Slicon carbide supported cobalt for Fischer-Tropsch synthesis: Probing into the cause of the intrinsic excellent catalytic performance

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Electronic Supplementary Information (ESI)

Experimental Section

Al$_2$O$_3$@SiC support synthesis.

The Al$_2$O$_3$@SiC support was synthesized via a two-step process. First, 13g β-SiC (Aladdin, 40 nm in diameter) was put into 500 mL NaOH solution (20 wt%) at 353 K under stirring for 24 h to remove the surface Si$_x$O$_y$ layer (3.5±0.5 wt%).[1] The obtained mixture was filtrated and washed thoroughly with deionized water for several times until the pH of the filtrate was 7. The filter cake was then dried in air at 393 K for 10 h in an oven and denoted as R-SiC. Second, the Al$_2$O$_3$ was coated on the R-SiC by a precipitation method. Specifically, 10 g R-SiC, 15 g polyvinylpyrrolidone (PVP, MW = 1,300,000, Aladdin), 3.68 g Al(NO$_3$)$_3$•9H$_2$O (Aladdin)and 5.88 g CO(NH$_2$)$_2$ (Aladdin) (n$_{(Al(NO3)3•9H2O)}$: n $_{(CO(NH2)2)}$ = 1:10) were added into 2 L H$_2$O and stirred for 2 h under ultrasonic treatment at RT. The adding of PVP was to make sure a homogeneous dispersion of SiC. Next, the mixture was kept stirring for 72 h at 343 K to guarantee the Al^{3+} precipitated. The mixture were then filtrated and washed with deionized water many times to remove the residual CO(NH$_2$)$_2$. Finally, the products were dried at 383 K for 12 h and calcined at 823 K for 10 h in an air flow and denoted as Al$_2$O$_3$@SiC.

Al$_2$O$_3$ support synthesis

In order to obtain similar chemical nature, the Al$_2$O$_3$ support was prepared by the same method with that Al$_2$O$_3$ species on Al$_2$O$_3$@SiC. In a typical synthesis, 147.2 g Al(NO$_3$)$_3$•9H$_2$O, 235.2 g CO(NH$_2$)$_2$ (n$_{(Al(NO3)3•9H2O)}$: n $_{(CO(NH2)2)}$ = 1:10) and 15g PVP were added into 2 L H$_2$O. After stirring for 72 h at 343 K, the mixture were filtrated and washed with deionized water many times. Finally, the products were dried at 383 K for 12 h and calcined at 823 K for 10 h in an air flow.

Catalysts synthesis

The preparation of catalyst was performed by excessive wetness impregnation method. At the beginning, the desirable supports (5 g) were added into the ethanol solution (20 ml) containing the required amounts of $Co(NO_3)_2 \cdot 6H_2O$ (Aladdin) to achieve nominal Co loading of 10 and 15 wt%. Then, the mixed solutions were stirred to dry at RT. The samples were further dried in an oven at 373 K overnight. Finally, the solid powders were calcined at 673 K for 6 h in air by increasing the temperature at a heating rate of 1 K/min.

Catalysts characterization

ICP-OES The content of Al in the $Al_2O_3@SiC$ was measured by ICP-OES method using the Thermo iCAP 6300 instrument. Before the experiment, about 20mg sample was completely dissolved in a $HNO_3/HF/HCl$ solution (1/1/3 volume ratio).

N_2 adsorption-desorption experiments were conducted at -195°C using a Micromeritics ASAP 2020 instrument to obtain specific surface area, total pore volume and pore size distribution. Prior to an experiment, the sample was outgassed at 200°C for 6 h. The BET surface areas were obtained for adsorption data in a relative pressure range from 0.05 to 0.30. The total pore volumes were calculated from the amount of N_2 vapor adsorbed at a relative pressure 0.99. The pore size distributions were evaluated from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

X-ray diffraction spectra for the supports and calcined catalysts were recorded with a DX-2700 diffractometer using monochromatized Cu Kα radiation. The spectra were scanned at a rate of 4°min^{-1} in the range 2θ = 5-85°. The average particle size of Co_3O_4 in the calcined catalysts was calculated from the most intense Co_3O_4 line (2θ =36.9°). The corresponding Co^0 particle size in reduced catalysts was then obtained from the Co_3O_4 particle size by applying the molar volume correction: d (Co^0) = 0.75 d (Co_3O_4).

Temperature-programmed NH_3 desorption (NH_3-TPD) was measured by an AutoChem II chemisorption analyzer (Micromeritics). 100 mg of the supports were first degassed under He flow at 873 K for 1 h and then saturated with NH_3 at 373 K during 1 h, using a flow of 1.65% NH_3 in He. The gas mixture was then switched back to He, and the sample was purged at 373 for 1 h to remove the weakly adsorbed NH_3 molecules. TP desorption was subsequently recorded under He flow, from 373 to 873 K. All flow rates were adjusted to 40 cm^3 min^{-1}, and the heating rates were 10 K min^{-1} during different stages of the experiment.

The reduction behavior of supported oxidized cobalt phases was studied by hydrogen temperature-programmed reduction in a TP-5080 multi-purpose automatic adsorption instrument. About 30 mg of sample were initially flushed with an N_2 flow at room temperature for 30 min, then a mixture of 10 vol% of H_2 in N_2 was passed through the catalyst and the temperature increased up to 1173 K at a heating rate of 10 K/min. The H_2 consumption rate was monitored in a thermal conductivity detector (TCD) calibrated previously using the reduction of CuO as standard. The extent of cobalt reduction was obtained from a method reported before, based on the fact that supported Co_3O_4 crystallites have been shown to be reduced to CoO at temperature typically below 673 K, while higher temperatures are needed to reduce CoO to

metallic cobalt.[2]

Cobalt dispersions were measured with H_2 chemisorption in an ASAP 2010C Micromeritics equipment by extrapolating the total gas uptakes in the H_2 adsorption isotherms at zero pressure. Prior to adsorption, the samples (*ca.* 250 mg) were pretreated in flowing Ar at 393 K for 30 min, and then were reduced *in situ* by flowing pure H_2 at a heating rate of 1 K/min^{-1} to 673 K and maintaining at this temperature for 6 h. Subsequently, the samples were evacuated at 673 K for 30 min, and then the temperature lowed to 373K. The H_2 adsorption was conducted at 373 K. The number of surface Co sites was calculated using the total (reversible + irreversible) amount of chemisorbed H_2 by assuming H/Co =1. Cobalt dispersion based on H_2 adsorption calculated from D = 96X/81.6/WR, with D being the cobalt dispersion, W the weight percentage of cobalt, X the total H_2 uptake and R the degree of cobalt reduction.[3]

The electronic states of cobalt on catalysts surface were characterized by X-ray photoelectron spectroscopy (AXIS-ULTRA DLD) using Al-Kα radiation. The fresh catalysts were pressed into thin disks and evacuated in the prechamber of the spectrometer at 10^{-9} mbar. The C_{1s} peak at 284.6 eV was used to correct for charging effects.

The surface morphologies of the samples were characterized by transmission electron microscopy (TEM) using a FEI Tecnai G2 F30 S-TWIN microscope operated at 300 KV. Before microscopy observation, the samples were suspended in ethanol under ultrasonic vibration for 10 minutes. Afterwards, a drop of this suspension was brought onto a holey carbon film on a copper grid.

2.3. Catalytic testing

The Fischer-Tropsch synthesis reaction was carried out in a tubular fixed-bed stainless steel reactor (I.D. = 10 mm). In a typical experiment, 2 g fresh catalyst (pellet size: 0.18-0.25 mm) was mixed with 2 g SiC and fixed into the reactor. Then, the catalyst was reduced *in situ* at 0.5 MPa in flowing pure H_2 at 673 K for 6 h at a heating rate of 1 K/min. After reduction, the temperature was cooled down to 373 K under the flow of H_2, and subsequently the reactant gas mixture (H_2/CO/N_2 in a volume ratio of 64/32/4, N_2 used as internal standard) was switched to pass through the reactor. Ultimately, the reaction pressure was slowly increased up to 2.0 MPa, and the temperature was raised up to the given temperature at a heating rate of 1 K/min. A constant gas hourly space velocity (GHSV) of 1.0 $L_{syngas}/(g_{cat}.h)$ was applied for all catalysts in each reaction.

During the experiment, liquid products and waxes were collected in a cold trap at *ca.* 278 K and hot trap at *ca.* 393 K, respectively. After separation from water, these liquid hydrocarbons as well as waxes were weighted, dissolved in CS_2, and analyzed offline on a GC-2010 chromatograph which was equipped with a 35 m OV-101 capillary column. The gas effluent was analyzed online on a GC-920 chromatographs equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). After a steady state was reached at time on stream (TOS) above 48 h, reaction parameters were started to be collected. Nitrogen balance, oxygen balance, carbon balance and total mass balance were satisfactory (100 ± 5%) to ensure reliable results.
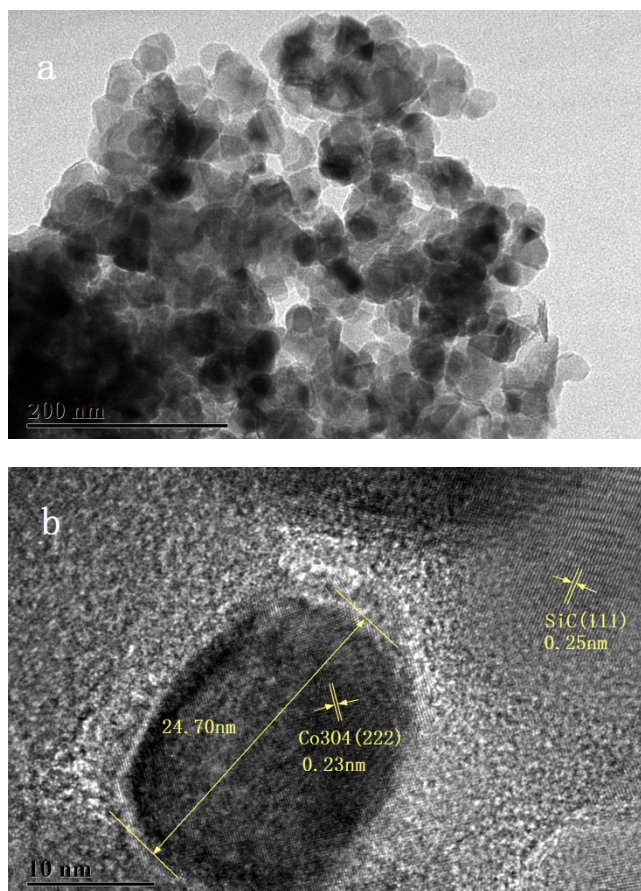
Figure S1. TEM images of the fresh Co/SiC catalyst: a) with low resolution; b) with high resolution.

SiC was low surface area material and no pore structure was exist on each SiC particle (Fig. 1 in the article). From the Fig. S1 a) we can see Co/SiC particles always gathered together to form agglomerates. Therefore, the measured pore structure from N_2 physisorption might be the interspace between each particle. From Fig. S1 b) we can see that the particle size of Co_3O_4 was larger than 20 nm, which was in the same scale with SiC support (40 nm). It should be mentioned that Co_3O_4 particle was contacted with SiC，not located inside pores. Hence, for the powdered Co/SiC catalyst, the pore structure effect on FTS should be negligible.
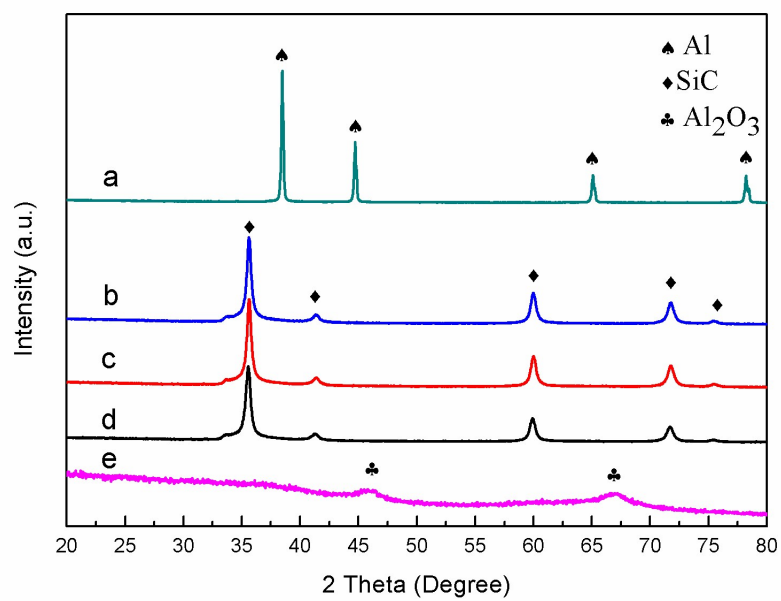
Figure S2. XRD patterns of the supports: a) Al; b) SiC; c) R-SiC; d) $Al_2O_3@SiC$; e) Al_2O_3
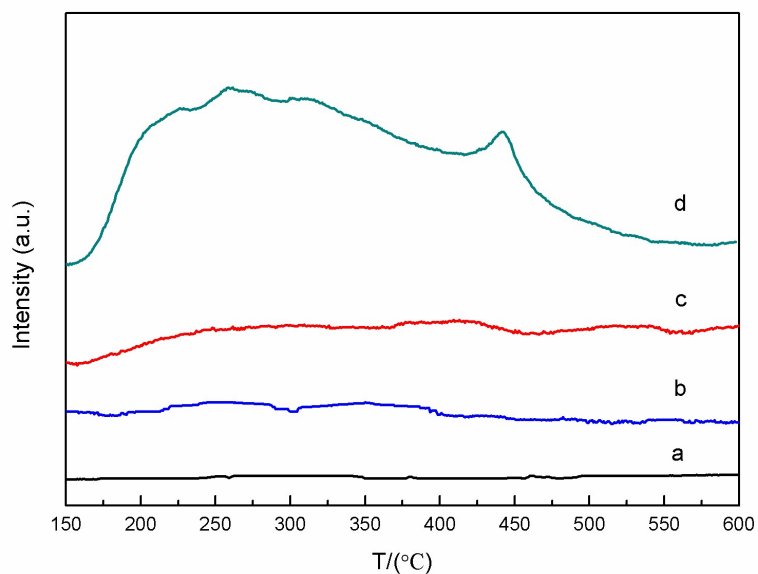
Figure S3. NH$_3$-TPD profiles of : a) SiC; b) Al; c) Al$_2$O$_3$@SiC; d) Al$_2$O$_3$

For SiC, no obvious NH$_3$ desorption peak was observed, indicating that SiC was a non-acid support. Two peaks at around 530 K and 710 K were observed for Al$_2$O$_3$. The first was known to arise from the weakly adsorbed NH$_3$ molecules, whereas the second one originated from the stronger Brønsted acid sites.[4] As far as the Al$_2$O$_3$@SiC and Al powders, the two peaks were also observed, indicating the formation of Al$_2$O$_3$ on the surface. However, the intensity of the peaks was weaker, which was due to the low content of Al$_2$O$_3$.
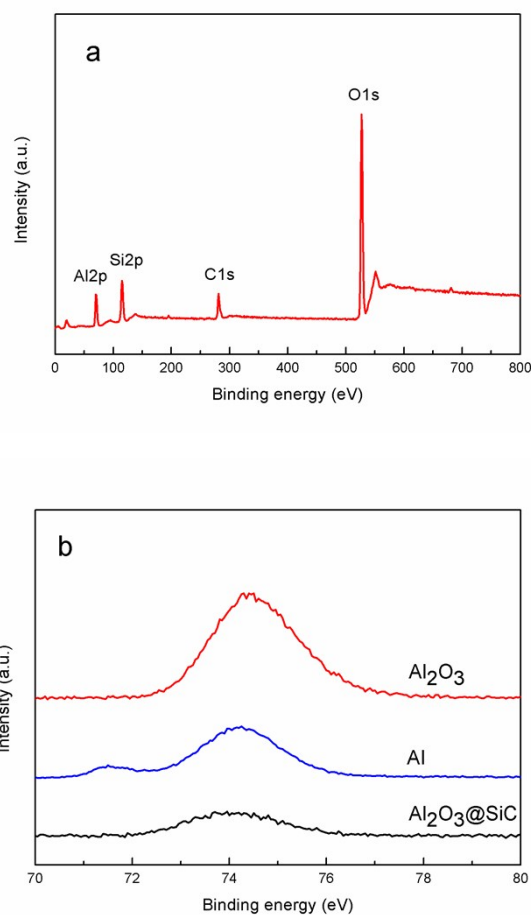
Figure S4. a) XPS wide spectra of $Al_2O_3@SiC$; b) Al 2p XPS spectra for Al_2O_3, Al powders and Al_2O_3.

As can be seen from Fig.S4a, the scan spectrum confirms the existence of Al, O, C and Si elements. Fig. S4b depicts the XPS spectra of Al2p for $Al_2O_3@SiC$, Al powders and Al_2O_3. The peak with a binding energy of 74.2 eV was observed for $Al_2O_3@SiC$, indicating that the Al_2O_3 was located on the surface of R-SiC. The XPS spectra of Al powders showed two peaks at BE of 71.5 and 74.2 eV, respectively. The first peak at BE of 71.5eV is the Al2p for metallic Al while the second peak at BE of 74.2 eV is the Al2p for Al_2O_3. This confirms us that there is a thin Al_2O_3 layer on the surface of Al powders.
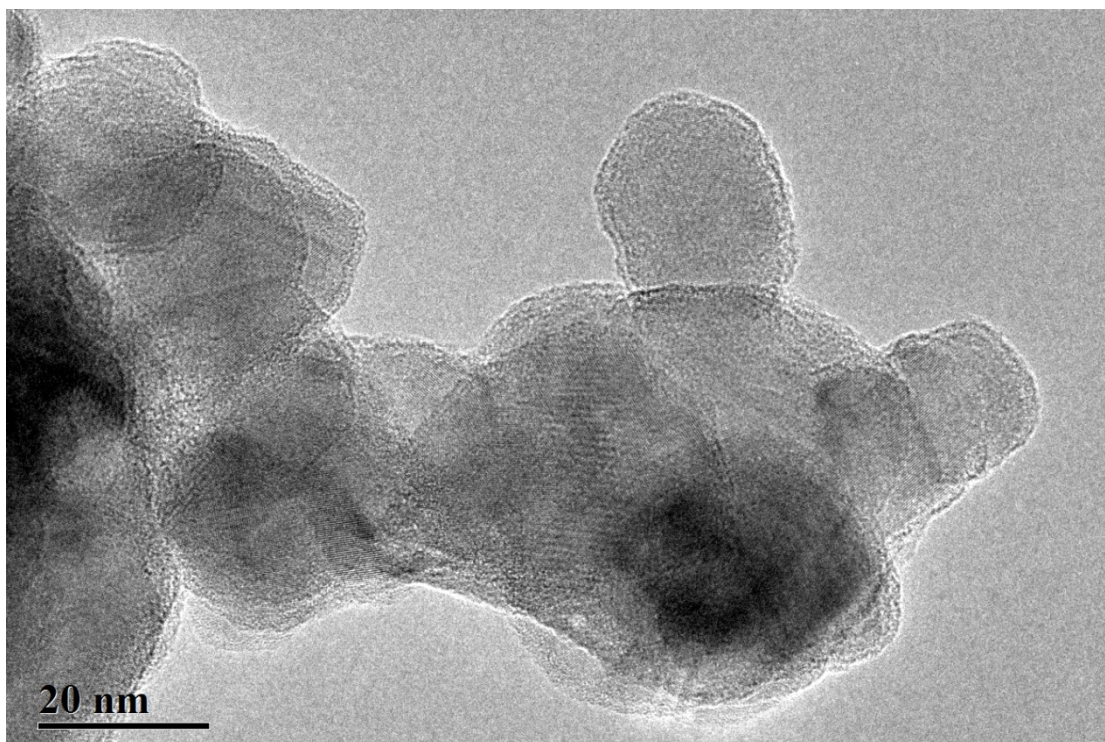
Figure S5. TEM images of Al$_2$O$_3$@SiC with low resolution.
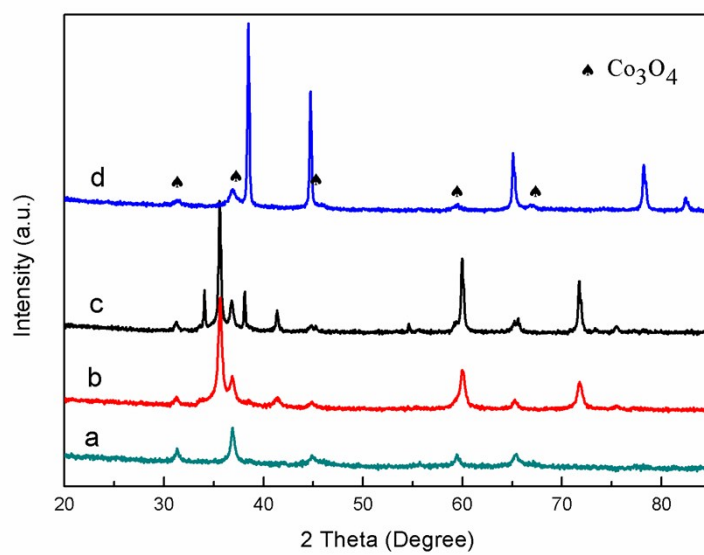
Figure S6. XRD patterns of catalysts: a) Co/Al$_2$O$_3$; b) Co/Al$_2$O$_3$@SiC; c) Co/SiC; d) Co/Al.

Table S1. FTS performance of Co/SiC with small and large particle size.[a]

catalyst	T	CO	Product selectivity[%]		
	(°C)	Conv.(%)	CH_4	C_{5+}	CO_2
15Co/SiC-S[b]	225	70.1	6.6	88.7	0.2
15Co/SiC-L[c]	225	58.2	12.5	76.8	2.7

[a] Reaction conditions: $n(H_2)/n(CO) = 2$, GHSV = 1.25 $L_{syngas}g_{cat}h^{-1}$, P = 2.0 Mpa, TOS = 48 h.
[b] Co/SiC with small pellet size (0.15-0.18 mm).
[c] Co/SiC with large pellet size (1.4-2.0 mm).

As can be see, the CO conversion of Co/SiC-L is lower, compared with Co/SiC-S. In addition, Co/SiC-L exhibits higher CH_4 selectivity and lower C_{5+} selectivity. This could be attributed to the serious intraparticle mass transfer limitation on Co/SiC-L. It is believed that the intraparticle diffusion limitation could alter the reaction rate and products selectivity of FTS.[5] During FTS reaction, the calatyst pores are filled with liquid waxes and reactants should diffuse in the waxes to arrive at the active sites. Thus, if the diffusion length is too long, the H_2/CO ratio will be much higher inside the catalyst particle because of the higher hydrogen diffusivity. And at lower CO concentrations, FT synthesis kinetics favors the formation of light paraffins, especially methane.[6] The bad catalytic performance of Co/SiC-L suggests that the mass teansfer limitation is existed on Co/SiC. Therefore, the traditional viewpoint that meso-macroporous structure of SiC could significantly enhance intraparticle mass transfer during FTS, favoring the production of heavy hydrocarbons is not applicable for the powdered Co/SiC.

Table S2. Al and Na elements content in Al_2O_3@SiC support.

Support	Na (ppm)	Al (wt%)	Al_2O_3[a] (wt%)
Al_2O_3@SiC	29	2.1	3.8

[a] $w(Al_2O_3) = w(Al) \times (27 \times 2 + 16 \times 3)/(27 \times 2)$

Table S3. Textural properties of the supports.

Support	B.E.T. (m^2/g)	PD (nm)[a]	PV (cm^3/g)[b]
SiC	32.1	12.5	0.11
R-SiC	33.8	12.3	0.11
Al_2O_3@SiC	38.5	11.2	0.15
Al	10.3	17.2	0.04
Al_2O_3	244.3	4.4	0.39

[a] Mean pore diameter estimated from the adsorption branches of the isotherms using the B.J.H method.
[b] Total pore volume of pores less than 300 nm.

Table S4. FTS catalytic performance over the low thermal conductive Co/Al_2O_3 and high thermal conductive Co/SiC tested with and without using heat disperser.

catalyst	T_{wall}[b] /K	$T_{centerline}$[c] /K	ΔT[d] /K	X_{CO} %	Products selectivity (wt%) CH_4	C_2-C_4	C_{5+}	CO_2
$30Co/Al_2O_3$ with disperser [a]	498	500.8	2.8	59.3	11.4	9.2	77.8	1.6
$30Co/Al_2O_3$ without disperser	498	502.1	4.1	78.4	11.6	9.4	76.6	2.4
$15Co/SiC$ with disperser	493	495.6	2.6	59.1	5.9	5.2	88.7	0.2
$15Co/SiC$ without disperser	493	495.7	2.7	59.5	6.2	5.5	88.1	0.2

Reaction conditions: $n(H_2)/n(CO) = 2$, GHSV = 1.25 $L_{syngas}g_{cat}h^{-1}$, P = 2.0 Mpa, TOS = 48 h.

[a] SiC is used as heat disperser.

[b] The wall temperature for Co/Al_2O_3 and Co/SiC is different in order to obtain a similar CO conversion.

[c] $T_{centerline}$ is the highest temperature in the center of the reactor observed during the FTS reaction.

[d] $\Delta T = T_{centerline} - T_{wall}$.

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