

Supporting information

Direct Conversion of Syngas to Aromatics

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Experimental Details

Catalyst preparation

The mixed metal oxide was prepared by co-precipitation method, similar to our previous report.^[1] Briefly, 12.48 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 5.61 g $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 5.27 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 ml distilled water and $(\text{NH}_4)_2\text{CO}_3$ aqueous solution was used as the precipitant. After precipitation, it was aged for 3 h at the same temperature, followed by filtration and washing by distilled water. The resulting product was dried over night at 383 K and then calcined at 773 K for 4 h.

ZSM-5 was synthesized hydrothermally. Typically, NaAlO_2 , 25% tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS) and urea were dissolved in 26.7 ml distilled water with a molar ratio of $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{TPAOH} : \text{H}_2\text{O} : \text{urea} = 1 : 0.0025 : 0.4 : 45 : 2.8$ unless otherwise stated.^[2] Then the mixture was transferred into a Teflon-lined autoclave, and kept for 4 days at 453 K. After filtering and washing by distilled water, the resulting product was dried over night at

383 K, and then it was calcined for 4 h at 773 K.

The composite catalyst is prepared by mixing and grinding of the two components in an agate mortar with the mass ratio of $\text{ZnCrO}_x/\text{ZSM-5} = 3/1$ unless otherwise stated.

Catalytic reaction tests

Catalytic reactions were performed with fixed-bed stainless steel reactor furnished with a quartz tube (outside diameter = 7 mm) lining in a continuous flow. Typically 280 mg composite catalyst (20 – 40 mesh) with $\text{ZnCrO}_x/\text{ZSM-5} = 3/1$ (mass ratio) was used. The catalyst was subjected to in situ reduction in H_2 for 4 h at 623 K. A premixed syngas was used as the feed with $\text{CO}/\text{H}_2 = 1/1$ (molar) containing 5% Ar as the internal standard for online gas chromatography (GC) analysis. Reaction was carried out at 4.0 MPa, 623 K and $1500 \text{ ml h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ unless otherwise stated. Data were collected after at least 4 hours on stream.

MTA was performed on the same ZSM-5 for comparison at atmospheric pressure. Methanol was introduced into the catalyst bed with He as the carrier gas. The weight hourly space velocity of methanol was 0.3 h^{-1} , equivalent to the CO converted in the OX-ZEO process assuming 100% methanol conversion.

Products were analyzed by an online GC (Agilent 7890B) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Porapak Q and 5 Å molecular sieves packed columns were connected to TCD while HP-FFAP and HP-AL/S capillary columns were connected to FID. Oxygen-containing compounds and hydrocarbons up to C_{17} were analyzed by FID, while CO, CO_2 , C_2H_4 , and C_2H_6 were analyzed by TCD. C_2H_4 and C_2H_6 were taken as a reference bridge between FID and TCD. CO conversion was calculated on a carbon atom basis, i.e.

$$\text{Con}_{\text{co}} = \frac{\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}}}{\text{CO}_{\text{inlet}}} \times 100\%$$

Where CO_{inlet} and $\text{CO}_{\text{outlet}}$ represent moles of CO at the inlet and outlet, respectively. CO_2 selectivity (Sel_{CO_2}) was calculated according to:

$$Sel_{CO_2} = \frac{CO_{2\text{outlet}}}{CO_{\text{inlet}} - CO_{\text{outlet}}} \times 100\%$$

Where $CO_{2\text{outlet}}$ denotes moles of CO_2 at the outlet.

The selectivity of individual hydrocarbon C_nH_m ($Sel_{C_nH_m}$) was obtained according to:

$$Sel_{C_nH_m} = \frac{nC_nH_m\text{outlet}}{\sum_1^n nC_nH_m\text{outlet}} \times 100\%$$

The selectivity to oxygenates were below 1% C and therefore were not reported in the product selectivity. The carbon balance was over 95%.

Catalyst characterization

Temperature-programmed-desorption of NH_3 (NH_3 -TPD) was performed on a Micromeritics AutoChem 2910 equipped with a thermal conductivity detector (TCD). The catalyst was first pretreated in a flowing He at 723 K for 1.5 h. After cooling down to 373 K under flowing He, the sample was exposed to 15% NH_3 /He at 373 K. Then the sample was swept by He at 373 K till a stable baseline was obtained. Subsequently, signal was recorded while the temperature was increased from 373 to 1073 K at a heating rate of 10 K/min.

X-ray diffraction (XRD) was measured on a PANalytical X'pert PPR diffractometer equipped with $CuK\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$), operated at 40 mA and 40 kV. XRD patterns were recorded in the range of $2\theta = 5 - 40^\circ$.

Scanning electron microscope (SEM) was performed on an FEI QUANTA 200FEG microscope at 20 kV.

X ray fluorescence (XRF) was measured on PANalytical ZETIUM operated at 3 kW.

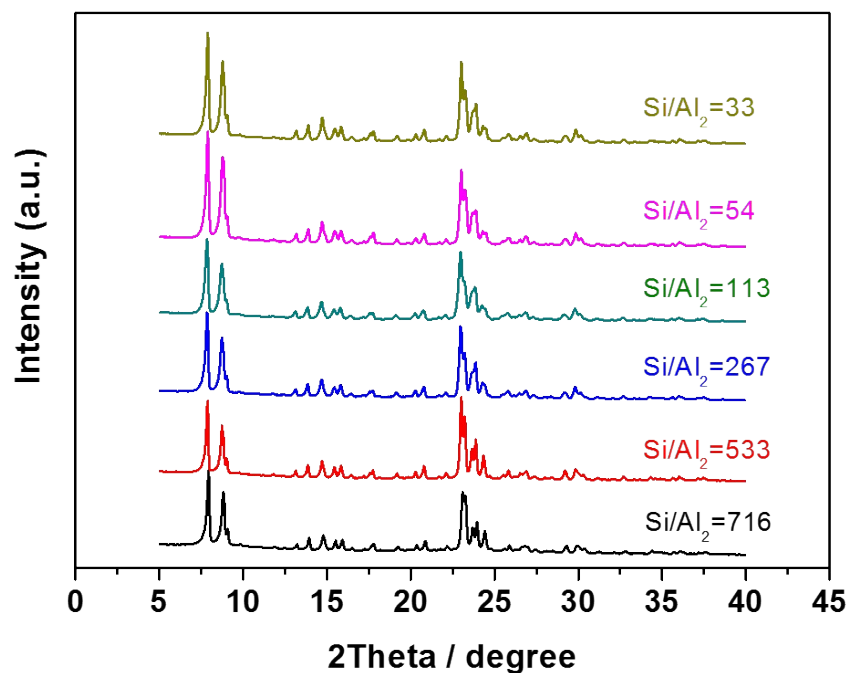


Figure S1. XRD patterns of ZSM-5 with different SiO₂/Al₂O₃ ratios.

Table S1. The specific production selectivity of syngas conversion over ZnCrO_x-ZSM-5-533.^[a]

CO Conversion [%]	16.0
CO ₂ Selectivity [%]	46.9
Selectivity in hydrocarbons [%]	
CH ₄	1.7
C ₂ =-C ₄ =	7.1
C ₂ -C ₄	8.0
Total C ₅₊	83.2
Toluene	1.7
Xylenes	13.0
Trimethylbenzenes	34.2
Tetramethylbenzenes	10.2
Other aromatics (C ₈ -C ₁₀)	14.8
Total aromatics	73.9
Non-aromatic C ₅₊	9.3

[a] Reaction conditions: ZnCrO_x-ZSM-5-533 (containing 50 wt% ZnCrO_x), 623 K, 4.0 MPa, GHSV = 1500 ml h⁻¹·g_{cat}⁻¹, H₂/CO = 1/1. There are no C₁₁₊ hydrocarbons detected.

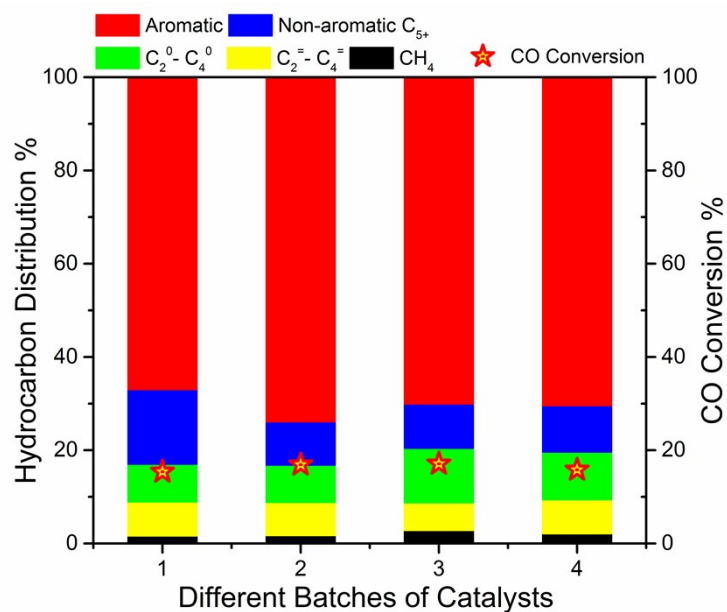


Figure S2. Reproducibility test of catalysts, which have been prepared and evaluated in different batches under the same reaction conditions. Reaction conditions: 623 K, 4.0 MPa and GHSV 1500 ml h⁻¹·g_{cat}⁻¹.

References

- [1] F. Jiao, J. J. Li, X. L. Pan, J. P. Xiao, H. B. Li, H. Ma, M. M. Wei, Y. Pan, Z. Y. Zhou, M. R. Li, S. Miao, J. Li, Y. F. Zhu, D. Xiao, T. He, J. H. Yang, F. Qi, Q. Fu, X. H. Bao, *Science* **2016**, *351*, 1065-1068.
- [2] Y. Liu, X. Zhou, X. Pang, Y. Jin, X. Meng, X. Zheng, X. Gao, F. S. Xiao, *Chemcatchem*. **2013**, *5*, 1517-1523.