Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Investigation of the deactivation behavior of Co catalysts in Fischer-Tropsch synthesis by using encapsulated Co nanoparticles with controlled SiO_2 shell layer thickness

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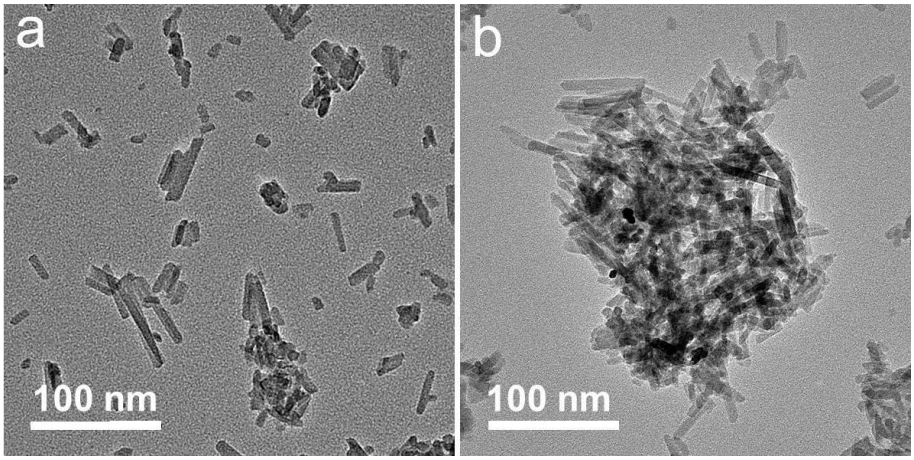

Fig. S1 TEM images of the Co_3O_4 nanorod precursors without calcination.

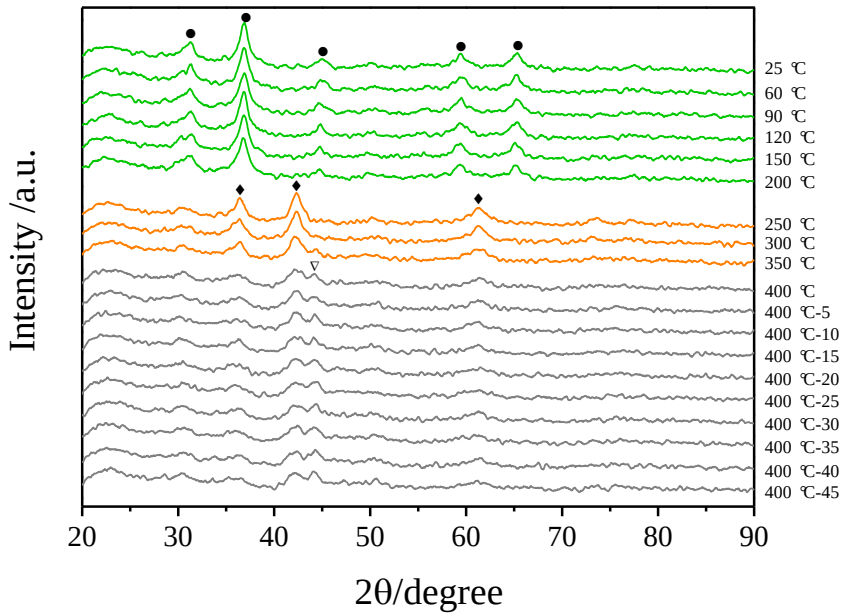

Fig. S2 In situ XRD patterns of 15Co10Zr/SiO_2 (Q50) catalyst. Note that: when conducting the in situ XRD experiment, the sample was in situ heated to 400 ℃ in a pure H_2 flow of 40 mL/min with a rate of 2 ℃ min^{-1}. It took about 7.5 min for each scanning. The x number in 400 ℃-x represents the scanning times when the reduction temperature reached to 400 ℃. ● Co_3O_4; ♦ CoO; ∇ Co.

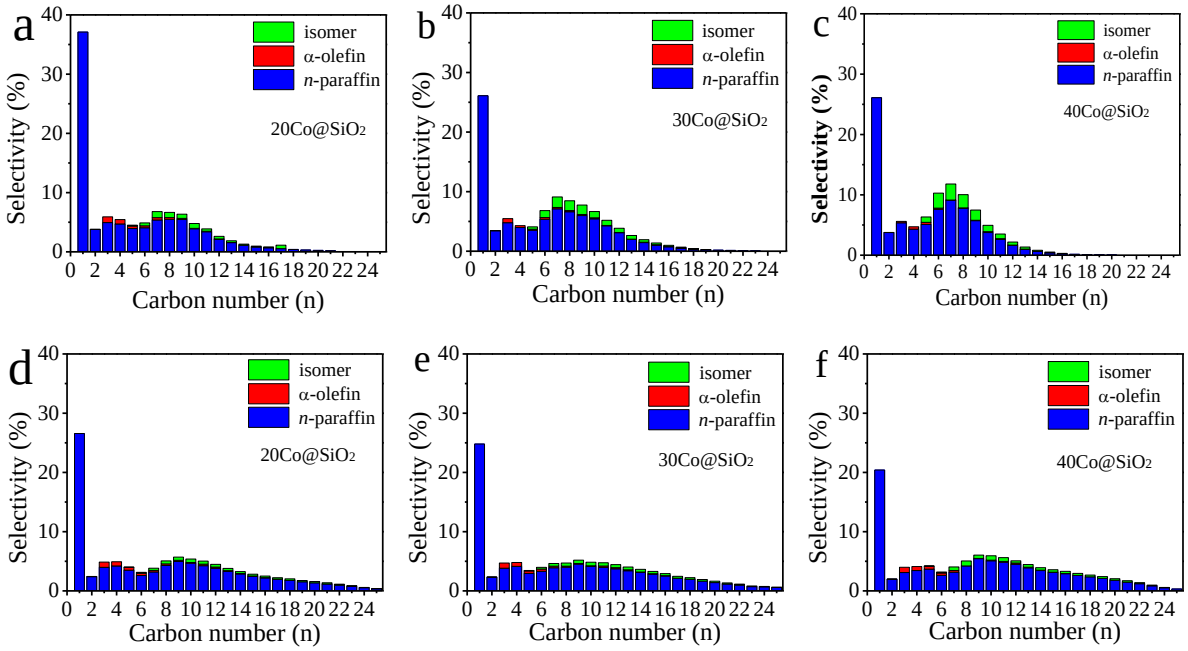

Fig. S3 Carbon number distributions of the FTS reactions over as-prepared catalysts at different reaction temperatures: (a-c) 240 ℃; (d-f) 220 ℃.

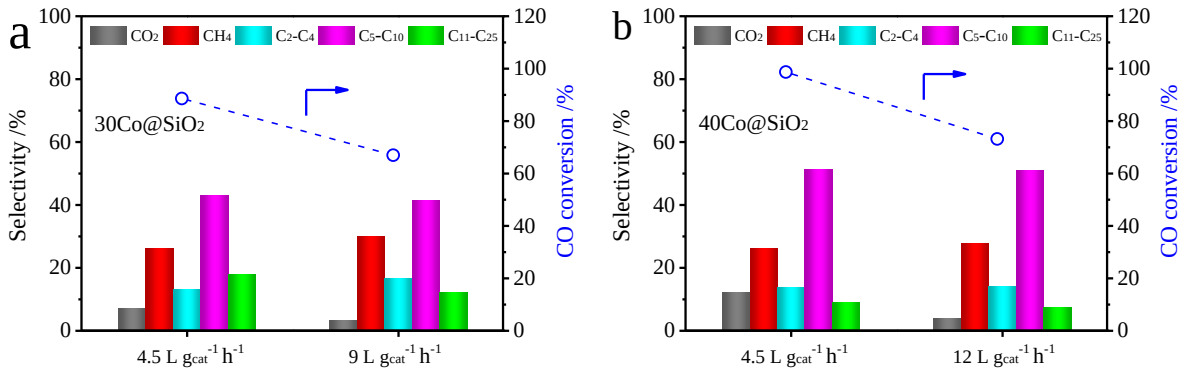

Fig. S4 Effects of GHSV on FTS activity and product distribution over as-prepared catalysts. Reaction conditions: 0.5 g of catalyst, 1 MPa, $H_2/CO/N_2$ =63.3/31.7/5, 240 ℃, 30Co@SiO_2 (a) and 40Co@SiO_2 (b). The values of CO conversion and selectivity were obtained as the average of last 5 h (46-50 h) in 50 h run stream.

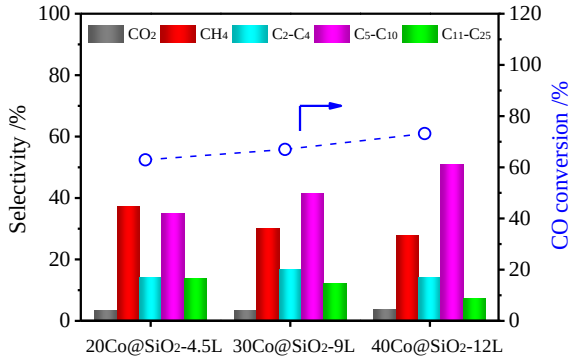

Fig. S5 Comparison of the FTS activity and product distribution over as-prepared catalysts with adjusted GHSV in order to obtain similar initial CO conversion. Reaction conditions: 0.5 g of catalyst, 1 MPa, $H_2/CO/N_2$ =63.3/31.7/5, and 240 ℃. The values of CO conversion and selectivity were obtained as the average of last 5 h (46-50 h) in 50 h run stream.

The calculation method of the water partial pressure can be described as below:

We can set the initial molar number of feeding gas H_2 = 63.3 mol, CO = 31.7 mol, and N_2 = 5 mol. And the CO conversion = x%, CO_2 selectivity = y%, CH_4 selectivity = z1%, ($C_2^{=}$+C_2^{o}) selectivity = z2%, ($C_3^{=}$+C_3^{o}) selectivity = z3%, ($C_4^{=}$+C_4^{o}) selectivity = z4%. Then, the molar number of gas in the reactor can be calculated according to the following equations:

1) Molar $_{H2}$ = 63.3 – 2×31.7×*x*% +31.7×*x*%×*y*%;
2) Molar $_{CO}$ = 31.7-31.7×*x*%;
3) Molar $_{N2}$ = 5;
4) Molar $_{CO2}$ = 31.7×*x*%×*y*%;
5) Molar $_{CH4}$ = 31.7×*x*%×(1-*y*%)×*z*1%;
6) Molar ($C_2^{=}$+C_2^{o}) = {31.7×*x*%×(1-*y*%)×z2%}/2;
7) Molar ($C_3^{=}$+C_3^{o}) = {31.7×*x*%×(1-*y*%)×z3%}/3;
8) Molar ($C_4^{=}$+C_4^{o}) = {31.7×*x*%×(1-*y*%)×z4%}/4;
9) Molar $_{H2O}$ = 31.7×*x*%-31.7×*x*%×*y*%×2

Based on the above obtained molar content of gas in the reactor, the partial pressure of water vapor can be calculated as following equation:

$$P_{H2O} = 1.0*\frac{Molar\ H2O}{(Molar\ H2+Molar\ CO+Molar\ N2+Molar\ CO2+Molar\ CH4+Molar\ C2+Molar\ C3+Molar\ C4+Molar\ H2O)}\ (MPa)$$