

Supporting Information

Stable co-production of ethylene and aromatics from ethane over Co²⁺-exchanged HZSM-5 zeolite

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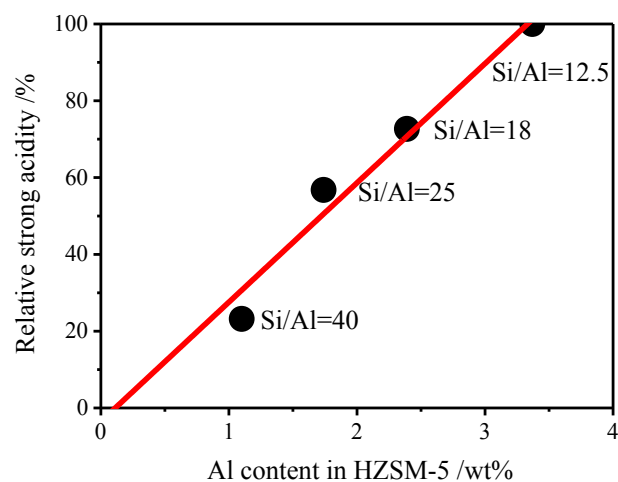


Fig. S1. The relative strong acidity in parent HZSM-5 zeolites as a function of Al content in zeolite based on that in the HZSM-5 (Si/Al = 12.5) supposed to be 100%.

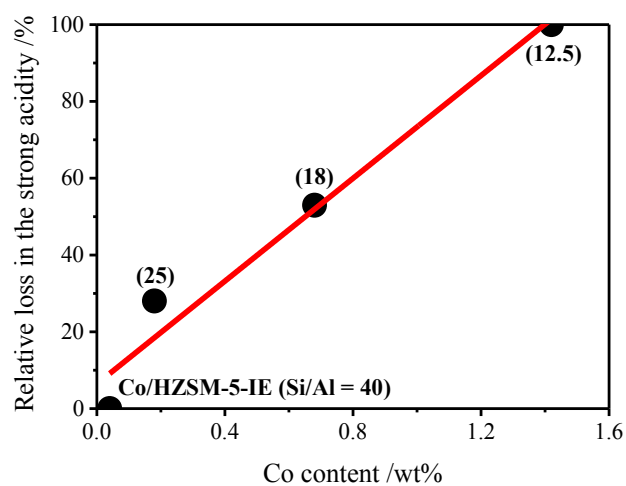


Fig. S2. The relative loss in the strong acidity in the Co/HZSM-5-IE catalysts as a function of Co content based on the loss in the Co/HZSM-5-IE (Si/Al = 12.5) supposed to be 100%.

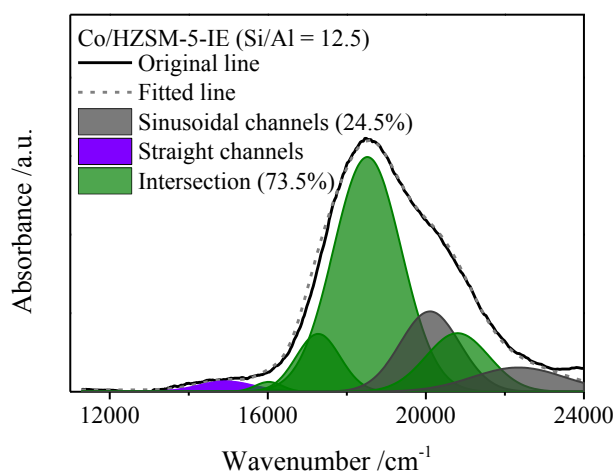


Fig. S3. Deconvolution of UV-vis DR spectrum of Co/HZSM-5-IE (Si/Al = 12.5) catalyst sample.

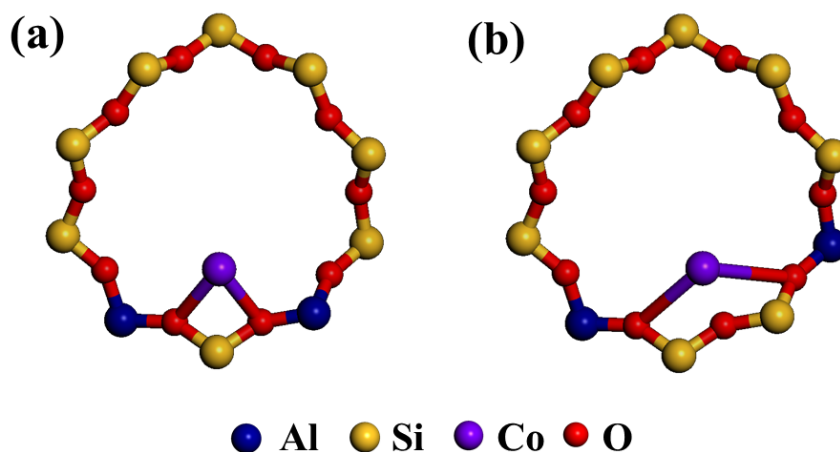


Fig. S4. The schematic location of Co ions in the ion-exchanged Co/HZSM-5 catalyst: (a) possibly existed in a zeolite with a very low Si/Al ratio; (b) commonly existed, especially, in a zeolite with a high Si/Al ratio.

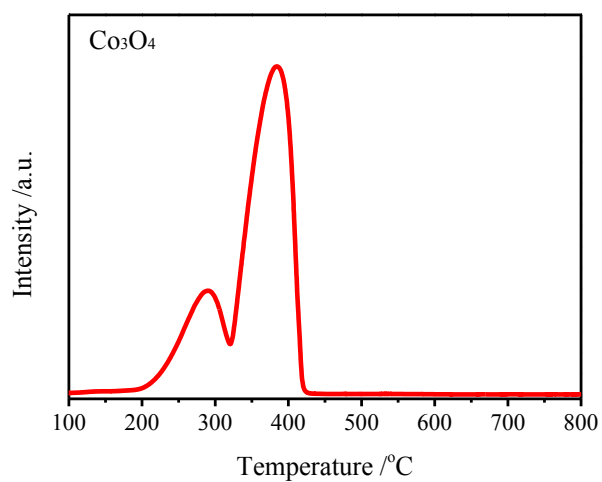


Fig. S5. H₂-TPR profile of a synthesized Co₃O₄ compound.

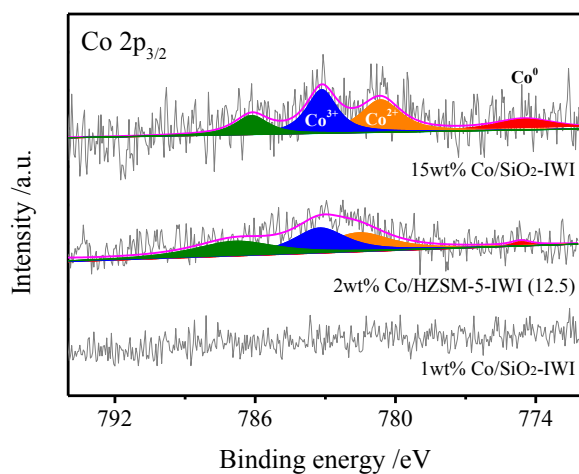


Fig. S6. XPS spectra of 1 wt%, 15 wt% Co/SiO₂-IWI and 2 wt% Co/HZSM-5-IWI (Si/Al = 12.5) catalysts reduced by H₂ at 600 °C for 30 min.

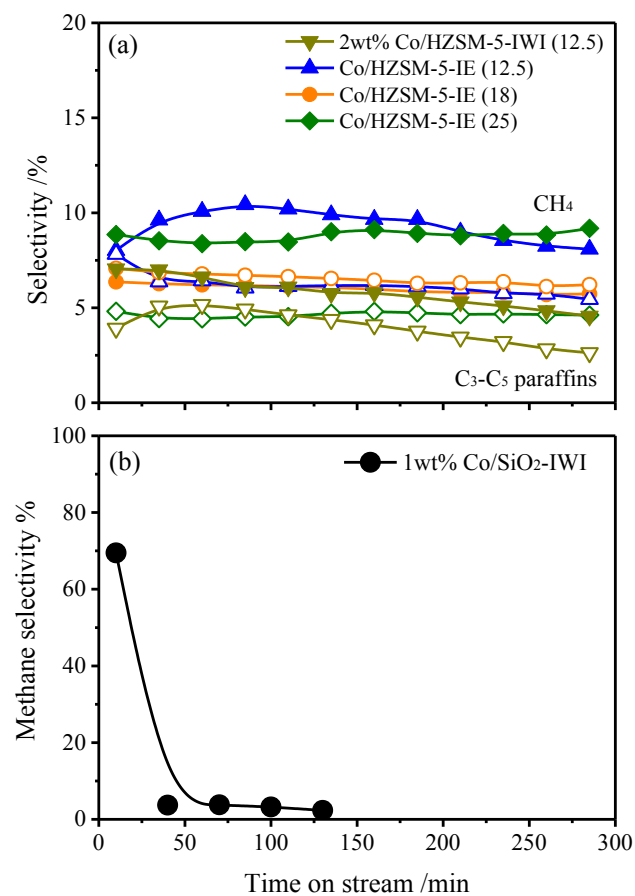


Fig. S7. The selectivities to paraffins for Co-based catalysts. Reaction conditions: 0.3 g of catalysts, 90% $\text{C}_2\text{H}_6/\text{N}_2$, 15 mL/min, 600 °C, pressure at 0.1 MPa.

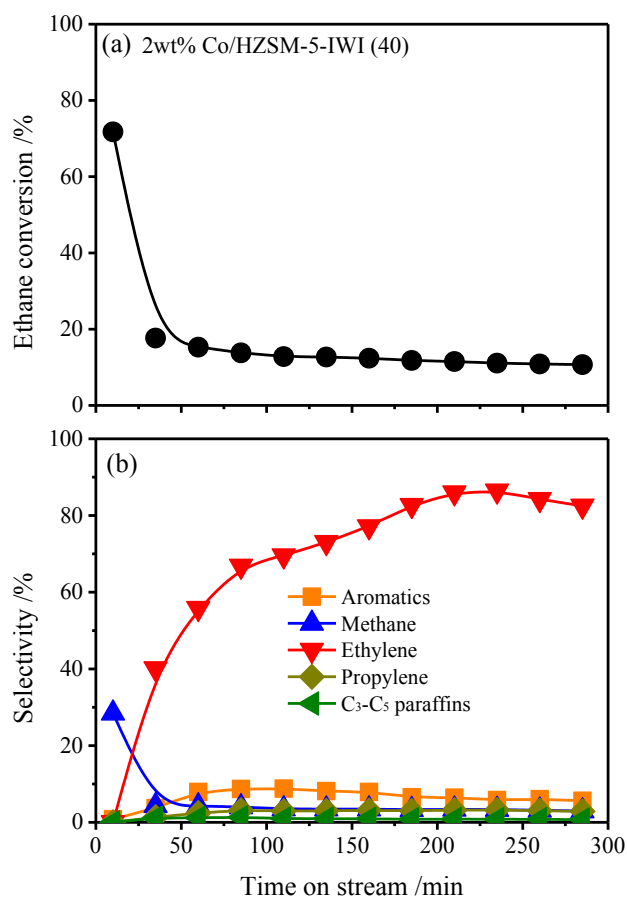


Fig. S8. Time-dependence of C_2H_6 conversion and the selectivity to various hydrocarbons for the 2 wt% Co/HZSM-5-IWI (40) catalysts at 600 °C, 0.1 MPa, 3000 mL/g/h and 90% C_2H_6 /10% N_2 .

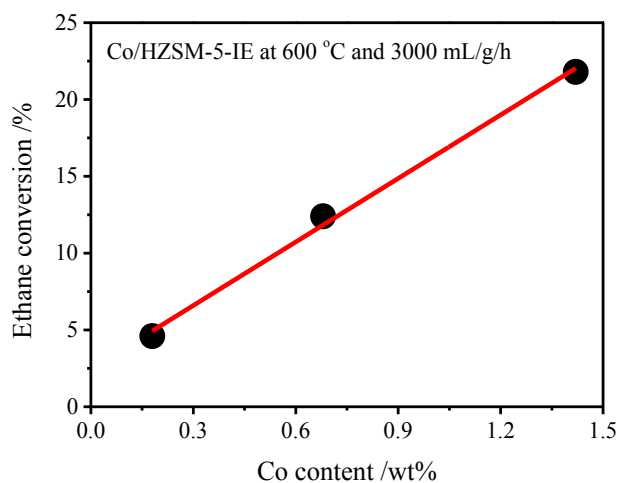


Fig. S9. The plotting of ethane conversion as a function of Co content in the Co-exchanged HZSM-5 catalyst. Reaction condition: 600 °C, 0.1 MPa, 3000 mL/g/h and 90% C_2H_6 /10% N_2 .

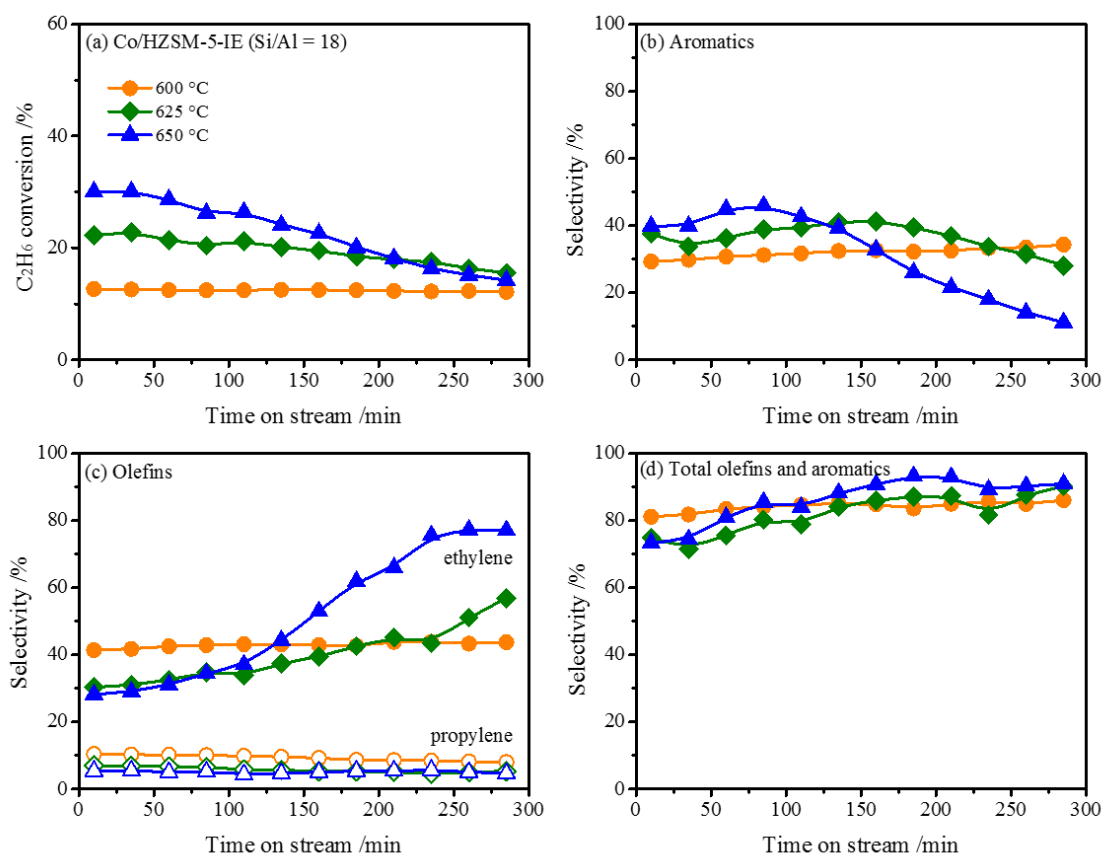


Fig. S10. The C₂H₆ conversion and selectivity to olefins and aromatics over Co/HZSM-5-IE (Si/Al = 18) catalyst at various reaction temperatures (600-650 °C) and 3000 mL/g/h.

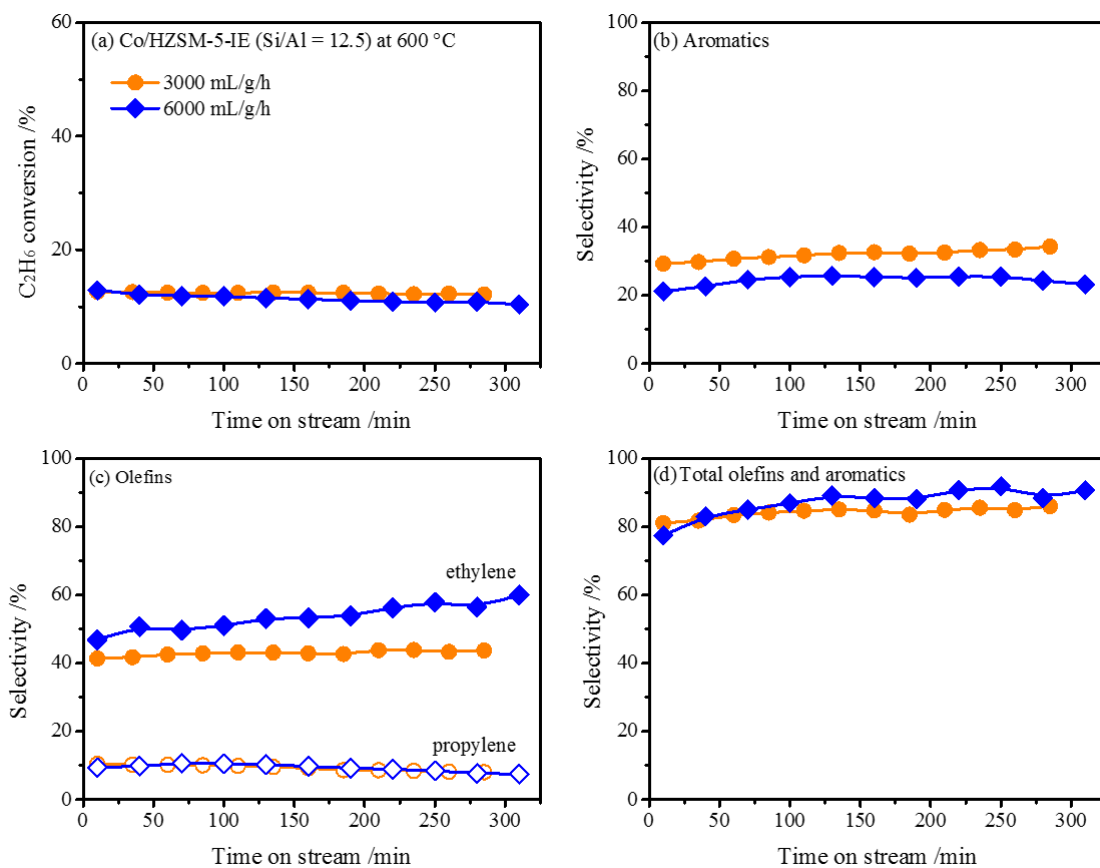


Fig. S11. The C₂H₆ conversion and selectivity to olefins and aromatics over Co/HZSM-5-IE (Si/Al = 18) catalyst at 600 °C and two space velocities of 3000 and 6000 mL/g/h.

Table S1. Ethane conversion and products selectivities over Co/HZSM-5 catalysts

| Catalyst | Ethane conv. ^{a)} /% | Selectivity ^{a)} /% | | | | | | | | | | | | Olefins /% | Aromatics /% |
|--------------------|-------------------------------------|------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|------|------|-----|-----|------|---------|--------------------|---------------|-----------------|
| | | CH ₄ | C ₂ H ₄ | C ₃ H ₆ | C ₃ H ₈ | C ₄ -C ₆ | Benz | Toul | Xyl | TMB | Naph | Me-Naph | Coke ^{b)} | | |
| Co/ZSM-5-IE (12.5) | 21.5 | 9.3 | 40.1 | 4.4 | 3.1 | 2.0 | 12.8 | 13.9 | 3.0 | 1.3 | 3.5 | 3.6 | 3.1 | 44.5 | 38.1 |
| Co/ZSM-5-IE (18) | 12.4 | 6.0 | 42.9 | 8.6 | 3.1 | 2.9 | 14.3 | 11.3 | 2.8 | 0.7 | 1.5 | 1.3 | 4.6 | 51.5 | 31.9 |
| Co/ZSM-5-IE (25) | 4.6 | 8.7 | 54.0 | 11.6 | 2.3 | 2.4 | 4.2 | 3.2 | 0.6 | 0.2 | 3.1 | 0 | 9.7 | 65.6 | 11.3 |

^{a)} The feed is 10%N₂/90%C₂H₆ and the reaction lasted for 300 min at 600 °C and 0.1 MPa.

^{b)} The selectivity to coke was obtained by subtraction method and carbon balance was confirmed to be 95-105% according to the coke amount in the spent samples.