

Electronic Supplementary Information

Cobalt-imbedded zeolite catalyst for direct syntheses of gasoline via Fischer-Tropsch synthesis

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Experimental details

Preparation of conventional precursor catalyst Co/SiO₂

The commercially available SiO₂ (Specific surface area 451 m²·g⁻¹, pore volume 1.061 cm³·g⁻¹, average diameter of pore 6.7 nm) was used as a support. The precursor catalyst Co/SiO₂ with nominal 20 wt% cobalt loading was prepared by incipient wet impregnation of the SiO₂ with an aqueous solution containing the required amount of Co(NO₃)₂·6H₂O. Then the catalyst was vacuuming for 1h, and then dried at 393 K for 12 h before its calcination in air from room temperature to 673 K for 2 h.

Preparation of cobalt-imbedded zeolite catalyst Co@HZSM-5

The cobalt-imbedded zeolite catalyst Co@HZSM-5 was prepared by a hydrothermal method. Tetrapropylammonium hydroxide (TPAOH) was selected as the structure-directing agent. The dissolved Si from the precursor catalyst Co/SiO₂ during the synthesis procedure served as the Si source for the crystallization of the zeolite, with Al(NO₃)₃·9H₂O as the Al source. NH₃·H₂O added to the synthesis system was used to improve the basicity of the solution to enforce the nucleation and growth

of HZSM-5. The molar ratio of the reactants in the precursor solution was 15 TPAOH: 500 EtOH: 1 $\text{Al}(\text{NO}_3)_3$: 50 SiO_2 : 1600 H_2O : 200 NH_3 . Firstly, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved by H_2O and EtOH in a Teflon-lined stainless steel autoclave, followed by the addition of the precursor catalyst power under stirring. Then TPAOH was added dropwise, and afterwards, the reaction mixture was further vigorously stirred at room temperature for 6 h. Finally, $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to the synthesis solution and allowed to stir for another 15 minutes, and then the autoclave was sealed and hydrothermally crystallized at 453 K for 100 h. After cooling the autoclave naturally, the product was separated by filtration and washed with deionized water and ethanol for several times. The as-synthesized sample was dried at 393 K for 12 h, and the final calcinations process was performed in air from room temperature to 773 K with a ramping rate of $2 \text{ K} \cdot \text{min}^{-1}$ and maintained at 773 K for 5 h to remove the organic template.

Preparation of zeolite-supported cobalt catalyst Co/HZSM-5

For comparison, the zeolite-supported cobalt catalyst Co/HZSM-5 was also prepared using the proton-type HZSM-5 support which was prepared via a traditional hydrothermal method. The template and Al source were the same as the preparation of Co@HZSM-5 catalyst except that the Si source was the silica used above. The molar composition of the mixture and the synthesis procedure was similar with the preparation of Co@HZSM-5. For the preparation of Co/HZSM-5 catalyst, the obtained HZSM-5 support was impregnated with excessive $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution. Thereafter, the suspension was left to rest overnight at ambient temperature before its continuously stirring and heating at 333 K to remove the residual water. The Co loading amount over the catalyst was 20 wt%. The sample was then dried at 393 K for 12 h before subjecting it for calcination at 673 K in air for 2 h.

Catalyst characterization

The power X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500VB2+/PC diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$). All the

samples were scanned at 40 KV and 200 mA within the 2θ range of $5-90^\circ$ at the rate of $5^\circ \cdot \text{min}^{-1}$. To avoid the disturbance of diffraction peaks of HZSM-5, the average crystalline size of cobalt oxide in the calcined samples were estimated from Scherrer equation by using the half-width of the diffraction peak of Co_3O_4 crystallites at $2\theta = 59.3^\circ$.

The chemical compositions of the samples were analyzed by X-ray fluorescence (XRF) on a XRF-1800 spectrometer.

The SEM images of the catalysts were obtained on a field-emission scanning electron microscope (SEM, Hitachi S-4700) equipped with an energy-dispersive X-ray spectroscopy attachment (EDAX, Genesis 60). The samples for this analysis were first deposited on a holder using an adhesive carbon tape and then coated with a platinum layer.

Transmission electron microscopy (TEM) was performed on a Hitachi H-800 microscope. The specimen was prepared by ultrasonically suspending the catalyst powder in ethanol. A drop of the suspension was deposited on a carbon-enhanced copper grid and dried in air.

²⁷Al MAS-NMR experiments of the powered samples were conducted on a 300 MHz solid-state Bruker AV300 spectrometer (7.05 T). The samples were packed into a ZrO_2 NMR rotor (4 mm o.d.). The spectra were recorded at a frequency of 78.2 MHz, with a spinning rate of 8 kHz and a recycling delay of 0.5s.

Hydrogen temperature programmed reduction (H_2 -TPR) was carried out in a quartz microreactor with a mixture of 10% H_2/Ar (vol.) as the reductive gas. The calcined catalysts (0.1 g) were reduced in a flow of $30 \text{ mL} \cdot \text{min}^{-1}$ and the temperature was raised from 323 K to 1173 K at the ramp rate of $10 \text{ K} \cdot \text{min}^{-1}$. The effluent gas was detected by a thermal conductivity detector after passing through a 5 Å molecular sieve trap to remove the produced water.

The temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out to test the acidic properties of the catalysts. The samples loaded in a quartz micro-reactor were first pretreated at 623 K in a flow of N_2 and then cooled down to 373 K. Afterwards, ammonia was introduced and kept at 373 K for 30 min. Prior to

desorption, the samples were purged with N₂ again to remove the gaseous and physically adsorbed NH₃ at 373 K for 1 h. The desorption profiles were obtained from 373 K to 873 K at a ramping rate of 10 K·min⁻¹. The effluent was detected by the down-stream gas chromatograph with a thermal conductivity detector (TCD).

Catalyst Test

The FTS reaction was conducted in a continuous-flow-type fixed-bed reactor. The catalysts were first pressurized and sieved to the desired grains of 20-40 mesh. The mixture of catalyst and quartz sand was loaded in the center of the stainless steel reactor tube. Prior to the reaction, the catalyst was reduced in situ in the flow of H₂ (80 mL·min⁻¹) at 673 K for 10 h. To prevent possible condensation of the heavy compounds, all the transfer lines were kept at 473 K. During the reaction, the effluent gas released from the reactor was analyzed by online gas chromatography (Shimadzu, GC-2014C). CO and CO₂ were analyzed with an active charcoal column equipped with a thermal conductivity detector (TCD). When testing the zeolite-involved catalyst Co@HZSM-5 and Co/HZSM-5, the hydrocarbons were analyzed using a flame ionization detector (FID) equipped with a capillary column (J&W Scientific GS-Alumina, i.d. 0.53 mm, length = 30 m). To check the possible formation of higher hydrocarbons, the liquid collected in the ice trap was also detected by a silicone SE-30 column, but no C₁₄₊ products can be distinguished. For the conventional Co/SiO₂ catalyst without zeolite, the capillary column was avoided due to the presence of heavy components in the effluent. In this system, the hydrocarbons were analyzed by FID for C₁-C₅ (Porapak Q, online) and for C₆-C₂₅ (SE-30, uniport), respectively. Moreover, to obtain the selectivity of *iso*-paraffins, the condensate hydrocarbons in the ice trap were also analyzed with the GC-FID mentioned above by injection. The results were summed up to obtain the selectivity of corresponding hydrocarbons. The selectivity of hydrocarbons in the reaction system was calculated in terms of carbon mol percentage (c-mol %). Argon was selected as an internal standard, with a concentration of 5 % in the feed gas. The selectivity and CO conversion were calculated using reaction data at 30 h. The temperature and pressure of the reaction were 533 K and 1.0 Mpa,

respectively. The mole ratio of H₂/CO was 2 and W_{catalyst}/F_{syngas} was 5 g·h·mol⁻¹.

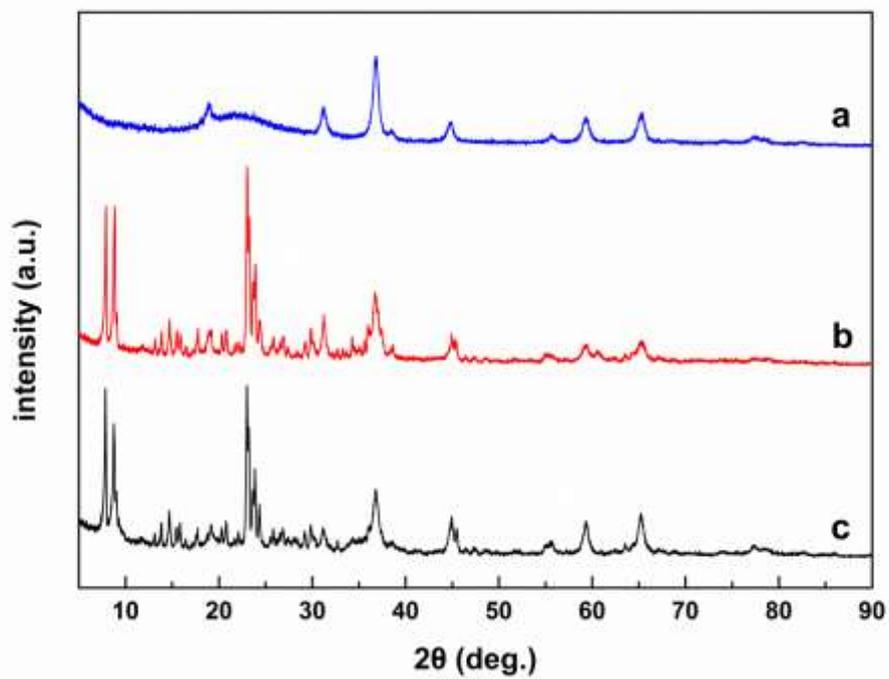


Fig. S1 XRD patterns of (a) Co/SiO₂; (b) Co/HZSM-5; (c) Co@HZSM-5.

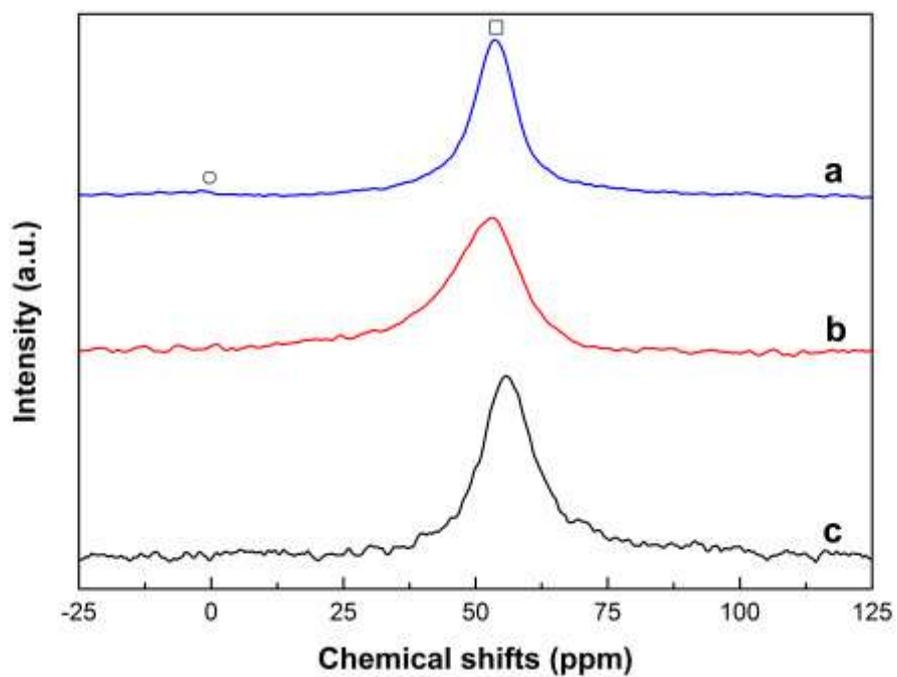


Fig. S2 ^{27}Al NMR spectra of the samples: (a) pure HZSM-5; (b) Co/HZSM-5; (c) Co@HZSM-5. (\square) tetrahedral aluminum, (\circ) octahedral aluminum.

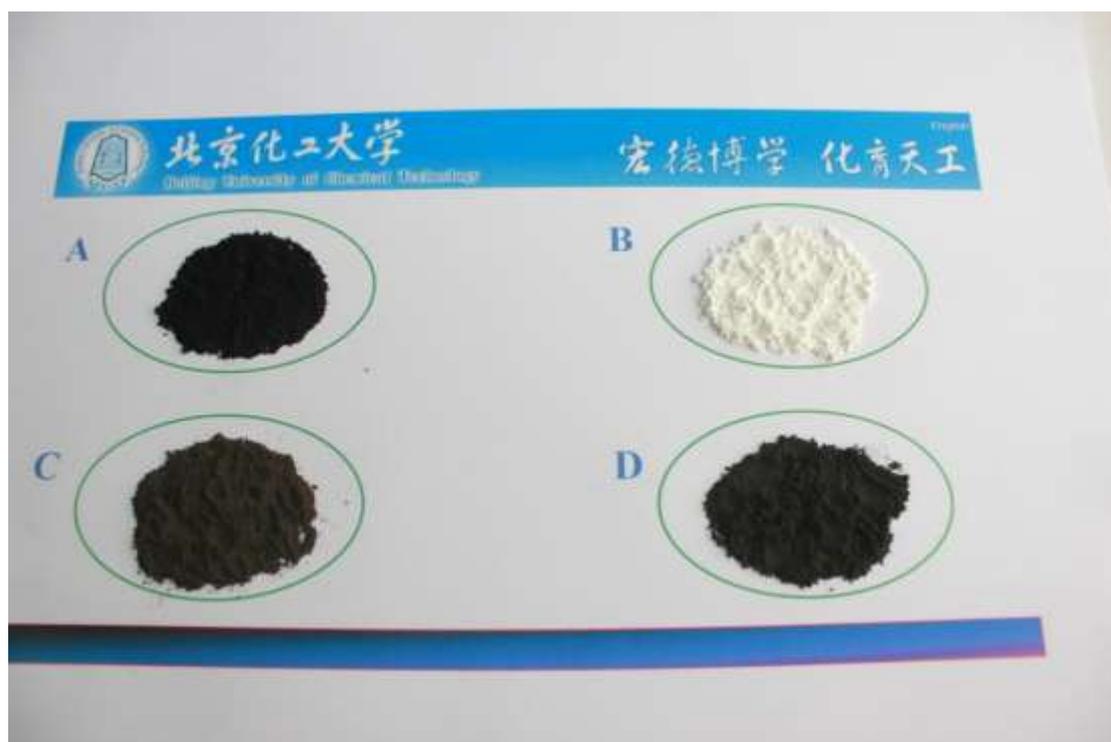


Fig. S3 Digital photos of the catalysts: (a) Co/SiO₂; (b) pure HZSM-5; (c) Co@HZSM-5; (d) Co/HZSM-5.

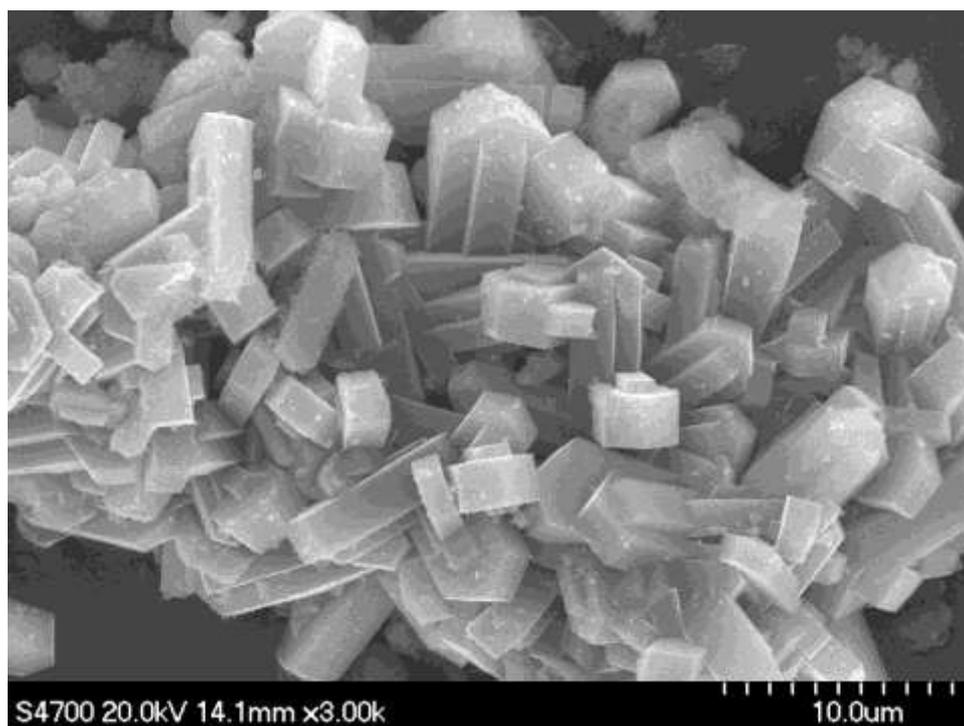


Fig. S4 SEM image of the as-synthesized pure HZSM-5 support

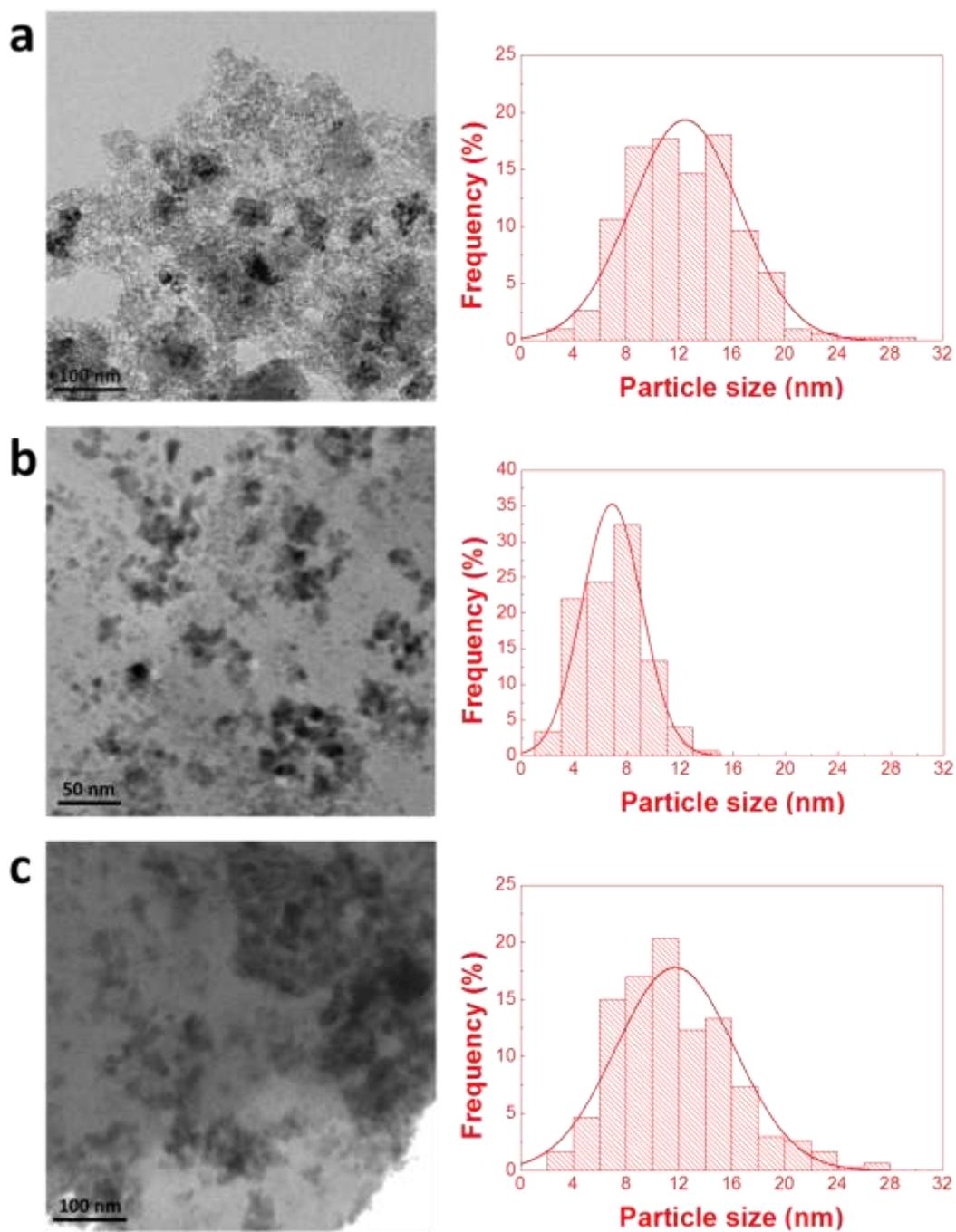


Fig. S5 TEM images of the catalysts and the corresponding particle size distribution of Co_3O_4 : (a) Co/SiO₂; (b) Co/HZSM-5; (c) Co@HZSM-5.

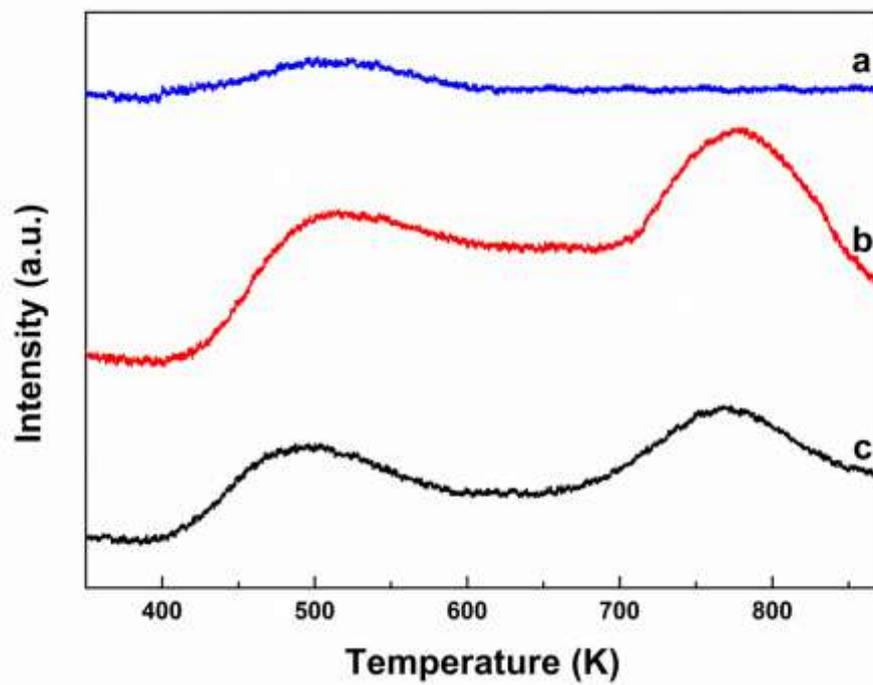


Fig. S6 NH₃-TPD profiles of (a) Co/SiO₂; (b) Co/HZSM-5; (c) Co@HZSM-5.

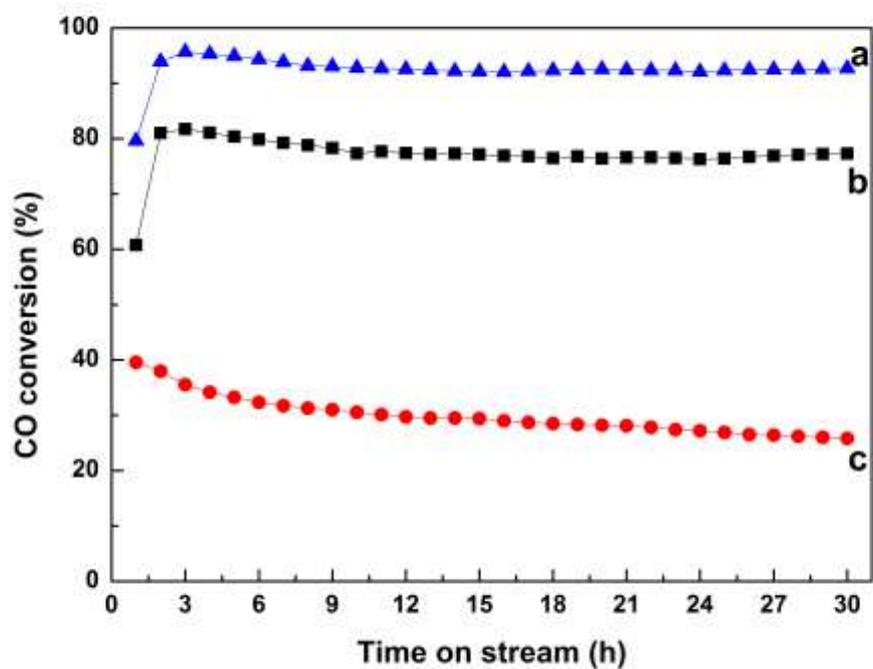


Fig. S7 CO conversion with time on stream over the catalysts: (a) Co/SiO₂; (b) Co@HZSM-5; (c) Co/HZSM-5. Reaction conditions: 1.0 MPa, 533 K, molar ratio of H₂/CO = 2.0, W/F=5 gcat·h·mol⁻¹.

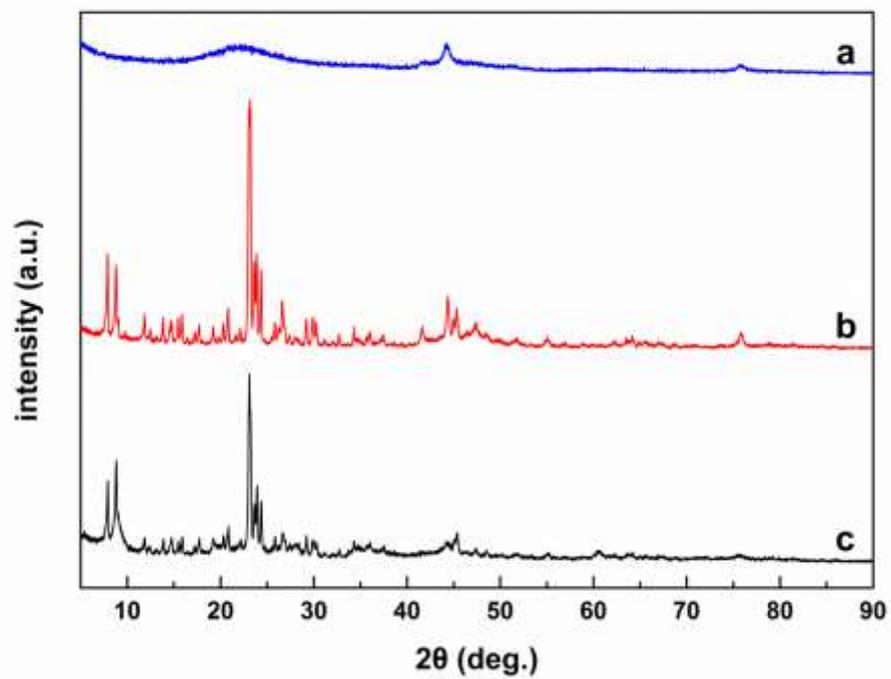


Fig. S8 XRD patterns of the used catalysts: (a) Co/SiO₂; (b) Co/HZSM-5; (c) Co@HZSM-5.