# Effect of Sodium on the Structure-Performance Relationship of Co/SiO<sub>2</sub> for Fischer-Tropsch Synthesis

Yuanyuan Dai,<sup>*a,b*</sup> Fei Yu,<sup>*a,b*</sup> Zhengjia Li,<sup>*a,c*</sup> Yunlei An,<sup>*a,d*</sup> Tiejun Lin,<sup>*a*</sup> Yanzhang Yang,<sup>*a,b*</sup> Liangshu Zhong,<sup>*s,a*</sup> Hui Wang,<sup>*a*</sup> and Yuhan Sun<sup>*s,a,e*</sup>

<sup>a</sup> CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, China

<sup>b</sup> University of the Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

<sup>d</sup> College of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

<sup>e</sup> School of Physical Science and Technology, Shanghai Tech University, Shanghai 201203, China

A series of Co/SiO<sub>2</sub> catalysts with different sodium (Na) loadings (0, 0.1, 0.2, 0.5 and 1 wt%) were prepared and evaluated for Fischer-Tropsch reaction to study the effect of Na on the catalyst structure and catalytic performance. The addition of Na was found to decrease the catalytic activity and hydrocarbon selectivity, but increase CO<sub>2</sub> selectivity due to the enhanced WGS activity. The addition of Na also resulted in higher selectivity to oxygenates (alcohols and aldehydes) and O/P ratio as well as the shift of hydrocarbons to lower carbon numbers. Structure characterization revealed a decrease in the surface area and particles size for the calcined samples with the addition of Na. Co<sub>2</sub>C was formed during the reaction process for the Na-promoted catalysts. As a result, a new Co/Co<sub>2</sub>C bifunctional active sites were generated for oxygenates formation leading to increasing oxygenates selectivity. In addition, the Co<sub>2</sub>C nanoparticles alone may also act as dual active sites for oxygenate formation at high reaction pressure over the promoted catalysts with high Na loading.

Keywords Fischer-Tropsch synthesis, structure-performance relationship, sodium, cobalt carbide, oxygenates

## Introduction

Fischer-Tropsch (FT) synthesis is a catalyzed surface polymerization process that produces major chemical building blocks such as paraffins, olefins and oxygenates from syngas.<sup>[1,2]</sup> FT synthesis has attracted much attention both in academia and industry due to the depletion of oil-based resource and the increase of global demand for clean fuel and various chemicals.<sup>[3,4]</sup> The group VIII metal elements such as Fe, Co and Ni, owing to their electronic properties, have been investigated for the FT reaction.<sup>[5]</sup> Co-based catalysts are considered optimal for the production of middle distillates and waxs from H<sub>2</sub>-rich syngas because of the high stability, and low activity for the water-gas-shift (WGS) reaction.<sup>[6,7]</sup> Compared with Fe-based FT catalysts, the products obtained from Co-based FT catalyst are mainly linear paraffins with few olefins and alcohols.

Electronic promoters are always used for FT catalysts to further improve the catalytic activity and product selectivity. Many promoters, such as calcium,<sup>[8]</sup> zirconia,<sup>[9]</sup> copper,<sup>[10,11]</sup> manganese<sup>[12-15]</sup> and alkali metals,<sup>[8,16-18]</sup> have been shown to exhibit different effects

on the catalytic performance. Previous studies show that the addition of alkali metals promotes catalyst carburization by facilitating the dissociation of CO on the catalyst surface.<sup>[18]</sup> Moreover, alkali metals accelerate the CO dissociative adsorption rate and result in an increase of the surface coverage of adsorbed CO.<sup>[19]</sup> The addition of alkali metals will also inhibit olefin readsorption, and thus increase olefin selectivity.<sup>[19]</sup>

Generally speaking, alkali metals are the common promoters of Fe-based catalysts for the FT synthesis.<sup>[17,20-22]</sup> However, the typical promoters for Co-based catalysts are noble metals, transition metals and some rare earth metal oxides. Alkali metals are always considered to possess a negative impact on Co-based FTS catalysts as the addition of alkali metals always leads to the decrease in catalytic activity. Lillebø *et al.*<sup>[23]</sup> have reported that there was not significant change of microcalorimetric measurements by H<sub>2</sub> and CO chemisorption for Co/Al<sub>2</sub>O<sub>3</sub> with 0.1 wt% Na concentration. However, the activity was 33%—43% lower than that of the catalyst without Na. Na could decrease the reducibility of cobalt oxide,<sup>[24]</sup> block active site<sup>[25]</sup> and promote catalyst



<sup>\*</sup> E-mail: zhongls@sari.ac.cn, sunyh@sari.ac.cn

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carburization. Anton et al.[16] have studied the effect of Na on Co/Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in FTS. They found that catalysts with low Na loading ( $\leq 0.6$  wt%) presented strong initial deactivation due to the phase change of  $Co^{\circ}$ . However, the catalytic activity remained almost constant with further increase of the Na loadings ( $\geq 0.8$ wt%). Close contact of metallic  $Co^0$  and  $Co_2C$  can occur, which was assumed to generate additional active sites for alcohols formation. This conclusion was also verified by other researchers.<sup>[26-29]</sup> Recently, a breakthrough in the selective production of lower olefins from syngas for CoMn catalysts has been reported by our group.<sup>[30]</sup> Using sodium carbonate as the precipitant, the obtained CoMn catalysts presented Co<sub>2</sub>C nanoprisms with exposed facets of (101) and (020) during the reaction process. Very high selectivity to lower olefins (60.8 C%) with low methane selectivity was detected. However, the catalysts using ammonium carbonate as the precipitant presented metallic cobalt and  $Co_x Mn_{1-x}O$  and exhibited typical FT performance. It was suggested that the residual Na enhanced the formation of Co<sub>2</sub>C. Although there are a lot of works concerning Na-promoted Co-based FT catalyst, detailed informations about the effect of Na on catalyst structure and catalytic performance (activity and selectivity) are still lacking. In this paper, Na-promoted Co/SiO<sub>2</sub> catalysts were chosen as model catalysts and the effect of Na on the structure-performance relationship was investigated in details.

## Experimental

#### **Catalysts** preparation

Commercially available SiO<sub>2</sub> with specific surface area of 200 m<sup>2</sup>•g<sup>-1</sup> was used as support. Co/SiO<sub>2</sub> was firstly prepared by the incipient wetness impregnation technique. Co weight loading was held constant at 20 wt% with respect to the sum of Co<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> support. 10 g of SiO<sub>2</sub> was impregnated with an aqueous solution (14 mL) of 13.57 g Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O. After impregnation, the sample was dried at room temperature for 12 h, then dried at 100 °C for 5 h, finally the catalyst was calcined at 330 °C for 3 h with a heating rate of 1 °C/min. The obtained catalyst was marked as Co/SiO<sub>2</sub>-0Na, and used for all further modification by Na impregnation.

The Na-promoted catalysts were obtained by further impregnation with aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. Na weight loadings were held 0.1 wt%, 0.2 wt%, 0.5 wt% and 1 wt% with respect to the sum of Co<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> support. The drying and calcination steps were performed as described for the unpromoted supported catalysts. According to the loading amount of Na, the catalysts were marked as Co/SiO<sub>2</sub>-0.1Na, Co/SiO<sub>2</sub>-0.2Na, Co/SiO<sub>2</sub>-0.5Na and Co/SiO<sub>2</sub>-1Na accordingly.

#### **Catalyst characterization**

The metal composition and the Na content were de-

termined by a PE Optima 2100DV inductive coupled plasma emission spectrometer (ICP). The surface area and pore structure of all the samples were determined by N<sub>2</sub> physical adsorption-desorption at –196 °C, using the multipoint BET analysis method, with a TriStar II 3020 instrument. Prior to the measurements, the samples were degassed at 200 °C for 6 h. The phase and average cobalt oxide crystallite size for the catalysts was determined by powder X-ray diffraction (XRD) performed on a Rigatku Ultima 4 X-ray diffractometer with Cu K $\alpha$  radiation (40 kV, 40 mA) in the range of 5°–90°. The identification of different phase was performed by comparing the patterns with JCPDS standard cards.

The reduction characteristics of the catalysts were studied by H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) on a Micromeritics ChemiSorb 2920 with a thermal conductivity detector (TCD). Typically, the catalyst sample (50 mg) was placed in a U-shaped quartz reactor and pretreated in flowing He of 40 mL•min<sup>-1</sup> at 200 °C for 1 h, followed by cooling down to 60 °C. After pretreatment, the temperature was raised to 800 °C at a rate of 10 °C•min<sup>-1</sup> with 50 mL•min<sup>-1</sup> of 5% H<sub>2</sub>/Ar mixture gas.

For semiquantitative analysis, the samples were scanned from  $30^{\circ}$  to  $50^{\circ}$  using a step scanning mode, of which the step size was  $0.02^{\circ}$ . The content of different phases was calculated by means of reference intensity ratios (RIR). Generally, the integrated intensities of the most intense peak of each phase were obtained from fitting and deconvolution results of XRD patterns. Then the mass fraction of *x* phase ( $w_x$ ) was calculated from the Eq. 1 as follows:

$$w_{x} = \frac{I_{x}}{\operatorname{RIR}_{x} \sum_{i=1}^{N} \frac{I_{i}}{\operatorname{RIR}_{i}}}$$
(1)

where *I* is the integrated intensity of the intensest peak and the RIR values were available from the PDF cards.

The spent catalysts were analyzed with transmission electron microscopy (TEM) to determine the size distribution and lattice fringe. The images were obtained using an accelerating voltage of 200 kV and a Tecnai G220 high-resolution microscope equipment. Samples for TEM were prepared by dispersing the sample in ethanol followed by ultrasonication.

#### **Catalytic evaluation**

The Fischer-Tropsch synthesis was performed in a fixed-bed reactor at 20 bar, 220-250 °C, H<sub>2</sub>/CO=2 *V*/*V* and GHSV=2000 mL g<sup>-1</sup>•h<sup>-1</sup> using 1.5 g catalyst (particle size of 40-60 mesh) diluted with 3 g quartz sand (particle size of 40-60 mesh). Prior to reaction, the catalyst was *in-situ* reduced by pure H<sub>2</sub> at 400 °C with gas flow rate of 200 mL/min for 5 h. After reduction, the reactor was cooled to 220 °C under He atmosphere with gas flow rate of 200 mL/min. Then the pressure was increased gradually up to 20 bar and syn-

gas (H<sub>2</sub>/CO=2, V/V) was introduced with gas flow rate of 50 mL/min. The tail gas after passing through a hot trap (120 °C) and a cold trap (0 °C), was analyzed on-line with an Agilent 7890B gas chromatograph by using a carbon molecular sieves column (TDX-1) with a thermal conductivity detector (TCD), using helium as the carrier gas. Hydrocarbons with carbon number from 1 to 7 ( $C_1$  to  $C_7$ ) were analyzed using a KCl-modified alumina capillary column (19095P-K25) with an argon carrier and a hydrogen flame ionization detector (FID). The aqueous products, oil products and wax products, collected from cold trap and hot trap, were analyzed off-line by GC. The aqueous products were analyzed with two Porapak Q columns equipped with a TCD (for H<sub>2</sub>O and MeOH detection) and FID (for C<sub>1</sub>-C<sub>5</sub> oxygenates detection), respectively. The oil products were analyzed through an HP-1 column with N<sub>2</sub> carrier by FID. The wax products were dissolved in CS<sub>2</sub> and analyzed through an MXT-1 column with N<sub>2</sub> carrier by FID. The CO conversion and product selectivities were determined after at least 24 h on-stream when the steady state was reached.

## **Results and Discussion**

#### Catalysts characterization

The content of cobalt and sodium, textural properties and particle size were measured by ICP, N<sub>2</sub>-adsorption and XRD as listed in Table 1. The cobalt and sodium concentrations determined with ICP were basically consistent with the nominal concentrations. With the addition of Na, the specific surface area ( $S_{\text{BET}}$ ) of the catalysts decreased from 198.2 m<sup>2</sup>·g<sup>-1</sup> for the unpromoted chinese journal o CHEMISTRY

Table 1 The composition and structure of  $Co/SiO_2$  catalysts with different Na loadings

Sample	Co <sup>a</sup> / wt%	Na <sup>a</sup> / wt%	BET surface area/ $(m^2 \cdot g^{-1})$	Particle size of Co <sub>3</sub> O <sub>4</sub> <sup>b</sup> /nm
Co/SiO <sub>2</sub> -0Na	21.1	_	198.2	18.3
Co/SiO <sub>2</sub> -0.1Na	21.3	0.13	193.1	17.2
Co/SiO <sub>2</sub> -0.2Na	21.6	0.35	161.4	17.3
Co/SiO <sub>2</sub> -0.5Na	21.9	0.58	132.2	17.5
Co/SiO <sub>2</sub> -1Na	21.4	1.11	88.9	17.6

<sup>*a*</sup> Measured by ICP; <sup>*b*</sup> calculated by XRD.

XRD patterns of Co/SiO<sub>2</sub> catalysts with different Na loadings at different stages were shown in Figure 1(a). After calcination, only crystalline Co<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> phases were observed by XRD, and no obvious diffraction peak belonging to the Na component was detected due to the low Na loading. The characteristic reflection peaks at 20 of 19.0°, 31.4°, 36.9°, 37.9°, 45.0°, 55.9° and 59.4° corresponded to the Co<sub>3</sub>O<sub>4</sub> phase (PDF# No. 42-1467), and the peak at  $2\theta$  of 21.9° was attributed to SiO<sub>2</sub> (PDF# No. 39-1425). The crystallite sizes of cobalt oxides were calculated from the Co<sub>3</sub>O<sub>4</sub> (311) peak according to the Scherrer equation and listed in Table 1. The average particle size of cobalt oxides for the unpromoted sample is 18.3 nm, while there is a slight decrease for the Na-promoted samples. Figure 1(b) showed the XRD patterns of reduced catalysts. The peaks at  $2\theta$  of 44.2°, 51.5° and 75.9° were ascribed to



Figure 1 XRD patterns of calcined (a), reduced (b) and spent (c) Co/SiO<sub>2</sub> catalysts; (d) TPR profiles of calcined Co/SiO<sub>2</sub> catalysts.

FCC Co (PDF# No. 15-0806), and the peaks at  $2\theta$  of 44.2°, 44.8°, 47.6°, 62.7°, 75.9° and 84.2° were assigned to HCP Co (PDF# No. 05-0727). After the reduction under 400 °C by H<sub>2</sub>, the Co<sub>3</sub>O<sub>4</sub> phase appeared to be converted into Co<sup>0</sup> (including FCC and HCP) and FCC Co was the dominant cobalt phase.<sup>[31]</sup>

The XRD patterns of spent catalysts were shown in Figure 1(c). For the spent Co/SiO<sub>2</sub>-0Na sample, only metallic phase was detected, while Co<sub>2</sub>C (PDF# NO. 50-1371) with the characteristic peaks at  $2\theta$  of  $37.6^{\circ}$ , 41.5°, 43.0°, 45.9°, 57.1° and 64.8° were clearly observed for Co/SiO<sub>2</sub>-0.1Na. By semiquantitative analysis, the proportion of Co<sub>2</sub>C among all Co-containing phases was 20%. The proportion of Co<sub>2</sub>C increased with the increase in Na loading. When the Na loading was higher than 0.2 wt%, the Co<sub>2</sub>C phase was the dominant Co species and the metallic Co phase was hardly observed from the XRD patterns. Obviously, the presence of Na promoted the formation of cobalt carbide. This phe-nomenon was also found by Anton *et al.*<sup>[16]</sup> and it was reported that Na enhanced the rate of CO dissociation resulting in carbonization. Na can acted as an electronic donator to cobalt resulting in stronger CO adsorption and enhanced CO dissociation, benefiting the formation and stabilization of Co<sub>2</sub>C. As a result, there was only the Co<sub>2</sub>C phase present in the sample with higher Na loading.

H<sub>2</sub>-TPR was carried out from room temperature to 800 °C under the flow of 5%  $H_2/Ar$  as shown in Figure 1(d). All catalysts exhibited two main peaks and the first peak was assigned to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO while the second peak was ascribed to the reduction of CoO to  $Co^0$ . For Co/SiO<sub>2</sub>-0Na, the first reduction stage from Co<sub>3</sub>O<sub>4</sub> to CoO ranged from 200 to 270 °C. The second reduction stage from CoO to Co<sup>0</sup> occurred from 270 to 360 °C. The addition of Na to the Co/SiO<sub>2</sub> catalyst slightly suppressed the reduction of Co<sub>3</sub>O<sub>4</sub> and CoO due to the interaction of cobalt oxide with Na. The second reduction stage of CoO to Co<sup>0</sup> also shifted to higher temperature with the increase of Na loading. When the Na loading was higher than 0.5 wt%, all reduction stages shifted to higher temperature resulting in the first reduction peak overlaped with the second re-duction peaks. Khobragade<sup>[25]</sup> claimed that alkali metals inhibited the dissociative adsorption of H<sub>2</sub> resulting in the suppression of the reduction, which was consistent with our H<sub>2</sub>-TPR results.

The TEM images of spent  $Co/SiO_2$  catalysts with different Na loadings were shown in Figure 2. All samples presented a certain degree of aggregation as the magnetic properties of the samples. The sample without Na showed metallic phases (FCC Co and HCP Co) and no Co<sub>2</sub>C phase was found. However, the Co<sub>2</sub>C phase was present in all Na-promoted samples, which was constant with the XRD results. For the Co/SiO<sub>2</sub>-0.1Na sample, both metallic phase and Co<sub>2</sub>C were found and metallic phase was the dominant cobalt phase. For samples with higher Na loading, only the Co<sub>2</sub>C phase



**Figure 2** TEM images of various spent catalysts. a: Co/SiO<sub>2</sub>-0Na; b: Co/SiO<sub>2</sub>-0.1Na; c: Co/SiO<sub>2</sub>-0.2Na; d: Co/SiO<sub>2</sub>-0.5Na; e: Co/SiO<sub>2</sub>-1Na.

could be found. In addition, all Co<sub>2</sub>C in the different Na-promoted samples showed sphere-like morphology. Recently, we have reported that Co<sub>2</sub>C nanoprisms with the specific exposed facets [(101) and (020)] were the effective active phase for Fischer-Tropsch to olefins (FTO) reaction.<sup>[30]</sup> As there was no obvious Co<sub>2</sub>C nanoprisms for the spent Na-promoted Co/SiO<sub>2</sub>, the catalytic performance of the Co<sub>2</sub>C on Na-promoted Co/SiO<sub>2</sub> samples might be different from Co<sub>2</sub>C nanoprisms. The particle sizes of Co<sub>2</sub>C for Co/SiO<sub>2</sub>-0.2Na, Co/SiO<sub>2</sub>-0.5Na and Co/SiO<sub>2</sub>-1Na were 17.7, 14.5 and 17.3 nm, respectively, suggesting the Na loading amount had little effect on the Co<sub>2</sub>C size.

STEM/EDX was also used to study the distributions

of different elements in spent  $Co/SiO_2$ -1Na catalyst as shown in Figure 3. Clearly, the cobalt phase was dispersed on SiO<sub>2</sub>. However, the signal for Na was rather weak and seemed as signal noise due to the very low Na loading.



**Figure 3** The elemental mapping of the spent Co/SiO<sub>2</sub>-1Na catalyst. Na (green), Co (red), Si (purple).

From the characterization results, it can be concluded that Na could suppress the reduction by inhibiting the dissociative adsorption of hydrogen, and promote the formation of  $Co_2C$  by enhancing CO adsorption and dissociation.

#### **Fischer-Tropsch synthesis**

Table 2 shows the catalytic performance over the studied Co/SiO<sub>2</sub> catalysts. The catalyst without Na displayed high activity for the FT reaction with low selectivity to both CO<sub>2</sub> and oxygenates but very high hydrocarbon selectivity. The activity and product distributions on this catalyst were in good agreement with the reported catalytic performance of typical Co-based FT catalyst with Co<sup>0</sup> as the active phase.<sup>[7]</sup> The addition of Na resulted in a decrease in the catalytic activity with a great change of product selectivity. For catalysts with low Na loading (Co/SiO<sub>2</sub>-0.1Na) at 250 °C, the oxygenates selectivity increased to 9.5 C% at a CO conversion of about 40%. With further increase of Na loading,

the promoter effect of Na became more remarkable. Co/SiO<sub>2</sub>-0.2Na sample exhibited lower CO conversion (28%) but higher oxygenates selectivity than Co/SiO<sub>2</sub>-0.1Na. Among all Na-promoted catalysts, Co/SiO<sub>2</sub>-0.5Na sample showed the highest oxygenates selectivity at about 14.5 C%. The aldehydes selectivity for the unpromoted sample was less than 1% but higher than 1.5% for Na-promoted samples. In addition, the alcohol selectivity of Na-promoted samples was much higher than that of the unpromoted sample, suggesting that the addition of Na improved both alcohols and aldehydes selectivity.

As far as the product distributions were concerned as shown in Table 3, the oxygenates distribution for the Co/SiO<sub>2</sub>-0Na sample was in the range of lower carbon  $(C_1 - C_{11})$  slate and no  $C_{12^+}$  oxygenates were obtained. However, the produced hydrocarbons exhibited higher carbon number and the C<sub>12+</sub> hydrocarbon selectivity was 31.7 wt%. With the addition of Na,  $C_{12^+}$  oxygenates could be obtained while the selectivity to  $C_{12^+}$  hydrocarbons decreased. The O/P ratios were also investigated as depicted in Figure 4. Obviously, the O/P ratios for the Na-promoted sample were much higher than that of the Na-free sample. For the Co/SiO<sub>2</sub>-0wt%Na sample, the O/P ratios with carbon number above 5 were almost zero. However, that values increased greatly with the addition of Na, indicating that Na could inhibit olefin re-adsorption and decrease the olefin hydrogenation rates.<sup>[18]</sup>



**Figure 4** Ratios of olefin to paraffin for Co/SiO<sub>2</sub> catalysts with different Na loadings.

Samula	Tommoroturo/°C	CO conversion/ $C0/$	Selectivity/C%						
Sample	Temperature/ C	CO conversion/C%	Oxygenates	CHn	$CO_2$	Alcohols	Aldehyde		
Co/SiO <sub>2</sub> -0Na	210	26.7	2.6	96.7	0.6	1.7	0.9		
	250	94.4	2.0	91.6	6.1	1.6	0.4		
Co/SiO <sub>2</sub> -0.1Na	250	39.6	9.5	81.5	9.0	6.7	2.8		
Co/SiO <sub>2</sub> -0.2Na	250	27.6	11.5	44.3	44.2	10.0	1.5		
Co/SiO <sub>2</sub> -0.5Na	250	29.2	14.5	38.4	47.1	12.7	1.8		
Co/SiO <sub>2</sub> -1Na	250	32.6	14.0	38.0	48.1	11.3	2.7		

**Table 2** The catalytic performance of various Co/SiO<sub>2</sub> catalysts (20 bar,  $H_2/CO=2$  and GHSV=2000 mL•g<sup>-1</sup>•h<sup>-1</sup>)

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<u>C</u> 1.	Oxygenates distribution/wt%				Hydrocarbon distribution (O&P, wt%)				
Sample	C <sub>1</sub>	$C_{2^{-4}}$	C <sub>5-11</sub>	$C_{12^{+}}$	$C_1$	$C_{2^{-4}}$	C <sub>5-11</sub>	$C_{12^{+}}$	
Co/SiO <sub>2</sub> -0Na	10.7	31.9	57.4	0	19.5	7.2	41.6	31.7	
Co/SiO <sub>2</sub> -0.1Na	6.3	55.2	35.7	2.8	13.2	27.8	37.7	23.0	
Co/SiO <sub>2</sub> -0.2Na	8.3	42.7	46.4	2.7	34.8	34.1	18.4	12.7	
Co/SiO <sub>2</sub> -0.5Na	12.7	47.6	32.7	7.0	36.6	39.0	170	7.5	
Co/SiO <sub>2</sub> -1Na	12.4	43.5	31.9	12.3	36.9	40.3	15.7	7.0	

**Table 3** The product distribution of various Co/SiO<sub>2</sub> catalysts (250 °C, 20 bar, H<sub>2</sub>/CO=2 and GHSV=2000 mL•g<sup>-1</sup>•h<sup>-1</sup>)

The chain growth probabilities ( $\alpha$ ) of the produced hydrocarbons and oxygenates were drawn in Figure 5. All products deviated from the ASF distribution, featuring two alpha-breaks distributions. For hydrocarbon distributions of Co/SiO<sub>2</sub>-0Na and Co/SiO<sub>2</sub>-0.1Na, the alpha breaks were located at C5 and C10 making the hydrocarbon selectivities into three segments, and the alpha breaks of other samples were located at  $C_9$  and  $C_{13}$ . The chain growth factor of hydrocarbons ( $\alpha = 0.87$  calculated from C<sub>13</sub>-C<sub>23</sub>) for Co/SiO<sub>2</sub>-0wt%Na was much higher than that of oxygenates ( $\alpha = 0.55$  calculated from  $C_4 - C_8$ ), suggesting that Co-based FT catalysts possessed higher selectivity to heavy paraffins than oxygenates. However, the addition of Na resulted in the shift of hydrocarbons to lower carbon numbers and the shift of oxygenates to higher carbon numbers. For example, when Na loadings were higher than 0.2 wt%, the proportion of  $C_{12^+}$  hydrocarbons was less than 23 wt%. For the oxygenates distributions, the addition of Na increased the fraction of the  $C_2-C_4$  at the expense of  $C_5 - C_{11}$ . The hydrocarbons chain growth factors of Na-promoted sample were about 0.8 calculated from the  $C_{13}-C_{23}$  slates and were lower than that of unprompted sample. However, the oxygenates chain growth factors slightly increased once Na was added. In addition, the chain growth factors of all products almost kept constant for the studied Na promoted samples with different Na loadings.

The effect of reaction temperature for different  $Co/SiO_2$  catalysts was also investigated. As shown in Figure 6, CO conversion increased with the increase of

temperature for all the studied catalysts as expected. CO<sub>2</sub> selectivity also increased with increasing temperature for all samples due to the severe WGS reaction. However, CO<sub>2</sub> selectivities for Co/SiO<sub>2</sub>-0Na and Co/SiO<sub>2</sub>-0.1Na were lower than those of other samples and still below 10 C% even at 250 °C. At low temperature (220-230 °C), Co/SiO<sub>2</sub>-0Na catalyst showed the lowest CH<sub>4</sub> selectivity of about 7.3% at 220 °C and 8.4% at 230  $^{\circ}$ C. At the same temperature, the catalysts with high Na loadings showed rather high CH<sub>4</sub> selectivity of about 15% – 19%, and the CH<sub>4</sub> selectivity slightly increased when the temperature further increased from 230 to 250 °C. However, Co/SiO<sub>2</sub>-0Na exhibited the highest CH<sub>4</sub> selectivity (about 20%) at 250 °C. The changing trend of  $C_{5+}$  + ROH selectivity of all catalysts, contrary to that of CH<sub>4</sub> selectivity, decreased with in-creasing temperature.<sup>[8]</sup> It seemed that higher temperature would favor surface species to desorb and resulted in high CH<sub>4</sub> selectivity and low selectivity to heavy products.<sup>[11]</sup>

As shown in Figure 7, the olefin to paraffin (O/P) ratio of C<sub>2-4</sub> decreased remarkably with increase of reaction temperature due to enhanced secondary hydrogenation of olefins for the sample without Na. When the Na loading was 0.1 wt%, the change in  $C_{2-4}^{-}/C_{2-4}^{0}^{0}$  with temperature was similar to that for Co/SiO<sub>2</sub>-0Na. However, for the sample with higher Na loadings,  $C_{2-4}^{-}/C_{2-4}^{0}$  ratios almost kept unchanged with the increase of reaction temperature. The changing trend of  $C_{2-4}^{-}$  selectivity with temperature was similar to  $C_{2-4}^{-}/C_{2-4}^{0}^{0}$  ratios.



Figure 5 Product distribution of hydrocarbons (a) and oxygenates (b) of various Co/SiO<sub>2</sub> catalysts with different Na loadings.



Figure 6 CO conversion (a), product selectivity to  $CO_2$  (b),  $CH_4$  (c) and  $C_{5^+}+ROH$  (d) over various  $Co/SiO_2$  catalysts at different reaction temperatures.



Figure 7  $C_{2-4}^{-a}/C_{2-4}^{-a}$  ratio (a) and  $C_{2-4}^{-a}$  selectivity (b) of various Co/SiO<sub>2</sub> catalysts at different reaction temperatures.

For the cobalt catalyst, the  $\text{Co}^0$  active phase will exhibit high activity for producing linear heavy hydrocarbons with low activity for the WGS reaction.<sup>[32]</sup> In all Na-promoted samples, Co<sub>2</sub>C was found after the reaction based on the XRD and TEM results, demonstrating that Na promoted the formation of cobalt carbide. Cobalt carbide formation is a possible cause for FT catalyst deactivation as it is less active than metallic Co.<sup>[33,34]</sup> According to the previous study, Co/Co<sub>2</sub>C presented as dual active sites for higher alcohols formation,<sup>[26]</sup> on which Co<sup>0</sup> functions for CO dissociation and chain propagation while Co<sub>2</sub>C for CO non-dissociative activation and insertion. Thus, for Na promoted sample containing metallic Co and Co<sub>2</sub>C phases, the performance showed high oxygenates selectivity. For those samples

with high Na loading, only the  $Co_2C$  phase was observed. However, oxygenates were still produced, suggesting that the  $Co_2C$  nanoparticles alone may also act as the dual active sites for oxygenate formation at high pressure.

From the TEM images of spent catalysts, Co<sub>2</sub>C was found in all Na-promoted samples with sphere-like morphology. In our previous study, there existed a strong facet effect for the Co<sub>2</sub>C nanostructure during syngas conversion.<sup>[30]</sup> Co<sub>2</sub>C nanoprisms had high selectivity to lower olefins at about 55 C% and the ratios of  $C_2^{=}/C_2^{\circ}$ ,  $C_3^{=}/C_3^{\circ}$  and  $C_4^{=}/C_4^{\circ}$  were 22, 45 and 30 respectively at atmospheric pressure. In order to compare the catalytic performance between Co<sub>2</sub>C nanoprisms and sphere-like Co<sub>2</sub>C nanoparticles, the Co/SiO<sub>2</sub>-0.2Na

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Sample	CO Conversion/C%	Product selectivity (C%, CO <sub>2</sub> -free)				Olefin/Paraffin ratio			
		$CH_4$	C <sub>2-4</sub> <sup>=</sup>	C <sub>2-4</sub> °	$C_{5^+}$ +ROH	C <sub>2</sub>	C <sub>3</sub>	$C_4$	
Co/SiO <sub>2</sub> -0Na	17.7	17.2	7.1	9.8	65.9	0.1	1.5	0.6	_
Co/SiO <sub>2</sub> -0.2Na	3.1	7.6	19.6	4.7	68.1	8.7	20.2	13.1	
Co/SiO <sub>2</sub> -1Na	2.8	10.2	27.6	2.0	60.2	10.8	19.8	13.6	

**Table 4** The catalytic performance of various Co/SiO<sub>2</sub> catalysts on atmospheric pressure (250 °C, 1 bar, H<sub>2</sub>/CO=2 and GHSV=2000  $mL \cdot g^{-1} \cdot h^{-1}$ )

and Co/SiO<sub>2</sub>-1Na catalysts were also evaluated at atmospheric pressure as showed in Table 4. All the samples with the Co<sub>2</sub>C phase in our study showed higher O/P ratios than unpromoted Co/SiO<sub>2</sub>. However, the O/P ratios were still lower than those of Co<sub>2</sub>C nanoprisms with exposed (101) and (020) facets.<sup>[30]</sup> In addition, higher CH<sub>4</sub> selectivity was obtained for sphere-like Co<sub>2</sub>C. It further illustrated that the morphology and exposed facet had strong effect on the catalytic performance of Co<sub>2</sub>C for syngas conversion.

### Conclusions

The effect of sodium on the structure and catalytic performance of  $Co/SiO_2$  for the Fischer-Tropsch synthesis was investigated in details. The samples with different Na loadings were characterized by various methods. The results showed that Na could change the structure of the catalyst, resulting in decreasing surface area and particles size and increasing the reduction temperature. From the XRD and TEM results of spent samples, the addition of Na promoted the formation of  $Co_2C$  with sphere-like morphology.

CO conversion and products selectivity were strongly influenced by the Na promoter. The addition of Na greatly decreased the catalytic activity and increased CO<sub>2</sub> selectivity. However, oxygenates selectivity, especially alcohol selectivity, increased when Na was added. It seemed that the addition of Na led to the transformation of the catalytic performance from typical FT reaction to oxygenate formation. The hydrocarbon products shifted to lower carbon numbers for Na-promoted samples. However, the oxygenate chain growth factors slightly increased once Na was added. In addition, the chain growth factors of all products almost kept as constant for the promoted samples with different Na loadings. The O/P ratios of samples with Na were much higher than those without Na. The metallic cobalt shifted to cobalt carbide during the reaction process due to the presence of Na, indicating that Na could promote the formation of Co<sub>2</sub>C serving as the active site for oxygenate and olefin formation.

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#### References

- [1] Iglesia, E. Appl. Catal. A **1997**, 161, 59.
- [2] Saul, E. C.; Richard, G. C.; Graham, J. H.; Terblanche, S. P.; Michael, M. T. *Nature* **1989**, *339*, 129.
- [3] Zhang, Q.; Deng, W.; Wang, Y. J. Energy Chem. 2013, 22, 27.
- [4] Bezemer, G. L.; Bitter, J. H.; Kuipers, H. P. C. E.; Ooster beek, H.; Holewijn, J. E.; Xu, X. D.; Kaptijn, F.; Dillen, A. J. V.; Jong, K. P. D. *J. Am. Chem. Soc.* **2006**, *128*, 3956.
- [5] Tian, H.; Li, X. Y.; Zeng, L.; Gong, J. L. ACS Catal. 2015, 5, 4959.
- [6] Xiong, H.; Zhang, Y.; Liew, K. Y.; Li, J. L. J. Mol. Catal. A: Chem. 2008, 95, 68.
- [7] Borg, O.; Eri, S.; Blekkan, E. A.; Storsaeter, S.; Wigum, H.; Rytter, E.; Holmen, A. J. Catal. 2007, 248, 89.
- [8] Dsa, A. R. D. L.; Lucas, A. D.; Valverde, J. L.; Romero, A.; Monteagudo, I.; Coca, P.; Sanchez, P. *Catal. Today* 2011, 167, 96.
- [9] Jongeomjit, B. J. Catal. 2003, 215, 66.
- [10] Xiang, Y. Z.; Barbosa, R.; Li, X. N.; Kruse, N. ACS Catal. 2015, 5, 2929.
- [11] Xiao, K.; Qi, X. Z.; Bao, Z. D.; Wang, X. X.; Zhong, L. S.; Fang, K. G; Lin, M. G; Sun, Y. H. Catal. Sci. Technol. 2013, 3, 1591.
- [12] Dinse, A.; Aigner, M.; Ulbrich, M.; Johnson, G. R.; Bell, A. T. J. Catal. 2012, 288, 104.
- [13] Johnson, G. R.; Werner, S.; Bell, A. T. ACS Catal. 2015, 5, 5888.
- [14] Shimura, K.; Miyazawa, T.; Hanaoka, T.; Hirata, S. Appl. Catal. A 2015, 494, 1.
- [15] Werner, S.; Johnson, G. R.; Bell, A. T. ChemCatChem 2014, 6, 2881.
- [16] Anton, J.; Nebel, J.; Song, H. Q.; Froese, C.; Weide, P.; Ruland, H.; Muhler, M.; Kaluza, S. J. Catal. 2016, 335, 175.
- [17] Cheng, K.; Ordomsky, V. V.; Legras, B.; Virginie, M.; Paul, S.; Wang, Y.; Khodakov, A. Y. *Appl. Catal. A* **2015**, *502*, 204.
- [18] Galvis, H. M. T.; Koejen, A. C. J.; Bitter, J. H.; Davidian, T.; Ruitenbeek, M.; Dugulan, A. L.; de Jong, K. P. J. Catal. 2013, 303, 22.
- [19] Ribeiro, M.; Jacobs, G.; Davis, B. H.; Cronauer, D. C.; Kropf, A. J.; Marshall, C. L. J. Am. Chem. Soc. 2010, 114, 7895.
- [20] Chun, D. H.; Park, J. C.; Lee, H.; Yang, J. G.; Hong, S. J.; Jung, H. Catal. Lett. 2013, 143, 1035.
- [21] Eliseev, O. L.; Tsapkina, M. V.; Dementeva, O. S.; Davydov, P. E.; Kazakov, A. V.; Lapidus, A. L. *Kinet. Catal.* **2013**, *54*, 207.
- [22] Xiong, H. F.; Motchelaho, M. A. M.; Moyo, M.; Jewell, L. L.; Coville, N. J. *Fuel* **2015**, *150*, 687.
- [23] Lillebø, A. H.; Patanou, E.; Yang, J.; Blekkan, E. A.; Holmen, A. *Catal. Today* 2013, 215, 60.
- [24] Ishida, T.; Yangihara, T.; Liu, X. H.; Ohashi, H.; Hamasski, A.; Honma, T.; Oji, H.; Yokoyama, T.; Tokunaga, M. *Appl. Catal. A* 2013, 458, 145.
- [25] Khobragade, M.; Majhi, S.; Pant, K. K. Appl. Energ. 2012, 94, 385.
- [26] Pei, Y. P.; Liu, J. X.; Zhao, Y. H.; Ding, Y. J.; Liu, T.; Dong, W. D.; Zhu, H. J.; Su, H. Y.; Yan, L.; Li, J. L.; Li, W. X. ACS Catal. 2015, 5, 3620.
- [27] Karaca, H.; Hong, J. P.; Fongarland, P.; Roussel, P.; Griboval con-

stant, A.; Lacroix, M.; Hortmann, K.; Safonova, O.; Khodakov, A. Y. Chem. Commun. 2010, 46, 788.

- [28] Fang, Y. Z.; Liu, Y.; Zhang, L. H. Appl. Catal. A 2011, 397, 183.
- [29] Tienthao, N.; Zahediniaki, M. H.; Alamdari, H. S.; Kaliaguine, S. J. Catal. 2007, 245, 348.
- [30] Zhong, L. S.; Yu, F.; An, Y. L.; Zhao, Y. H.; Sun, Y. H.; Li, Z. J.; Lin, T. J.; Lin, Y. J.; Qi, X. Z.; Dai, Y. Y.; Gu, L.; Hu, J. S.; Jin, S. F.; Shen, Q.; Wang, H. *Nature* **2016**, *538*, 84.
- [31] Gnanamani, M. K.; Jacoba, G.; Shafer, W. D.; Davis, B. H. Catal. Today 2013, 215, 13.
- [32] Chen, L.; Shen, J. Y. J. Catal. 2011, 279, 246.
- [33] Karaca, H.; Safonova, O. V.; Chambrey, S.; Fongarlang, P.; Roussel, P.; Gribovalconstant, A.; Lacroix, M.; Khodakov, A. Y. J. Catal. 2011, 277, 14.
- [34] Tsakoumis, N. E.; Ronning, M.; Borg, O.; Rytter, E.; Holmen, A. *Catal. Today* 2010, 154, 162.

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