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

Supporting Information

Building Premium Secondary Reaction Field with a Miniaturized Capsule Catalyst to Realize Efficient Synthesis of Liquid Fuel Directly from Syngas

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Experimental Section

Preparation of capsule catalyst

Miniaturized and traditional large SiO_2 cores were purchased from Fuji Silysia Chemical Ltd. They possessed similar specific surface area (300 m^2/g), pore volume (1.0 cm^3/g) and average pore diameter (10 nm). However, the average volume size of the two cores were about 7×10^{-4} mm^3 (diameter range of 75-150 μm) and 1.1 mm^3 (diameter range of 0.85-1.70 mm), respectively. To load cobalt on the SiO_2 cores, an aqueous solution of $Co(NO_3)_2{\bullet}6H_2O$ was used to prepare the Co/SiO_2 cores with 10 wt% Co content by incipient wetness impregnation method. After the impregnation, the Co/SiO_2 cores were dried at 393 K for 12 h, followed by calcination in air at 673 K for 2 h. The miniaturized and large core catalysts are separately denoted as Co/SiO_2-M and Co/SiO_2-L. Unless otherwise specified, Co on the core has the same weight of 10 wt%.

In order to coat zeolite ZSM-5 on the Co/SiO_2 core, a hydrothermal method was employed in our coating processes.[1] In brief, $Al(NO_3)_3{\bullet}9H_2O$ was added into a Teflon container at room temperature, which contains the mixture of TPAOH (tetrapropylammonium hydroxide), deionized water and ethanol. Then the sol was stirred in the container for several minutes. After this, TEOS (tetraethylorthosilicate) was slowly added into the above sol, followed by stirring for 6 h. Then, a clear precursor sol with molar composition of 1.0 SiO_2: 0.25 TPAOH: 0.0125 Al_2O_3: 6.0 EtOH: 60 H_2O was obtained. Before hydrothermal treatment, the Co/SiO_2 core pellets were added into above precursor sol. Then the mixture was sealed in a stainless steel autoclave lined by Teflon for hydrothermal treatment at 453 K and 2 day with rotation speed of 2 rpm. After hydrothermal synthesis, the capsule catalysts separated from the mother liquor were washed repeatedly by deionized water and dried at 393 K for 12 h. The capsule catalysts were finally obtained after calcination at 773 K for 5 h. At the same concentration of mother liquor, the capsule catalysts (denoted as Co/SiO_2-M-Z_{6ET} and Co/SiO_2-L-Z) were prepared by adding the same weight of Co/SiO_2-M and Co/SiO_2-L, respectively. The pure zeolite ZSM-5 was prepared without adding Co/SiO_2 core in the hydrothermal process. The miniaturized capsule catalysts prepared by different ethanol dosage and Co content are denoted by Co/SiO_2-M-Z_{4ET}, Co/SiO_2-M-Z_{8ET}, $15Co/SiO_2$-M-Z_{6ET} and $20Co/SiO_2$-M-Z_{6ET}. The Co/SiO_2-M-Z_{4ET} and the Co/SiO_2-M-Z_{8ET} were synthesized by separately using the EtOH ratio of 4.0 and 8.0 in the mother liquor, while the other treatment conditions remained unchanged. The $15Co/SiO_2$-M-Z_{6ET} and the $20Co/SiO_2$-M-Z_{6ET} were prepared by altering cobalt loading weight into 15 and 20 wt% on miniaturized Co/SiO_2 core, and the other synthesis processes were still the same with the Co/SiO_2-M-Z_{6ET}.

Catalyst characterization

The X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (RINT 2400, Rigaku Co.) with Cu-K_α radiation (40 kV and 40 mA). The average size of cobalt oxide in the precursor catalysts was calculated by the Scherrer equation at $2\theta = 37^o$. The sample surface morphology observation was obtained by the scanning electron microscopy (JEOL, JSM-6360LV) combined with the energy-diffusive

X-ray spectroscopy (EDS) (JEOL, JED-2300). The samples used for this analysis were firstly pretreated by an auto fine coater (JEOL, JFC-1600) to coat a platinum layer. The temperature-programmed desorption of ammonia (NH_3-TPD) measurements were carried out with a BELCAT-B-TT (BEL Co.) instrument. Typically, the sample (0.03 g) in a quartz reactor was pretreated by a He gas with a flow rate of 30 mL min^{-1} at 673 K for 1 h. The adsorption of NH_3 was performed at 353 K in an NH_3-He mixture (5 vol% NH_3) for 1 h. Then the TPD was tested in helium flow by raising the temperature to 1073 K with a rate of 10 K min^{-1}. The H_2-TPR was also performed by using BELCAT-B-TT (BEL Co.) instrument. The sample (0.03 g) was firstly pretreated in flowing helium at 423 K for 1 h. After cooling down to 323 K, a H_2-Ar gas mixture (5 vol% H_2) was introduced into the quartz reactor, and then the temperature was raised to 1073 K with the rate of 10 K min^{-1}. H_2 chemisorption measurements were carried out with a Quantachrome Autosorb-1 (Yuasa Co.) instrument. The samples were reduced for 6 h in H_2 gas flow at 673 K. After reduction, the temperature was cooled down to 423 K. The H_2 adsorption isotherms were measured at 423 K. The total H_2 uptake at zero pressure was obtained by extrapolating the linear part of the isotherm. The Co dispersions were calculated by assuming one hydrogen atom on per cobalt surface atom. The diameter of Co particles was estimated from the dispersion by hypothesizing spherical metal particles of uniform diameter with a site density of 14.6 atom nm^{-2} for the supported cobalt particles.[2]

Catalytic reaction

Model reactions of n-hexadecane (n-C_{16}) were performed in a stainless-steel reactor (inner diameter = 10 mm). In short, 0.5 g catalyst mixed with 2.0 g quartz sand was pretreated by a H_2 gas with flow rate of 80 mL min^{-1} at 673 K for 8 h. Then the reactor was cooled down to 423 K and the pressure of H_2 was raised to 1.0 MPa with a H_2 flow rate of 18 mL min^{-1}. After the reaction temperature was raised to 533 K, the n-hexadecane with mole ratio of H_2/n-C_{16} = 30 was introduced into the reactor by a Hitachi CM5110 pump to start the reaction.

Fischer-Tropsch (FT) synthesis was measured by the same reactor operated at 533 K and 1.0 MPa. Before reaction, 0.5 g catalyst mixed with 2.0 g quartz sand were pretreated in H_2 gas with flow rate of 80 mL min^{-1} at 673 K for 8 h. After the reactor was cooled down to 423 K, the syngas with the H_2/CO ratio = 2 and flow rate of 18 mL min^{-1} ($W_{cat.}/F_{CO+H2}$ = 10 gh mol^{-1}) was introduced into the reactor. Then, the temperature and pressure were raised to 533 K and 1 MPa to test the FT performance.

After cracking reactions and FT synthesis, the effluent gas released from the reactor was analyzed by two online gas chromatographs (Shimadzu GC-8A, TCD and Shimadzu GC-14B, FID). An ice trap was used to capture the heavy hydrocarbons between reactor and back pressure regulator. This portion of products was analyzed by an offline gas chromatograph (Shimadzu GC-2014, FID). The selectivity was calculated on a molar carbon basis and catalytic performances after 6 h were used for discussion.

Supplementary Figures and Table

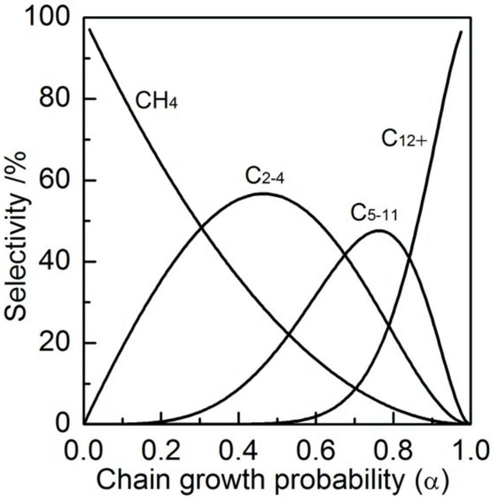

Fig. S1 Anderson-Schulz-Flory (ASF) model for the product distributions.[3] The maximum selectivity of gasoline (C_{5-11}) is only 45 %, if the chain growth probability (α) is 0.75. By the prediction for chain growth probability of 0.86, the selectivity of CH_4, C_{2-4}, C_{5-11}, and C_{12+} is 2.0, 13, 37, and 48 %, respectively.

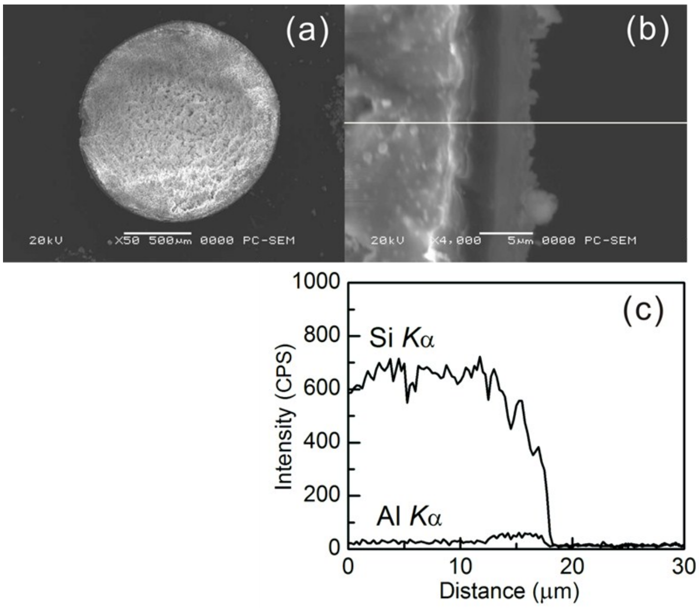

Fig. S2 SEM images and EDS linear scan analysis over the conventional capsule catalyst Co/SiO_2-L-Z. (a) cross section of Co/SiO_2-L-Z, (b) shell section of Co/SiO_2-L-Z, (c) EDS linear scan analysis of Co/SiO_2-L-Z.

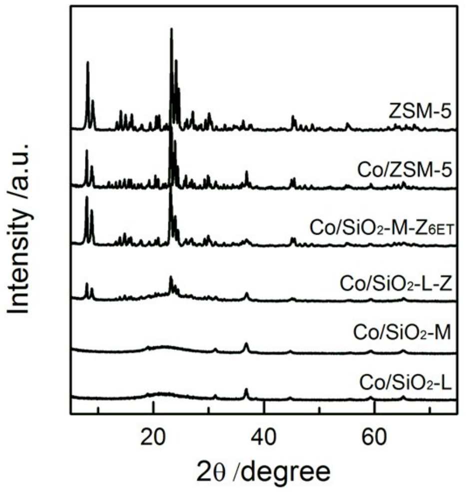

Fig. S3 XRD patterns for the miniaturized capsule and other reference samples. The average size of cobalt oxide in the precursor catalysts was calculated by the Scherrer equation at $2\theta = 37^{o}$.

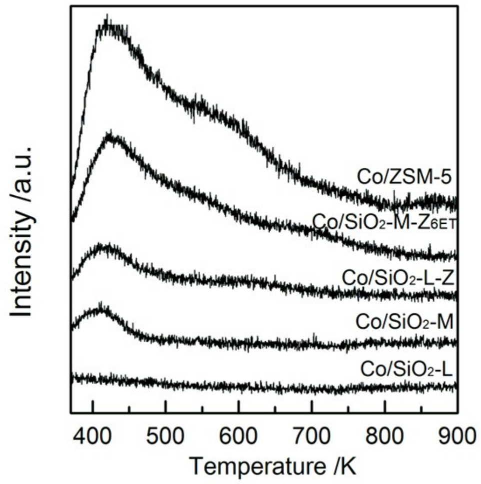

Fig. S4 NH_3-TPD profiles for the miniaturized capsule and other reference catalysts. The peak blow than 500 K should correspond to physical adsorption of NH_3 and weak interaction between NH_3 molecules and zeolite such as hydrogen bond or Lewis acid. The desorption of NH_3 at high temperature higher should be assigned to NH_3 molecules adsorbed on the strong Brønsted acid sites in the zeolite.[4] Only the low temperature peak is displayed on the Co/SiO_2-M and there is no peak on Co/SiO_2-L. Therefore, there is no Brønsted acidity on both Co/SiO_2-M and Co/SiO_2-L core catalysts.

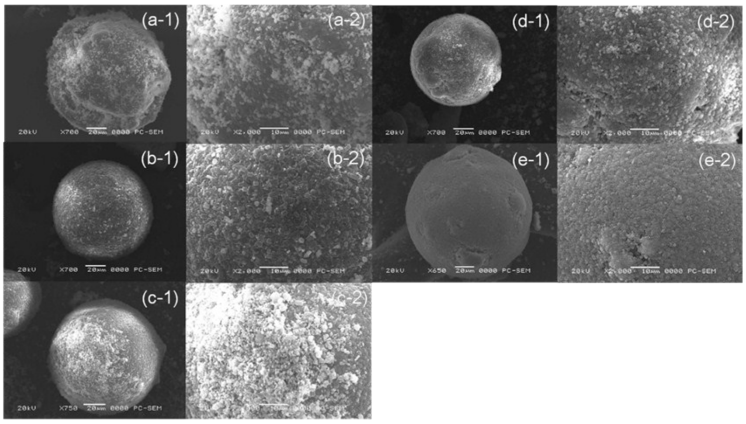

Fig. S5 SEM images of the miniaturized capsule catalysts with different ethanol dosage and cobalt loading weight. (a-1) Co/SiO_2-M-Z_{4ET}, (a-2) outer surface of Co/SiO_2-M-Z_{4ET}; (b-1) Co/SiO_2-M-Z_{6ET}, (b-2) outer surface of Co/SiO_2-M-Z_{6ET}; (c-1) Co/SiO_2-M-Z_{8ET}, (c-2) outer surface of Co/SiO_2-M-Z_{8ET}; (d-1) 15Co/SiO_2-M-Z_{6ET}, (d-2) outer surface of 15Co/SiO_2-M-Z_{6ET}; (e-1) 20Co/SiO_2-M-Z_{6ET}, (e-2) outer surface of 20Co/SiO_2-M-Z_{6ET}.

Table S1 The EDS analysis for the miniaturized capsule catalysts with different ethanol dosage and cobalt weight.

Sample	Al	Si	Si/Al
Co/SiO_2-M-Z_{4ET}	0.39	32	83
Co/SiO_2-M-Z_{6ET}	0.39	30	79
Co/SiO_2-M-Z_{8ET}	0.38	27	72
15Co/SiO_2-M-Z_{6ET}	0.29	30	105
20Co/SiO_2-M-Z_{6ET}	0.21	30	142

These EDS results show the slight decreases of Si/Al ratios with increasing ethanol dosage and the significant increases with increasing cobalt weight.

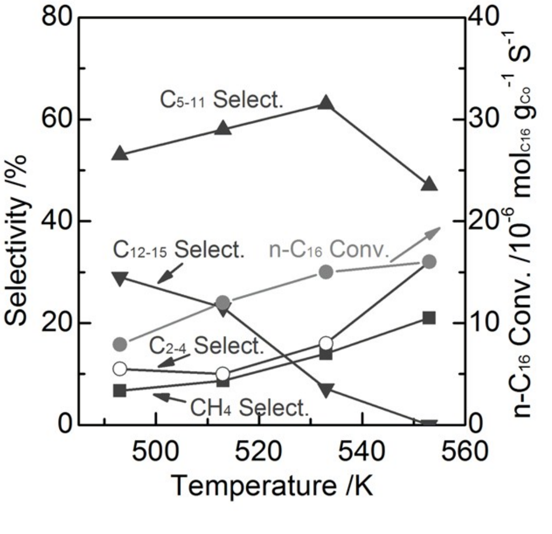

Fig. S6 Model reactions over Co/SiO_2-M-Z_{6ET} with different reaction temperature. Reaction conditions: *T* = 493 ~ 553 K; *P* = 1.0 MPa; flow rate, $W_{cat.}$/F = 10 gh mol^{-1}; H_2/n-C_{16} = 30; catalyst, 0.5 g.

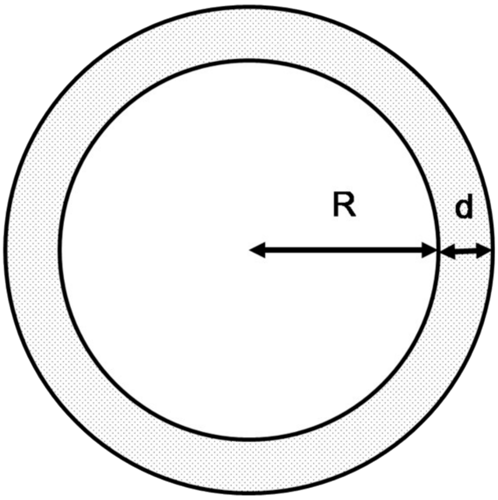

Fig. S7 Capsule model for calculation of the capsule size effect on different average volume size. The parameters of R and d represent the core radius and shell thickness, respectively. According to the parameters, the core volume is $(4/3)\ \pi\ R^3$ and the shell volume of the capsule is $4\ \pi\ R^2d$. Thus, the volume ratio of shell to core is 3d/R. Because it represnts that the core per unit volume can share the amount of shell, we employ this volume ratio to indicate the capsule size effect. By supposing that the thickness d of the shell is same, the capsule size effect of Co/SiO_2-M-Z_{6ET} is increased by more than 10 times when compared with Co/SiO_2-L-Z. It dramatically enhances hydrocracking/isomerization reaction contribution.

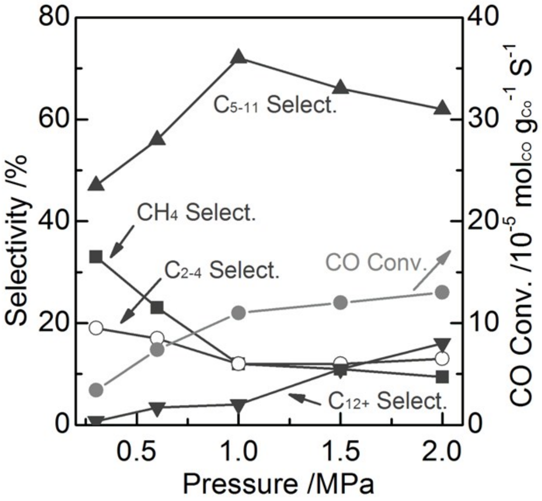

Fig. S8 Fischer-Tropsch synthesis over Co/SiO_2-M-Z_{6ET} with different reaction pressure. Reaction conditions: $T = 533$ K; $P = 0.3 \sim 2.0$ MPa; $H_2/CO = 2.0$; flow rate, $W_{cat.}/F = 10$ gh mol^{-1}; catalyst, 0.5 g.

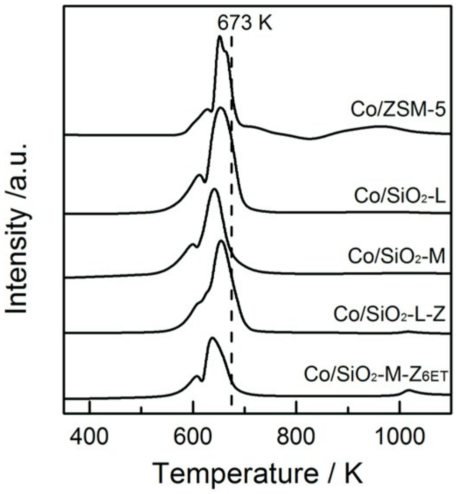

Fig. S9 H_2-TPR profiles for the pure Co/ZSM-5, two core catalysts and two capsule catalysts. Reduction degrees were calculated by the peak areas before 673 K. Due to high reduction degree on our capsule catalysts Co/SiO_2-L-Z and Co/SiO_2-M-Z_{6ET}, the relative Co contents were separately calculated by comparing total peak areas over large core Co/SiO_2-L and miniaturized core Co/SiO_2-M.

Table S2 The physicochemical properties and the conversions over the miniaturized capsule and other reference catalysts.

Sample	Reduction degree [%][a]	Co content [%][b]	H_2 chemisorption amount [mmol g_{Co}^{-1}][c]	Size of Co_3O_4 [nm][d]	Co dispersion [%][e]	Mean Co size [nm][f]	n-C_{16} Conv. [%][g]	CO Conv. [%][h]
Co/ZSM-5	67	10	0.41	17	7.2	13	99	90
Co/SiO_2-L	83	10	0.61	14	8.7	11	89	95
Co/SiO_2-M	87	10	0.69	13	9.4	10	93	98
Co/SiO_2-L-Z	81	8.2	0.65	12	9.4	10	96	90
Co/SiO_2-M-Z_{6ET}	85	5.6	0.70	12	9.6	10	93	70
Co/SiO_2-M+Z	/ [i]	/	/	/	/	/	75	62

[a] Calculated by the peak areas before 673 K. [b] Calculated from total peak areas. [c] Evaluated from the H_2 chemisorption measurement on per gram cobalt. [d] Calculated by the XRD at $2\theta = 37^o$. [e] Calculated using the H_2 chemisorption amount and Reduction degree. [f] Calculated using the hypothesis of spherical Co model. [g] The results of n-C_{16} conversion from model reactions. [h] The results of CO conversion from FT synthesis. [i] Not detected.

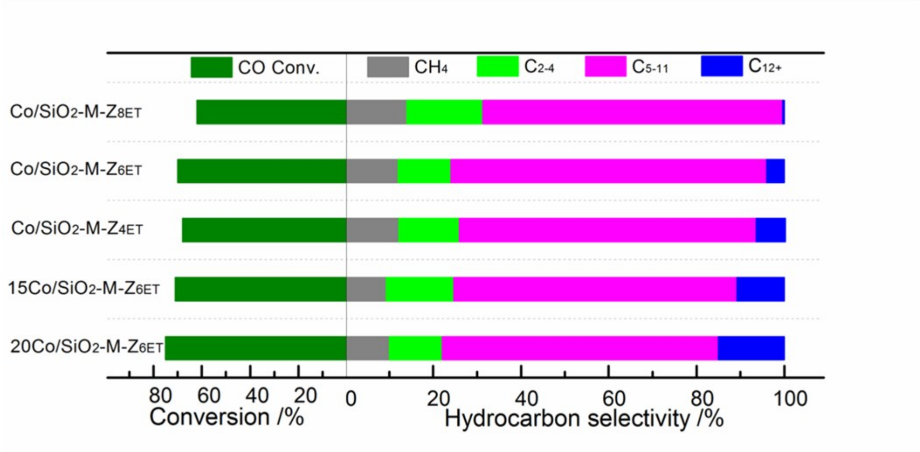

Fig. S10 Fischer-Tropsch synthesis on the miniaturized capsule catalysts with different ethanol dosage and cobalt loading weight. Reaction conditions: T = 533 K; P = 1.0 MPa; H_2/CO = 2.0; flow rate, $W_{cat.}$/F = 10 gh mol^{-1}; catalyst, 0.5 g.

References

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