outlet}}{\sum_1^n (nC_nH_m\text{outlet})} \times 100\% \quad (4).$$

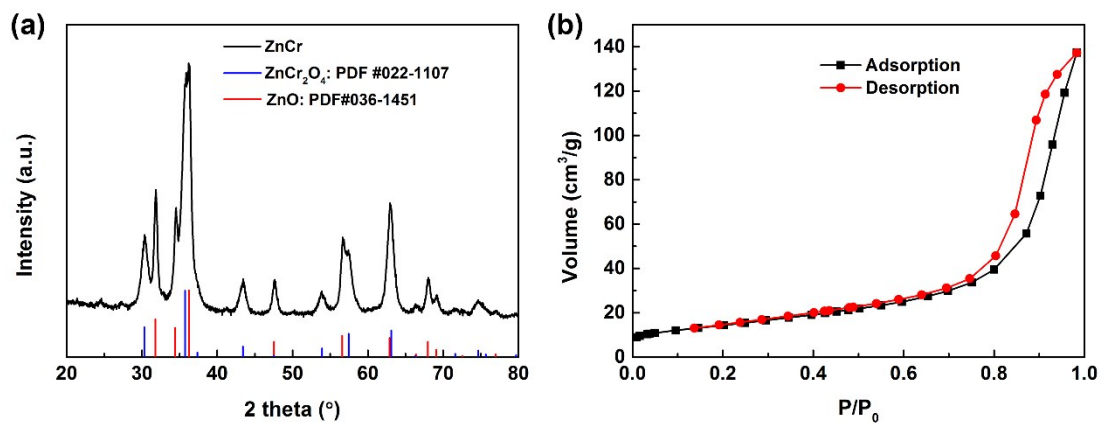


Fig. S1. (a) XRD pattern and (b) N₂ adsorption-desorption isotherm of ZnCr oxide.

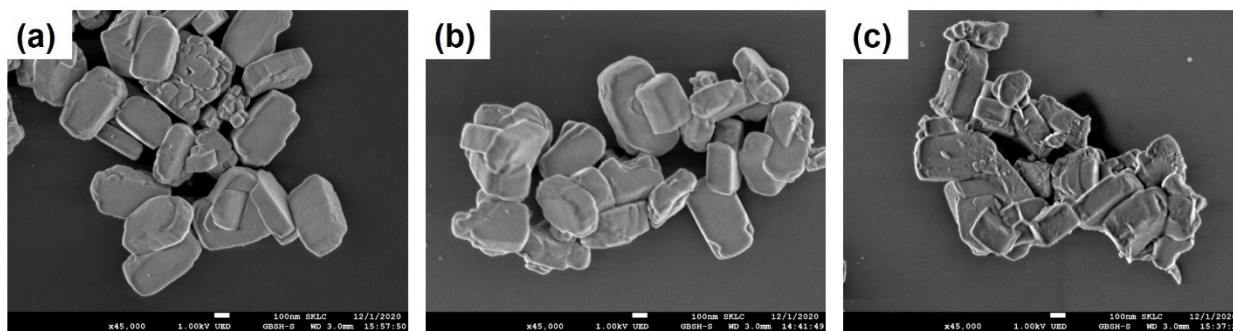


Fig. S2. SEM images of (a) Z5-pristine; (b) 3P/Z5; and (c) 3P/Z5-Si₃.

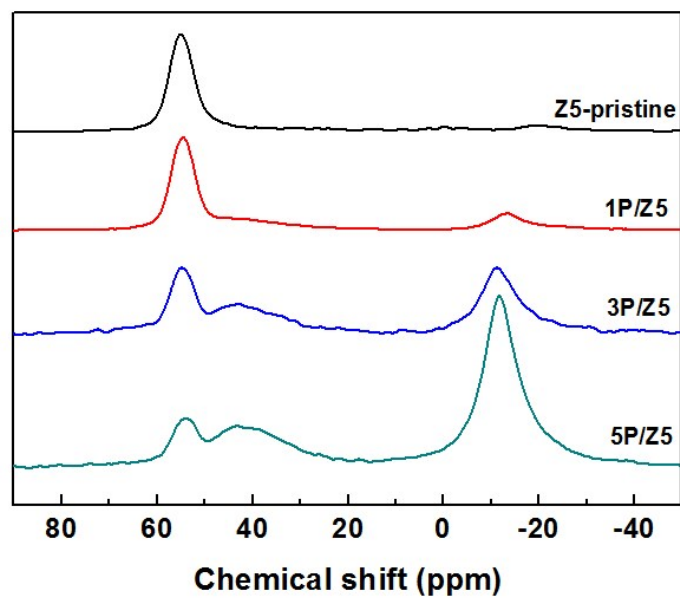


Fig. S3. ^{27}Al NMR spectra of phosphorus-modified ZSM-5.

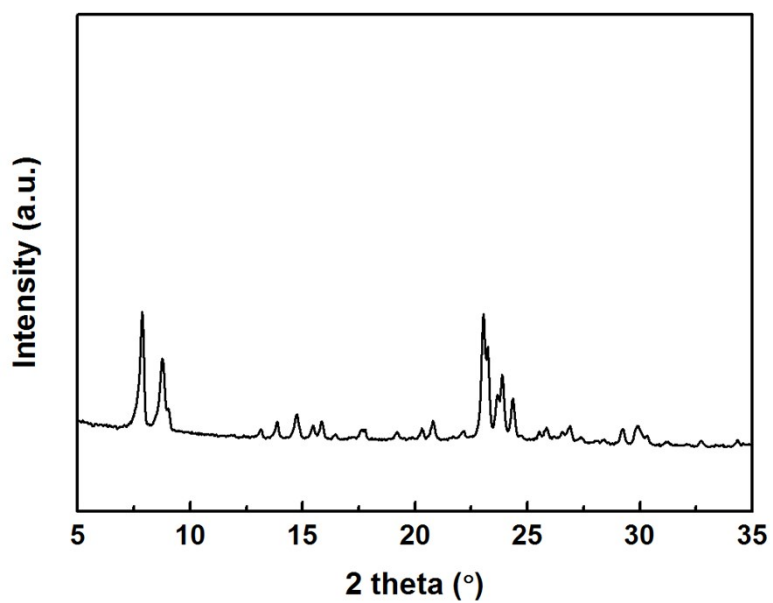


Fig. S4. XRD pattern of 3P/Z5-Si₃.

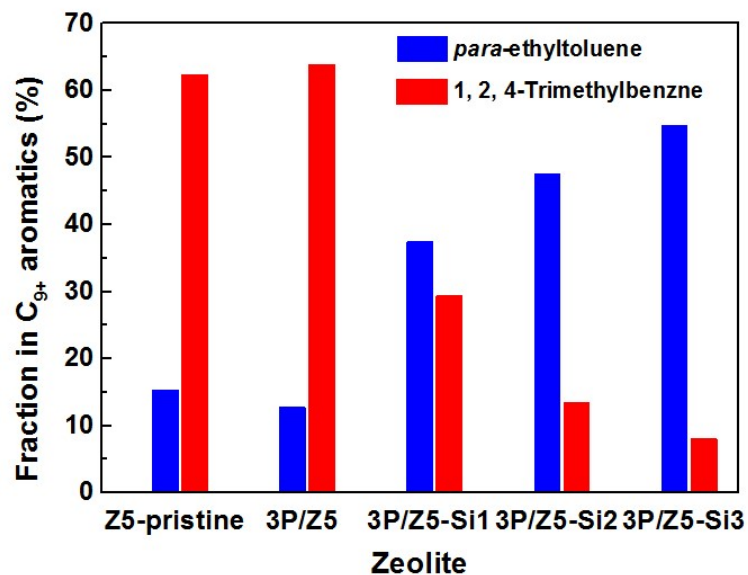


Fig. S5. Fractions of *para*-ethyltoluene and 1,2,4-trimethylbenzene in C₉₊ aromatics. Reaction conditions are the same as those in Fig. 7.

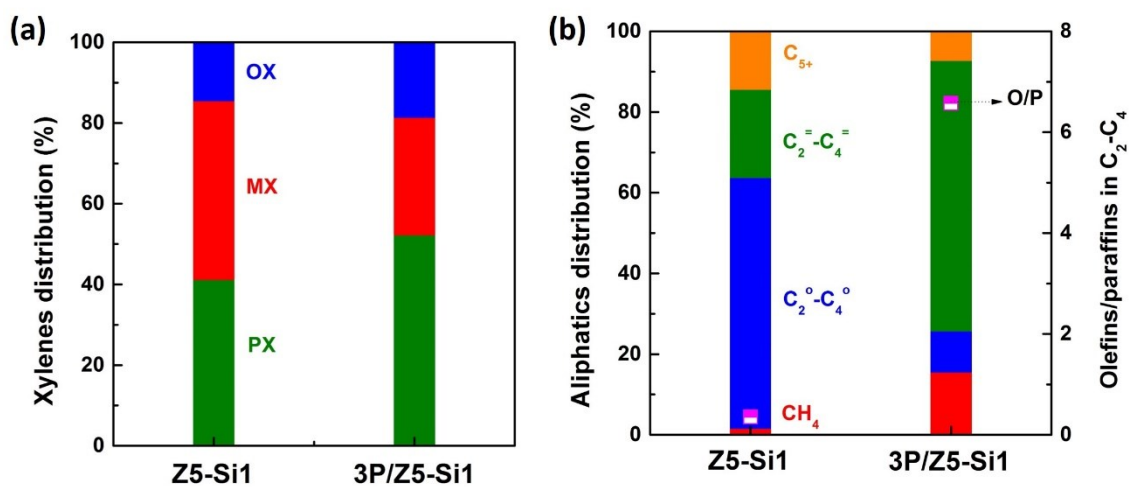


Fig. S6. (a) Xylenes distribution and (b) aliphatics distribution over ZnCr-Z5-Si1 and ZnCr-3P/Z5-Si1. Reaction conditions is the same as in Fig. 7.

Table S1. CO₂ hydrogenation in the presence of toluene over ZnCr-modified ZSM-5.

Zeolite	X_{CO2} (%)	S_{CO} (%)	X_T (%)	S_{Aro.} (%)
Z5-pristine	22.0	70.4	31.4	97.3
3P/Z5	21.3	74.7	25.7	92.6
3P/Z5-Si1	23.7	73.0	18.8	87.7
3P/Z5-Si2	23.2	75.5	11.2	75.5
3P/Z5-Si3	20.9	74.0	10.6	69.5

Reaction conditions: ZnCr/ZSM-5 = 1/1 mass ratio, granule mixing, 40-60 mesh, GHSV_{CO₂/H₂} = 15000 ml/g/h, WHSV_{toluene} = 0.87 h⁻¹, 390 °C, 4 MPa, H₂/CO₂ = 3/1.

Reference

1. F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, M. Li, S. Miao, J. Li, Y. Zhu, D. Xiao, T. He, J. Yang, F. Qi, Q. Fu and X. Bao, *Science*, 2016, **351**, 1065-1068.
2. D. Miao, Y. Ding, T. Yu, J. Li, X. Pan and X. Bao, *ACS Catal.*, 2020, **10**, 7389-7397.