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Journal Name

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

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The thin Si_xO_y layer on SiC surface is changed to Al_2O_3 to form Al_2O_3@SiC. Co/Al_2O_3@SiC shows distinct different catalytic behaviour with Co/SiC, indicating that the Si_xO_y layer on the surface of SiC plays a great role in the intrinsic excellent catalytic performance of Co/SiC.

Fischer-Tropsch synthesis (FTS) is a key technology in the gas-to-liquids (GTL) process, which transforms synthesis gas derived from natural gas, coal or biomass into high quality ultra-clean fuels or valuable chemicals.[1-3] The FTS is a high exotheric reaction, which could cause an adiabatic temperature rise of up to 1750 K.[4] High temperature gradient might exist within catalyst bed, which could threaten the safety of the plant particularly for large scale commercial production, provided that the generated heat could not be removed effectively.[5,6]

Recently, high thermal conductive silicon carbide (β-SiC) has been reported as support for FTS and the prepared catalyst exhibits excellent catalytic performance, that is, high C_{5+} (> 90%) and low CH_4 selectivity.[7-11] According to the most accepted viewpoint at present, two factors are responsible for the good catalytic performance of Co/SiC. On one hand, it is assumed that the heat generated during reaction could not be completely evacuated to the entire body of traditional insulated supports (Al_2O_3, SiO_2, TiO_2), leading to the formation of "hot spots" on the surface of catalyst, which favors the formation of light products.[8] For Co/SiC, the high thermal conductivity of SiC facilitates heat dissipation throughout the catalyst body, avoiding the formation of "hot spots" on catalyst surface, thus enhances the selectivity to long-chain hydrocarbons.[10] However, no research has verified the correctness of the explanation at present. On the other hand, it is reported that the meso-macroporous structure of SiC

could significantly enhance intraparticle mass transfer during FTS, which favors the production of heavy hydrocarbons.[8] However, many research results, both experimental and computational have pointed out that the intraparticle mass transfer limitation could only affect the intrinsic reactive behavior for those catalysts with large pellet sizes.[12,13] Therefore, the pore structure effect on powdered Co/SiC catalysts should be negligible (Fig. S1 and Table S1, ESI†). On the silicon carbide surface, there is a thin amorphous Si_xO_y (3.5±0.5 wt%) layer.[14,15] No research has focused on the effect of the Si_xO_y layer on the FTS performance so far. In brief, the traditional explanations for the remarkable catalytic performance of Co/SiC are not very persuasive.

Actually, it is of great significance to probe into the cause of the intrinsic excellent catalytic performance for Co/SiC, as the obtained research findings could be utilized to guide the preparation of FTS catalysts with remarkable performance similar to Co/SiC. Herein, we have systematically investigated the possible reasons for the good performance of Co/SiC. SiC support was treated with NaOH to remove the Si_xO_y layer, the obtained material was denoted as R-SiC. Then the prepared R-SiC was coated a layer of Al_2O_3 using precipitation method, the obtained sample was denoted as Al_2O_3@SiC. In order to obtain similar surface chemical nature with Al_2O_3@SiC, traditional low thermal conductive Al_2O_3 support was also prepared by precipitation method. Co/Al_2O_3 and Co/Al_2O_3@SiC catalysts are used to investigate the effect of thermal conductivity on FTS performance. Co/SiC and Co/Al_2O_3@SiC catalysts are used to investigate the effect of the Si_xO_y layer on FTS performance. Co/Al catalyst is also used as comparison because of the similar structure with SiC.

The content of Al_2O_3 on Al_2O_3@SiC is 3.8 wt%, which is close to the content of amorphous Si_xO_y on SiC (Table S2, ESI†). The specific surface area of Al_2O_3@SiC is a little higher than SiC, which could be attributed to the introduction of Al_2O_3 layer on the surface (Table S3, ESI†). No characteristic diffraction patterns of Al_2O_3 are detected for Al_2O_3@SiC and Al powder, which might be attributed to the lower content of alumina or the alumina particles are too small to be detected (Fig. S2

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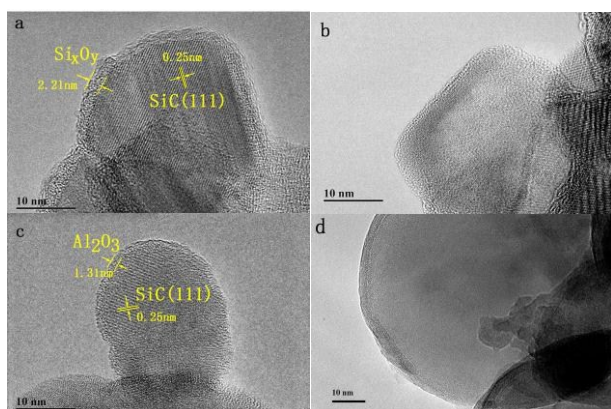

Fig.1 Typical HRTEM images of the materials: a) SiC; b) R-SiC; c) Al_2O_3@SiC; d) Al powders.

ESI†). From NH_3-TPD result, two peaks at around 530 and 680 K are observed for Al_2O_3@SiC and Al powders, indicating the existence of Al_2O_3 phase. However, no obvious NH_3 desorption peak is observed for SiC, indicating that SiC is a non-acid support (Fig. S3, ESI†). XPS technique is also used to investigate the surface character of the supports. The peak centered at 74.2 eV can be observed for Al_2O_3@SiC and Al powders, which is assigned to the Al2p of Al_2O_3 (Fig. S4, ESI†).[16] This suggests that Al_2O_3 phase is located on the surface of Al_2O_3@SiC and Al powders. The morphology of the support materials has been studied by TEM. As shown in Fig. 1, there is a thin amorphous layer with a thickness of about 2.21 nm on the surface of SiC, which could be Si_xO_y layer. After treating with NaOH, the amorphous layer could not be seen on R-SiC any more, demonstrating that the amorphous Si_xO_y layer is removed. For Al_2O_3@SiC, a new layer with a thickness of about 1.31 nm can be observed on the surface of Al_2O_3@SiC. According to the XPS result talked above, Al_2O_3 phase is located on the surface of Al_2O_3@SiC, thus the new formed layer must be Al_2O_3. In addition, from the low resolution TEM image (Fig. S5, ESI†) we can observe that the new Al_2O_3 layer is homogeneously coated on Al_2O_3@SiC surface. Likewise, a thin layer of Al_2O_3 is also observed on the Al powders from high resolution TEM image. It should be mentioned that the structure of Al powders is similar with SiC and Al_2O_3@SiC, that is, a thin Al_2O_3 layer is formed on the outer surface and underneath is high thermal conductive metallic Al.

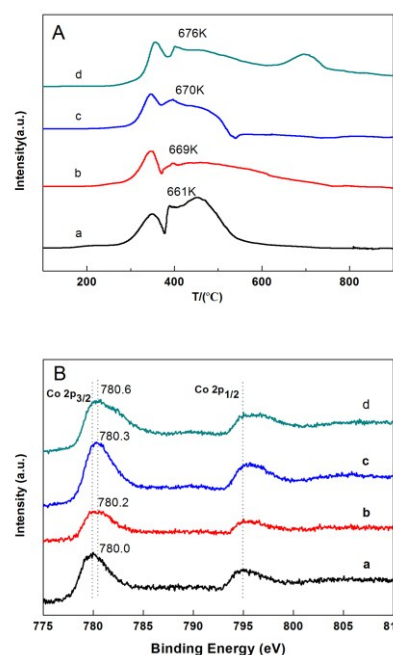The spinel Co_3O_4 is the only crystalline cobalt species in the

Fig.2 A) H_2-TPR profiles of the catalysts: a) Co/SiC, b) Co/Al_2O_3@SiC, c) Co/Al, d) Co/Al_2O_3; B) Co2p XPS spectra of the catalysts: a) Co/SiC, b) Co/ Al_2O_3@SiC, c) Co/Al, d) Co/Al_2O_3.

fresh catalysts according to the XRD result (Fig. S6).[17] Table 1 shows the textural and chemical properties of the prepared catalysts. The Co_3O_4 particle sizes of the catalysts are in the range of 15.4-24.2 nm, which are calculated from Scherrer equation.[18] The corresponding Co^0 crystalline sizes are in the range of 11.6-18.2 nm. Co^0 crystalline sizes are also calculated from H_2 chemisorption result, which is in line with the XRD result. It is reported that the cobalt particle sizes smaller than 6 nm can significantly affect the intrinsic selectivity and activity of FTS.[19] As can be seen, the Co^0 crystalline sizes of the prepared catalysts are all larger than 10 nm, indicating that the cobalt sizes effect should be negligible.

The H_2-TPR profiles of the calcined catalysts are shown in Fig. 2A. Three main reduction peaks centered at approximately 620, 661 and 723 K are observed for Co/SiC. The first two peaks are typically assigned to the two-step reduction of Co_3O_4 to CoO and CoO to Co, the third peak could be attributed to the

Table 1 Textural and chemical properties of the prepared catalysts.

Catalyst	B.E.T. (m^2/g)	PD (nm)	PV (nm)	XRD (nm)		H_2 ads.[c]	d(Co^0)[d] (nm)	R[e] (%)
				d(Co_3O_4)[a]	d(Co^0)[b]			
10Co/SiC	28.6	14.2	0.12	24.2	18.2	29.6	19.6	73
10Co/Al	16.3	17.9	0.08	19.5	14.6	26.5	15.1	59
10Co/Al_2O_3@SiC	33.5	13.5	0.12	21.2	15.9	31.9	14.3	56
15Co/Al_2O_3	160.1	4.1	0.27	15.4	11.6	41.2	10.4	35

[a] The average particle size of Co_3O_4 in the calcined catalysts was calculated from the most intense Co_3O_4 line (2θ =36.8°). [b]d(Co^0) =0.75 d(Co_3O_4). [c] H_2 ads. in $\mu mol H_2 g_{cat}^{-1}$. [d] Calculated from H_2 chemisorption. [e] Reducibility calculated by TPR from 400 to 673 K.

COMMUNICATION

Table 2 FTS performance of the catalysts.[a]

Catalyst	X_{CO} (%)	Products selectivity (wt%)				CTY^b	TOF ($10^{-2}s^{-1}$)
		CH_4	C_2-C_4	C_{5+}	CO_2		
10Co/SiC	39.3	6.5	4.9	88.4	0.2	1.6	2.7
10Co/Al	45.9	11.2	9.1	78.1	1.6	1.9	2.9
10Co/Al$_2$O$_3$@SiC	53.8	11.8	9.0	78.3	0.9	2.2	2.6
15Co/Al$_2$O$_3$	49.0	12.3	7.9	77.6	2.2	1.4	2.9

[a] Reaction conditions: $n(H_2)/n(CO) = 2$, GHSV = 1.0 $L_{syngas}g_{cat}h^{-1}$, T = 503 K, P = 2.0 Mpa, TOS = 48 h. [b] Cobalt time yield (10^{-5} $mol_{CO}g_{Co}^{-1}s^{-1}$, molar CO conversion rate per gram of cobalt per hour).

reduction of bulk cobalt species.[20,21] The H_2-TPR profile shapes of Co/Al$_2$O$_3$@SiC and Co/Al are similar but different with Co/SiC, indicating that the surface species layer on SiC could affect the reduction behavior of Co$_3$O$_4$. The second reduction peak of Co/Al$_2$O$_3$@SiC shifts to higher temperature than Co/SiC. This suggests that the interaction between Co$_3$O$_4$ and support becomes stronger after changing the surface Si$_x$O$_y$ species to Al$_2$O$_3$. The degrees of Co reduction estimated by H_2-TPR experiments are also shown in Table 1. Co/SiC catalyst possesses the highest Co reduction degree, but it decreases to 56% for Co/Al$_2$O$_3$@SiC catalyst. This suggests that the Co$_3$O$_4$ is difficult to reduce after altering the surface Si$_x$O$_y$ species on SiC. The cobalt reduction degree for Co/Al$_2$O$_3$@SiC and Co/Al is at the same level, which could be attributed to the similar structure of the two supports, that is, a thin layer of Al$_2$O$_3$ is existed on the surface of the two materials. Figure 2B shows the XPS results of the catalysts. Two peaks centered at about 780 and 795 eV are observed, which can be ascribed to the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks of Co$_3$O$_4$.[12] For the Co/Al$_2$O$_3$@SiC, the peak of Co $2p_{3/2}$ shift to a higher binding energy than Co/SiC, indicating that the interaction between Co$_3$O$_4$ and support becomes stronger after changing the Si$_x$O$_y$ to Al$_2$O$_3$ on the surface of SiC.

The catalytic results of the catalysts are listed in Table 2. Reaction data were collected after 48 h time-on stream in order to obtain the steady state. The Co/Al$_2$O$_3$@SiC and Co/Al$_2$O$_3$ are compared to investigate the effect of support thermal conductivity on the intrinsic reaction behavior of FTS. The Al$_2$O$_3$ and Al$_2$O$_3$@SiC supports are all prepared by precipitation method, thus the two supports could possess similar surface chemical nature. In addition, 15wt% cobalt is impregnated into Al$_2$O$_3$ in order to rule out cobalt particle sizes effect. Hence the major variable between them is the thermal conductivity property, as Al$_2$O$_3$ is insulator but Al$_2$O$_3$@SiC is high thermal conductive material. As can be seen, Co/Al$_2$O$_3$@SiC and Co/Al$_2$O$_3$ exhibit similar catalytic performance, namely the CH_4 selectivity is 11.8% and 12.3% while C_{5+} selectivity is 78.3% and 77.6%. This suggests that the thermal conductivity of catalyst support makes no effect on the intrinsic reaction behavior of FTS. Actually, inert solid heat disperser was often used in FTS and the temperature gradient in the catalyst bed could be negligible, especially for our laboratory fixed-bed reactor.[12,22] At the reaction steady state, the generated and transferred heat could also be in equilibrium on each catalyst particle, regardless of the thermal

conductive property for catalysts. Therefore, the traditional speculation that "hot spots" exist on the surface of insulated supports but do not form on high thermal conductive SiC surface thus can enhance heavy hydrocarbon selectivity may be inaccurate.

The dilution experiment results of low thermal conductive Co/Al$_2$O$_3$ and high thermal conductive Co/SiC are shown in Table S4. As can be seen, the temperature difference between the reactor wall and the centerline (ΔT) for the undiluted Co/Al$_2$O$_3$ is 1.3 K higher than the diluted Co/Al$_2$O$_3$. This is because that the heat transfer condition is bad for the undiluted Co/Al$_2$O$_3$ and the generated heat is accumulated in the catalyst bed, leading to a higher temperature gradient between reactor wall and the centerline.[23] As a consequence, the undiluted Co/Al$_2$O$_3$ displays higher CO conversion than the diluted Co/Al$_2$O$_3$, i.e. 78.4% instead of 59.3%. The CO conversion of 59.1% is chosen for diluted Co/SiC, in order to make sure that the generated heat during reaction is similar with diluted Co/Al$_2$O$_3$. No obvious temperature difference (ΔT) is observed for the diluted and undiluted Co/SiC. This is because that Co/SiC catalyst possesses well heat transfer ability thus a homogenous temperature gradient inside the reactor could be maintained even without using heat disperser. Therefore, the real effect of the high thermal conductive SiC support is to improve heat transfer efficiency inside the reactor, thus maintaining a homogeneous temperature gradient within catalyst bed, which is beneficial to the safety of fixed-bed reactor particularly for large scale commercial plants.

The only difference between SiC and Al$_2$O$_3$@SiC is the species on the surface. Hence Co/SiC and Co/Al$_2$O$_3$@SiC are compared to investigate the effect of SiC surface Si$_x$O$_y$ species on the intrinsic reaction behavior of FTS. As can be seen, Co/SiC shows remarkable catalytic performance, that is, a lower CH_4 selectivity of 6.5% and higher C_{5+} selectivity of 88.4%. However, after the Si$_x$O$_y$ layer on SiC surface is changed to Al$_2$O$_3$, obvious different reaction result is observed for the prepared Co/Al$_2$O$_3$@SiC. The CH_4 selectivity increases to 11.8% and C_{5+} selectivity decreases to 78.3%. It is accepted that the metallic Co^0 is the active phase in FTS.[22,24] For Co/Al$_2$O$_3$@SiC, the interaction between Co$_3$O$_4$ and Al$_2$O$_3$ layer is stronger thus lead to a lower cobalt reduction degree, which enhances CH_4 selectivity.[25,26] After reduction, the stronger interaction could also change the electronic state of the Co^0 and affect the CO dissociation ability, thus influencing the product selectivity.[12,27] For Co/SiC, the interaction between Co$_3$O$_4$ and

surface Si_xO_y layer is relative weaker thus could own appropriate cobalt reduction degree. Furthermore, the electronic state of the Co^0 might not be significantly affected because of the relative weaker interaction. Therefore, we believe that the surface Si_xO_y layer on SiC is the main cause for the intrinsic good catalytic performance of Co/SiC. To further confirm our conclusion, Co/Al catalyst is also tested under the same reaction condition. The structure of Al powders is similar with SiC and Al_2O_3@SiC, that is, a thin layer of Al_2O_3 is formed on the outer surface and underneath is high thermal conductive metallic Al. As can be seen, the CH_4 selectivity is 11.2% and C_{5+} selectivity is 78.1% for Co/Al, which is similar with Co/Al_2O_3@SiC but different with Co/SiC. This could be attributed to the different surface species on these supports. For Al_2O_3@SiC and Al powders, the surface species is Al_2O_3 but for SiC is Si_xO_y. The result confirms our conclusion that the surface Si_xO_y layer on SiC is the main cause for the intrinsic good catalytic performance of Co/SiC.
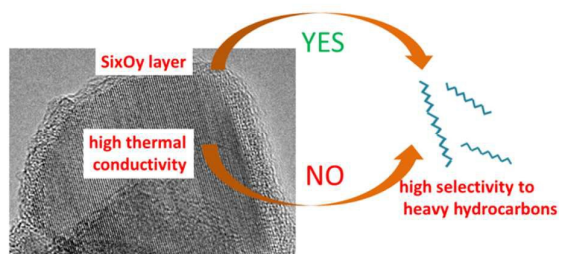
In summary, we have demonstrated that the traditional explanations for the intrinsic excellent catalytic performance of Co/SiC are not reliable. The high thermal conductive property is not the cause for the intrinsic good FTS performance of Co/SiC. The real effect of the high thermal conductivity is to increase heat transfer efficiency and maintain a homogeneous temperature gradient inside the fixed-bed reactor, thus avoiding the formation of "hot spots", which could improve the security of plants. The surface Si_xO_y layer on SiC is the main cause for the intrinsic good catalytic performance of Co/SiC, which possesses proper interaction between cobalt phase and Si_xO_y. Therefore, the attempt to utilize other high thermal conductive materials as supports to prepare FTS catalysts with good catalytic performance similar with Co/SiC might not be working. Regulating the interaction between cobalt phase and support might be an effective approach to prepare FTS catalysts with excellent catalytic performance.

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The Si_xO_y layer on the surface of SiC plays a great role in the intrinsic excellent catalytic performance of Co/SiC.