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Article

Effect of the support on cobalt carbide catalysts for sustainable production of olefins from syngas

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ABSTRACT

Co₂C-based catalysts with SiO₂, γ-Al₂O₃, and carbon nanotubes (CNTs) as support materials were prepared and evaluated for the Fischer-Tropsch to olefin (FTO) reaction. The combination of catalytic performance and structure characterization indicates that the cobalt-support interaction has a great influence on the Co₂C morphology and catalytic performance. The CNT support facilitates the formation of a CoMn composite oxide during calcination, and Co₂C nanoprisms were observed in the spent catalysts, resulting in a product distribution that greatly deviates from the classical Anderson-Schulz-Flory (ASF) distribution, where only 2.4 C% methane was generated. The Co₃O₄ phase for SiO₂- and γ-Al₂O₃-supported catalysts was observed in the calcined sample. After reduction, CoO, MnO, and low-valence CoMn composite oxide were generated in the γ-Al₂O₃-supported sample, and both Co₂C nanospheres and nanoprisms were identified in the corresponding spent catalyst. However, only separated phases of CoO and MnO were found in the reduced sample supported by SiO₂, and Co₂C nanospheres were detected in the spent catalyst without the evidence of any Co₂C nanoprisms. The Co₂C nanospheres led to a relatively high methane selectivity of 5.8 C% and 12.0 C% of the γ-Al₂O₃- and SiO₂-supported catalysts, respectively. These results suggest that a relatively weak cobalt-support interaction is necessary for the formation of the CoMn composite oxide during calcination, which benefits the formation of Co₂C nanoprisms with promising catalytic performance for the sustainable production of olefins via syngas.

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1. Introduction

Olefins, as basic building blocks of the chemical industry, are extensively used to synthesize various products such as polymers, solvents, drugs, cosmetics, and detergents [1–5]. Traditionally, olefins are produced by thermal or catalytic cracking

of petroleum products such as naphtha, gas oil, and condensates. Due to the expected depletion of limited petroleum reserves, it is necessary to develop new processes that can produce olefins from alternative feedstocks. Syngas, a mixture of carbon monoxide and hydrogen, can be obtained from various carbon-containing sources such as coal, natural gas, biomass,

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and even organic waste [6–11]. Many value-added products, including methanol, gasoline, diesel, alcohols, and olefin chemicals, can be obtained from syngas conversion.

Owing to the simplified operation and low energy consumption, direct production of olefins from syngas has attracted increased attention. The typical routes of direct production of olefins from syngas include bifunctional catalytic reactions and the Fischer-Tropsch to olefin (FTO) process. During bifunctional catalytic processes, methanol-like intermediates are generated first, which are then further converted into olefins using molecular sieve catalysts [3,12–14]. Jiao et al. [13] and Li et al. [15] developed a $\text{ZnCrO}_x/\text{MSAPO}$ bifunctional catalyst and obtained a C_{2-4} selectivity as high as 80 C% at a CO conversion of 17% at 400 °C and 2.5 MPa. Cheng et al. [14] reported a $\text{Zn-Zr}/\text{SAPO-34}$ catalyst with a CO conversion of 10% and C_{2-4} selectivity of 70 C% at 400 °C and 1 MPa. In addition, it was found that the integration manner and proximity of the two components are crucial for the C_{2-4} selectivity [16–18]. Traditional studies of the FTO process mainly focused on Fe-based catalysts [1,19,20]. Torres Galvis et al. [4] studied supported iron FTO catalysts and found that Fe/CNF and $\text{Fe}/\alpha\text{-Al}_2\text{O}_3$ catalysts exhibit a high selectivity toward lower olefins (~60 C%) with relatively low methane selectivity (<25 C%). The effects of the iron particle size, sodium, and sulfur on the catalytic performance of supported iron catalysts during the FTO reaction were also investigated [5,21,22]. The results showed that the nature and concentrations of the promoters play a key role in the design of FTO catalysts with optimum catalytic performance. However, Fe-based FTO catalysts usually require a very high temperature (>300 °C), which may cause catalyst deactivation due to particle sintering and carbon deposition.

Recently, we discovered that Co_2C nanoprisms derived from the CoMn composite oxide could catalyze syngas conversion to lower olefins with a high selectivity of 60.8 C% under mild reaction conditions (250 °C, 1–5 bar) [23–25]. Low methane (<5 C%) and high olefin selectivities with a high olefin/paraffin ratio were simultaneously obtained. Catalyst characterization and theoretical calculations indicated that Co_2C nanoprisms play a key role in syngas conversion, which favors olefin production and inhibits methane formation. The effects of alkali and manganese on the catalytic performance of Co-based catalysts during the FTO reaction were also studied [24,25]. It was found that Na, acting as an electronic donor to cobalt, promotes

the formation of Co_2C . Manganese not only acts as typical electronic and structural promoter but also has a strong influence on the morphology of Co_2C nanoprisms with special exposed (101) and (020) facets.

Supported catalysts are usually used for the Fischer-Tropsch reaction to enhance the mechanical stability and thermal conductivity and improve the dispersion of the active phase [26–28]. The effect of the chemical nature of the oxide support on the cobalt FT catalysts was investigated by Reuel et al. [29], who reported a decline in the catalytic activity per surface Co atom (or turnover frequency, TOF) in the order $\text{Co}/\text{TiO}_2 > \text{Co}/\text{SiO}_2 > \text{Co}/\text{Al}_2\text{O}_3 > \text{Co}/\text{MgO}$. Keyvanloo et al. [30] reported a supported Fe-FT catalyst using γ -alumina doped with silica as the support. The catalytic performance was greatly improved compared with bulk and traditionally supported Fe-FT catalysts. Prieto et al. [31] studied the effect of the chemical nature of the oxide support on the performance of cobalt FT catalysts and observed a volcano dependence of the metal-specific activity on the nature of the support. A marked support effect on the hydrocarbon selectivity pattern was also reported by Borg et al. [7], who found that the porosity size of the $\gamma\text{-Al}_2\text{O}_3$ support affects the size of the Co_3O_4 nanoparticles and product selectivity.

In our previous work, Co_2C -based FTO catalysts were usually prepared by coprecipitation. Whether a supported Co-based catalyst prepared by impregnation is available for FTO remains unclear, in addition to its effect on the catalytic performance. In this study, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and carbon nanotubes (CNTs) were selected as supports and their effects were investigated. The detailed structure of the catalysts was studied with a combination of several characterization techniques such as nitrogen adsorption, temperature-programmed reduction (TPR), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The effect of the cobalt-support interaction on the Co_2C morphology and catalytic performance was also discussed.

2. Experimental

2.1. Catalyst preparation

Supported Co catalysts with a nominal loading of 30 wt% Co (as metal Co), 14 wt% Mn (the atomic ratio of Co/Mn is 2), and

Liangshu Zhong (Shanghai Advanced Research Institute, Chinese Academy of Sciences) **received the 6th Young Chemist Award in 2018**, which was presented by Chinese Chemical Society and Royal Society of Chemistry. Professor Liangshu Zhong received his Ph.D. degree in Physical Chemistry from Institute of Chemistry, Chinese Academy of Sciences in 2008. After two years in Technical University of Munich as a post-doctoral fellow, he joined Shanghai Advanced Research Institute, Chinese Academy of Sciences in 2010 where he was promoted to a full professor in 2015. He has also received several awards and honours, including the Young Scientist Award of Chinese Academy of Sciences in 2017, and Outstanding Advisor Award of Chinese Academy of Sciences in 2017. His research interests are mainly focused on development of new catalyst systems with high selectivity for C1 conversion via the design of new active sites and the investigation of nanoeffects.

2 wt% Na were prepared by multi-step incipient wetness impregnation of the selected support with an aqueous solution of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd.), manganese nitrate (50 wt% $\text{Mn}(\text{NO}_3)_2$, aq, Sinopharm Chemical Reagent Co., Ltd.), and Na_2CO_3 (Sinopharm Chemical Reagent Co., Ltd.). Different support materials were used including SiO_2 (480 m^2/g , Aladdin), $\gamma\text{-Al}_2\text{O}_3$ (180 m^2/g , Sasol), and CNT (170 m^2/g , Sinopharm Chemical Reagent Co., Ltd.). Before impregnation, the CNT support was pretreated using the following procedure. The CNT (30 g) and 65%–68% HNO_3 (600 mL, Sinopharm Chemical Reagent Co., Ltd.) were added to a flask (1000 mL), the mixture was stirred at 100 °C for 5 h, and the resulting suspension was filtered. The filter cake was washed with deionized water eight times and dried at 80 °C for 12 h.

The solution was added to the support until the pore volume was completely filled. After each impregnation step, the catalysts were dried at 80 °C for 2 h. Impregnation and drying steps were repeated until the total volume of the solution was incorporated. The dried samples supported on SiO_2 or $\gamma\text{-Al}_2\text{O}_3$ were calcined at 400 °C for 3 h with a heating rate of 1 °C/min in static air, while the CNT sample was calcined under nitrogen flow.

2.2. Catalyst characterization

Nitrogen adsorption measurements were performed on a Micromeritics TriStar 3020 instrument. Approximately 50 mg sample was degassed at 200 °C in vacuum for 10 h and then moved to the analysis station for adsorption-desorption at −196 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The total pore volume and average pore size were determined by the Barrett-Joyner-Halenda (BJH) method. The adsorption branches were employed for the calculations [32].

The XRD patterns of the catalysts were obtained with a Rigaku Ultima IV X-ray powder diffractometer (40 kV, 40 mA) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at a scanning rate of 4°/min. Subsequently, H_2 -TPR experiments were carried out on a Micromeritics Autochem-II 2920 instrument equipped with a thermal conductivity detector (TCD). The samples (30 mg) were pretreated under a helium flow at 200 °C for 120 min and then cooled to 50 °C. The gas stream was then switched to 5% (v/v) H_2/Ar and the temperature was raised from 50 to 800 °C at a rate of 10 °C/min.

TEM measurements were performed on a JEOL JEM 2011 electron microscope with a 200 kV accelerating voltage. The samples were prepared by dispersing the powder in ethanol followed by ultrasonication and then one droplet of the suspension was dropped on a carbon-coated copper grid for the measurement. The nanoparticle size distribution of each sample was determined using samples of ~300 nanoparticles.

2.3. Catalytic evaluation

The FTO reaction was carried out in a stainless fixed-bed reactor with an inner diameter of 8 mm. A total of 1.5 g of the

catalyst (40–60 mesh) was mixed with 3 g silica of the same size. Prior to the reaction, the catalysts were reduced *in situ* at 300 °C and 1 bar for 5 h in a flow of 10% CO/N_2 (v/v) with a weight hourly space velocity (WHSV) of 6000 $\text{mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ (where g_{cat} denotes the mass of the catalyst). The heating ramp was 1 °C/min. After the reduction, the temperature was dropped to 265 °C. A mixture of 97 vol% syngas with different H_2/CO (v/v) ratios ($\text{H}_2/\text{CO} = 0.5, 1, \text{ or } 2$) and 3 vol% N_2 (as an internal standard) was introduced to the reactor as the feed gas. The reaction pressure was then increased to 5 bar, and the reaction was conducted at a WHSV of 2000 $\text{mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$. The pressure of the system was kept at 5 bar using a pressure controller (TESCOM). Data were recorded after 100 h of reaction when reaction stability was reached.

The outlet gas was analyzed online with a GC after passing through hot (120 °C) and cold (0 °C) traps and the liquid and wax products were collected and analyzed offline (also using the GC). During the reaction, the reactor effluent was analyzed online by an Agilent 7890B gas chromatograph equipped with two columns and two detectors. The H_2 , N_2 , CO , CH_4 , and CO_2 concentrations were analyzed by employing a TDX-1 carbon molecular sieve column with a TCD using He as the carrier gas. The $\text{C}_1\text{--C}_7$ hydrocarbons were analyzed with a KCl-modified alumina capillary column (Agilent 19095P-K25) with Ar carrier gas and a hydrogen flame ionization detector (FID). Aqueous, liquid oil, and solid wax products collected from the cold and hot traps were analyzed offline with a GC (Shimadzu GC2010 plus). The H_2O , methanol, and $\text{C}_1\text{--C}_5$ oxygenates of the aqueous products were analyzed by using two Porapak Q columns equipped with a TCD and FID. The liquid oil products were analyzed with an HP-1 column with N_2 carrier gas and FID. The solid wax products were dissolved in CS_2 and analyzed with an MXT-1 column with N_2 carrier gas and FID. The mass, carbon, and oxygen balances calculated for each test were 100% $\pm$ 5%. Further details of the GC analysis can be found in our previous studies [23,33].

For a typical FTO reaction, the CO conversion (X_{CO}) and product selectivity (S_{CO_2} , S_i) were calculated based on the following equations:

$$X_{\text{CO}} = (n_{\text{CO,inlet}} - n_{\text{CO,outlet}}) / n_{\text{CO,inlet}} \times 100\%$$

$$S_{\text{CO}_2} = n_{\text{CO}_2} / (n_{\text{CO,inlet}} - n_{\text{CO,outlet}}) \times 100\%$$

$$S_i = (N_i \times n_i) / \sum (N_i \times n_i) \times 100\%$$

where $n_{\text{CO,inlet}}$ and $n_{\text{CO,outlet}}$ represent the moles of CO at the inlet and outlet, respectively, n_{CO_2} represents the moles of CO_2 at the outlet, N_i is the molar fraction of product i , and n_i is the carbon number of product i .

3. Results and discussion

3.1. Structure characterization

3.1.1. Textural properties

The BET surface area, pore size, and pore volume of the supports and the corresponding supported catalysts are listed in Table 1. The SiO_2 support exhibits the highest specific surface area of 459.0 m^2/g . The specific surface areas of $\gamma\text{-Al}_2\text{O}_3$

Table 1

Textural properties of various supports and the corresponding catalysts.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)
SiO ₂	459.0	0.78
γ-Al ₂ O ₃	184.6	0.52
CNT	170.6	0.57
CoMnNa/SiO ₂	60.7	0.23
CoMnNa/γ-Al ₂ O ₃	72.7	0.21
CoMnNa/CNT	98.4	0.37

and CNT are 184.6 and 170.6 m²/g, respectively. After impregnation, the specific surface area and pore volume decrease dramatically due to the coverage and/or blocking of the pore structure [34]. The specific surface areas of CoMnNa/SiO₂, CoMnNa/γ-Al₂O₃, and CoMnNa/CNT decrease to 60.7, 72.7, and 98.4 m²/g, respectively. The pore volumes of SiO₂, γ-Al₂O₃, and CNT are 0.78, 0.52, and 0.57 cm³/g, respectively. However, the pore volumes of the corresponding catalysts decrease to 0.23, 0.21, and 0.37 cm³/g after impregnation, respectively.

3.1.2. XRD

The XRD patterns of the calcined cobalt catalysts with different supporting materials are presented in Fig. 1(a). In addition to weak diffraction peaks of the corresponding support materials, the XRD measurements of CoMnNa/SiO₂ and CoMnNa/γ-Al₂O₃ reveal the presence of diffraction peaks corresponding to Co₃O₄ (JCPDS #74-2120) and MnO₂ (JCPDS #81-2261). The CoMnNa/CNT shows diffraction peaks of CoMn₂O₄ (JCPDS #77-0471) and CoO (JCPDS #74-2391) [24,25,35].

After reduction at 300 °C (Fig. 1(b)), CoMnNa/SiO₂ shows diffraction peaks of MnO (JCPDS #75-0257) and CoO (JCPDS #71-1178), indicating the separation of the cobalt and manganese phases. The average crystallite size of CoO is 9.5 nm based on Scherrer's equation using the (200) peak located at 2θ = 42.4°. For CoMnNa/γ-Al₂O₃, diffraction peaks of Co_xMn_{1-x}O with a low degree of crystallinity at 2θ of 36°, 42°, and 61° were observed in addition to that of CoO and MnO. However, only the Co_xMn_{1-x}O phase was found in the reduced CoMnNa/CNT catalyst. The average Co_xMn_{1-x}O crystallite size in the reduced CoMnNa/γ-Al₂O₃ and CoMnNa/CNT is 15.4 and 23.3 nm, respectively.

With respect to the spent catalysts (Fig. 1(c)), all samples

show diffraction peaks of Co₂C (JCPDS # 65-1457) at 2θ of 41.3°, 42.6°, and 45.7°. Based on the calculation using Scherrer's equation and the (111) peak located at 2θ = 42.8°, the average sizes of the Co₂C nanoparticles are 15.4, 20.8, and 23.9 nm for CoMnNa/SiO₂, CoMnNa/γ-Al₂O₃, and CoMnNa/CNT, respectively. Diffraction peaks of Co_xMn_{1-x}O were also observed in the spent CoMnNa/γ-Al₂O₃ and CoMnNa/CNT samples. In addition, diffraction peaks assigned to MnCO₃ (JCPDS #44-1472) at 2θ of 31.4°, 37.5°, and 51.7° were found for CoMnNa/CNT.

3.1.3. TPR

The TPR results for the supported catalysts are presented in Fig. 2(a). The outlet gas was detected online using a mass spectrometer. Fig. 2(b) shows the evolution of the MS signal of *m/z* = 18 (H₂O) vs. the reduction temperature during the TPR process. The TPR profiles fit the MS signal well, suggesting that all TPR peaks are involved in the consumption of hydrogen and formation of water. For the CoMnNa/SiO₂ and CoMnNa/γ-Al₂O₃ catalysts, three distinct peaks centered at 372, 427, and 566 °C and at 326, 400, and 604 °C were identified, respectively. Based on the combination with the XRD results and previous studies [23–25,35], the first two peaks of CoMnNa/SiO₂ and CoMnNa/γ-Al₂O₃ correspond to a two-step reduction of Co³⁺ to Co²⁺ and Co²⁺ to metallic Co⁰. The peak at the higher reduction temperature is mainly due to highly dispersed cobalt species that strongly interact with the oxide support. Notably, the TPR peaks in Fig. 2(a) reveal that the metal-support interaction of SiO₂ is stronger than that of γ-Al₂O₃. The third peak of the CoMnNa/SiO₂ catalyst at 566 °C is due to the reduction of cobalt silicates [36]. The third peak of CoMnNa/γ-Al₂O₃ at 604 °C corresponds to the reduction of cobalt aluminate species [27,37]. The CoMnNa/CNT catalyst shows two distinct peaks centered at 372 and 447 °C, corresponding to the reduction of CoO and CoMn composite oxides, respectively.

3.1.4. (HR)TEM

The (HR)TEM images of the reduced samples are shown in Fig. 3. Both CoO (with a *d*-spacing of 2.13 Å of the (200) facet) and MnO (with a *d*-spacing of 2.54 Å of the (111) facet) phases were found in the reduced CoMnNa/SiO₂ sample. The average size of CoO is only 10.2 nm, with a very narrow distribution (Fig. 3(a3)). Sphere-like nanoparticles were observed in the reduced samples of CoMnNa/γ-Al₂O₃ and CoMnNa/CNT, with a

Fig. 1. XRD patterns of various catalysts after calcination (a), reduction (b), and reaction (c). (1) CoMnNa/SiO₂; (2) CoMnNa/γ-Al₂O₃; (3) CoMnNa/CNT.

Fig. 2. (a) TPR profiles of various supported catalysts; (b) MS signals of $m/z = 18$ (H₂O) of the outlet gas during the TPR. (1) CoMnNa/SiO₂; (2) CoMnNa/ γ -Al₂O₃; (3) CoMnNa/CNT.

Fig. 3. TEM images ((1) and (2)) and particle size distributions (3) for various reduced supported catalysts. (a) CoMnNa/SiO₂; (b) CoMnNa/ γ -Al₂O₃; (c) CoMnNa/CNT.

size distribution of 5–40 nm. The d -spacings of 2.13 and 2.47 Å correspond to the (200) and (111) facets of Co_xMn_{1-x}O, respectively. The average particle sizes of Co_xMn_{1-x}O on the γ -Al₂O₃ and CNT supports are 17.5 and 26.4 nm, respectively, much

greater than that on SiO₂. In addition, most of the Co_xMn_{1-x}O nanoparticles are located outside of the channels of CNT.

The (HR)TEM images of the spent catalysts are presented in Fig. 4. A large number of spherical nanoparticles from 5 to 30

Fig. 4. (HR)TEM images of various spent catalysts. (a) CoMnNa/SiO₂; (b) CoMnNa/γ-Al₂O₃; (c) CoMnNa/CNT.

nm were observed in the SiO₂-supported catalyst. Magnified images of randomly selected areas are shown in Fig. 4(a2)–(a3). Nanoparticles with lattice spacings of 2.12 and 2.18 Å corresponding to the (111) and (020) planes of Co₂C, respectively, were detected. Fig. 4(b1)–(b3) shows the (HR)TEM images of the CoMnNa/γ-Al₂O₃ catalyst; both Co₂C nanospheres and nanoprisms were identified. Many Co₂C nanoprisms with *d*-spacings of 2.19 and 2.45 Å corresponding to the (020) and (101) exposed facets, respectively, were observed in the CoM-

nNa/CNT catalyst (Fig. 4(c1)–(c3)), with most of the Co₂C nanoparticles located outside of the CNT channels.

3.2. Catalytic performance

The supported catalysts were evaluated at 265 °C and 5 bar to determine the influence of the support on the catalytic activity and product selectivity, as shown in Table 2. With a H₂/CO ratio of 0.5, the studied catalysts exhibit similar CO conversions

Table 2

Catalytic FTO reaction performance of various supported catalysts.

Catalyst	H ₂ /CO	X _{CO} (C%)	S _{CO₂} (C%)	Product selectivity (C%, CO ₂ -free)			Olefin/paraffin ratio			
				Olefins	Oxygenates	Paraffins (CH ₄) ^a	C ₂	C ₃	C ₄	O/P
CoMnNa/SiO ₂	0.5	10.8	35.1	68.5	11.9	19.6 (12.0)	4.8	12.1	9.7	3.5
	1.0	32.2	38.7	64.4	9.8	25.9 (14.5)	1.7	8.5	6.4	2.5
	2.0	63.2	36.5	50.5	10.8	38.7 (20.4)	0.3	4.4	4.2	1.3
CoMnNa/γ-Al ₂ O ₃	0.5	12.2	38.1	64.7	22.7	12.6 (5.8)	7.2	16.9	11.9	5.1
	1.0	32.7	45.1	66.2	14.0	19.8 (10.2)	2.3	10.9	8.1	3.3
	2.0	60.6	42.3	51.5	14.7	33.8 (17.6)	0.6	5.3	5.0	1.5
CoMnNa/CNT	0.5	12.8	46.1	66.6	25.4	7.9 (2.4)	12.9	16.4	10.4	8.4
	1.0	26.6	50.0	60.0	27.2	12.8 (5.4)	5.8	10.9	7.4	4.7
	2.0	42.8	48.9	54.7	26.4	18.9 (9.2)	3.4	8.2	5.7	2.9

Reaction conditions: 265 °C, 5 bar, 2000 mL h⁻¹ g_{cat}⁻¹.

^a The values in the brackets represent the methane selectivity of the total product.

Fig. 5. (1) Hydrocarbon distributions of various supported catalysts with the chain growth probability (α) obtained by fitting the results generated for chains of three to seven carbons using the ASF model; (2)–(4) Detailed distributions of hydrocarbons. (a) CoMnNa/SiO₂; (b) CoMnNa/ γ -Al₂O₃; (c) CoMnNa/CNT.

(10.8%–12.8%), while the product selectivity differs greatly. The CO₂ selectivity of various catalysts follows the order CoMnNa/SiO₂ (35.1 C%) < CoMnNa/ γ -Al₂O₃ (38.1 C%) < CoMnNa/CNT (46.1 C%). For the FTO process, it is necessary to

maximize the olefin fraction and minimize the methane selectivity. Although the SiO₂-supported catalyst shows 68.5 C% of olefin selectivity and 11.9 C% of oxygenates selectivity, the methane selectivity is too high (12.0 C%) and the ratio of olefin

to paraffin is only 3.5. The olefin and oxygenate selectivities of the γ - Al_2O_3 -supported catalyst are 64.7 C% and 22.7 C%, respectively, whereas the methane selectivity is 5.8 C% and the ratio of olefin to paraffin is higher (5.1). The CNT-supported catalyst, however, displays optimal product fractions of olefins and oxygenates. The total olefin and oxygenate selectivities are as high as 92.1 C% (66.7% and 25.4 C%, respectively) and the olefin to paraffin ratio reaches 8.4 with the least amount of methane formed (2.4 C%).

The detailed hydrocarbon distributions of various catalysts are shown in Fig. 5. A remarkable deviation from the typical ASF distribution was observed for the CNT-supported catalyst. With respect to the C_2 component, reabsorption of olefins is the main reason for the much lower value of the C_2 component compared with the prediction. However, the hydrocarbon distribution of the SiO_2 -supported catalyst follows the ASF law, while the γ - Al_2O_3 -supported catalyst slightly deviates from the traditional ASF model. The chain growth probabilities for the SiO_2 -, γ - Al_2O_3 -, and CNT-supported catalysts are 0.51, 0.57, and 0.65, respectively. The slightly higher chain growth probability for the CNT-supported catalyst suggests a stronger chain

propagation probability. The hydrocarbon distributions of the catalysts are plotted in Fig. 5(a2), (b2), and (c2). The CNT-supported catalyst shows the highest olefin content, reaching as high as 88.7 wt% of the total hydrocarbons with a methane fraction of only 3.7 wt%. In addition, the obtained olefins are mainly in the range of C_2 to C_{12} , with a C_{2-10} selectivity as high as 91%, while the C_{13+} selectivity is as low as 5%, indicating a much narrower distribution. The olefin fraction of the SiO_2 - and γ - Al_2O_3 -supported catalysts drops to 76.1 wt% and 81.4 wt%, respectively. The methane fractions of the SiO_2 - and γ - Al_2O_3 -supported catalysts are as high as 15.2 wt% and 8.3 wt%, respectively.

The effect of the H_2/CO ratio on the catalytic performance was also investigated. Table 2 shows that the CO conversion of all supported catalysts increases with increasing H_2/CO ratio. However, the olefin selectivity and O/P ratio dramatically decrease due to the intensive hydrogenation at a higher H_2/CO ratio and increasing methane selectivity. For example, at a H_2/CO ratio of 2, the olefin selectivity decreases to 50.5 C% over $\text{CoMnNa}/\text{SiO}_2$ and the methane and paraffin selectivities increase to 20.4 C% and 38.7 C%, respectively. The olefin selec-

Fig. 6. (a) Oxygenate product distributions of CNT-supported catalysts with different H_2/CO ratios with the chain growth probability (α) obtained by fitting the results generated for chains of five to nine carbons using the ASF model; Oxygenate product distributions at H_2/CO ratios of (b) 0.5, (c) 1, and (d) 2.

tivity of the γ - Al_2O_3 -supported catalyst also decreases to 51.5% and the methane and paraffin selectivities increase to 17.6 C% and 33.8 C%, respectively. The CNT-supported catalysts still exhibit a promising catalytic performance, even at a higher H_2/CO ratio. The total olefin and oxygenate selectivities are still as high as 81.1 C%, with a H_2/CO ratio of 2. The undesired methane and paraffin selectivities only slightly increase to 9.2 C% and 18.9 C%, respectively.

The hydrocarbon distributions under various H_2/CO ratios are plotted in Fig. 5. Due to the enhanced hydrogenation ability under a high H_2/CO ratio, the chain growth probability decreases. For example, the chain growth probability of the SiO_2 -supported catalysts decreases from 0.51 to 0.46 as the H_2/CO ratio increases from 0.5 to 2. In addition, the olefin fraction in hydrocarbons drops dramatically from 76.1 wt% to 54.4 wt% with increasing H_2/CO ratio of the SiO_2 -supported catalyst and from 81.4 wt% to 58.1 wt% for the γ - Al_2O_3 -supported catalyst. However, the olefin content of the CNT-supported catalyst only slightly decreases from 88.7 wt% to 72.7 wt%. The methane content of the hydrocarbons also increases with increasing H_2/CO ratio. At a H_2/CO ratio of 2, the methane con-

tent of the hydrocarbons of the SiO_2 - and γ - Al_2O_3 -supported catalysts increase to 25.1 wt% and 22.7 wt%, respectively. However, the methane fraction of the CNT-supported catalyst only increases to 14.0 wt%.

In addition to the formation of olefins, a large amount of oxygenates was also detected in the CNT-supported catalyst. Ding et al. [38–41] reported that a high activity and high alcohol selectivity could be obtained on activated carbon-supported cobalt catalysts from syngas via FT reaction. They attributed this to the high dispersion of Co and the formation of Co_2C species. The DFT calculations suggest that the activation energies for CO dissociation of various Co_2C facets are quite different. In our previous study [35], we showed that Co_2C nanoparticles with certain exposed facets can act as dual sites for oxygenate formation. The Co_2C facets with a lower CO dissociation activation energy might act as the active site to form alkyl species, while those with a higher CO dissociation activation energy are responsible for CO insertion. Oxygenate products may be generated at the interface of two adjacent Co_2C facets with distinct CO dissociation energies. Fig. 6 shows the oxygenate distribution of the CoMnNa/CNT catalyst at different H_2/CO ratios. The

Fig. 7. Catalytic FTO process performance of CoMnNa/CNT catalysts. (a) CO conversion and product selectivity as a function of the time-on-stream; (b) Ratio of olefin to paraffin as a function of the time-on-stream; (c) Product plots ($\ln(W_n/n)$ and n) with the time-on-stream for hydrocarbons; where W_n is the weight fraction of a product with n number of carbon atoms; (d) Chain growth probability (α) as a function of the time-on-stream obtained by fitting the results generated for chains of three to seven carbons using the ASF model. Reaction conditions: 265 °C, 5 bar, 2000 $\text{mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$, and $\text{H}_2/\text{CO} = 0.5$.

C₂–C₁₀ oxygenate fraction accounts for more than 93.6 wt% of all oxygenate products. With the H₂/CO ratio increasing from 0.5 to 2, the chain growth probability of the oxygenates decreases from 0.70 to 0.58 and the aldehyde fraction decreases from 78.3 wt% to 34.6 wt%. In addition, the methanol content increases from 0.8 wt% to 5.1 wt%.

The catalytic stability of the CNT-supported catalyst was also tested (Fig. 7). After an initial activation period, the CO conversion reaches 12 C% and no notable deactivation is found within 150 h of the time-on-stream. The product selectivity remains unchanged with a ~43 C% CO₂ selectivity. With respect to the product selectivity, the methane and C_{2–4} selectivities are maintained at approximately 2.2 C% and 30 C%, respectively, while the C₅₊ + oxygenate selectivity remains ~56 C%. The ratio of C₂/C₂^o, C₃/C₃^o, and C₄/C₄^o stays at ~15, 19, and 13, respectively. The hydrocarbon product distribution as a function of the time-on-stream is plotted in Fig. 7(c). The ln(*W_n*/*n*) value of C₁ shows a significant deviation from the typical ASF distribution and is much lower than the predicted value based on the ASF law. Fig. 7(d) shows the variation of the chain growth probability (α) for hydrocarbons as a function of the time-on-stream. The chain growth probability remains at a value of ~0.58 during the stability test.

3.3. Effect of the catalyst support

Based on the combination of the catalyst characterization and FTO performance, the support has a great effect on the catalyst structure and catalytic properties. The strong metal-support interaction hinders the formation of the CoMn composite oxide, which is required for the generation of the specific Co₂C morphology [23–25]. Inert CNT contributes to the formation of the CoMn composite oxide during the calcination process, while the Co₃O₄ and MnO₂ of the SiO₂- and γ -Al₂O₃-supported catalysts separate. The support also influences the reducibility of the supported catalyst, as shown by the H₂-TPR characterization. The reduction temperature of the SiO₂-supported catalyst is higher than that of the γ -Al₂O₃-supported catalysts due to the stronger cobalt-support interaction of the SiO₂-supported catalyst. After the reduction, a CoMn composite oxide with low valence was found in the CNT-supported catalyst, while separated phases of CoO and MnO were detected in the SiO₂-supported catalyst. In addition to CoO and MnO phases, low-valence CoMn composite oxide forms in the γ -Al₂O₃-supported catalysts. The formation of the CoMn composite oxide contributes to the formation of Co₂C nanoprisms with special, exposed (101) and (020) facets [23–25]. As confirmed by TEM, the CNT-supported catalyst contains many Co₂C nanoprisms, while most of the Co₂C nanostructures of the SiO₂-supported catalyst are in the form of nanospheres and both Co₂C nanospheres and nanoprisms are found in the γ -Al₂O₃-supported catalysts.

Manganese has been reported to be an electronic promoter that alters the chemisorption species on the catalyst surface and a structural promoter that enhances the dispersion of the active phase during the FTO process [9,42,43]. The necessity for the addition of Mn during the FTO process was reported in

our previous work [23–25]. The Mn acts as a structural promoter and the formation of the CoMn composite oxide precursor benefits the cobalt dispersion. In addition, Co₂C nanoprisms with special exposed facets can be generated from the CoMn composite oxide in the presence of the sodium promoter. The Co₂C (101) surface benefits the olefin formation, while the formation of methane on both Co₂C (101) and Co₂C (020) is unfavorable. It is well known that Co₂C nanospheres possess a lower catalytic activity during the FT reaction and the formation of Co₂C is often considered to be one of the main reasons for the deactivation [44–46]. Notably, Co₂C nanostructures play an important role in the syngas conversion and morphological control of Co₂C nanostructures is essential for the selective formation of lower olefins. In this study, many Co₂C nanoprisms with exposed (020) and (101) facets were found in CoMnNa/CNT, which contributes to the excellent FTO performance with high olefin selectivity and low methane selectivity. On the other hand, most of the Co₂C species have a spherical morphology, mostly exposing the (111) facet in the spent CoMnNa/SiO₂ catalysts, resulting in a high methane selectivity. We thus conclude that the support has a great influence on the Co₂C morphology and corresponding catalytic performance.

4. Conclusions

A series of CoMn catalysts with different support materials (SiO₂, γ -Al₂O₃, and CNT) were synthesized using the impregnation method. The influence of the support on the FTO reaction was investigated in detail in this study. It was found that the interaction between the support and cobalt species has a great impact on the formation of active Co₂C sites. Inert CNT facilitates the formation of the CoMn composite oxide, which contributes to the generation of Co₂C nanoprisms with special, exposed (111) and (020) planes. These Co₂C nanostructures display an excellent FTO performance. Under conditions of 265 °C, 5 bar, 2000 mL h⁻¹ g_{cat}⁻¹, and a H₂/CO ratio of 0.5, the total selectivity of olefin and oxygenate products is higher than 92 C% (66.7 C% and 25.4 C% for olefins and oxygenates, respectively) and the undesired paraffin product fraction is less than 8 C%. The olefin to paraffin ratio reaches a very high value of 8.4 and the product distribution greatly deviates from the classical ASF distribution, with a methane selectivity of only 2.4 C%. No notable catalyst deactivation was observed within the 150 test hours. Support materials with high specific surface areas, such as SiO₂ and γ -Al₂O₃, interact strongly with cobalt species and inhibit the formation of the CoMn composite oxide; Co₃O₄ and MnO₂ were identified in calcined catalysts. After the reduction, CoO, MnO, and low-valence CoMn composite oxides are generated in the γ -Al₂O₃ supported sample. Both Co₂C nanospheres and nanoprisms were identified in the corresponding spent catalysts, which cause the formation of undesired paraffins with selectivities as high as 12.6 C%. The total olefin and oxygenate product fraction drops to 87.4 C% and the methane selectivity reaches 5.8 C%. Only a slight deviation from the traditional ASF distribution was found in the γ -Al₂O₃-supported catalyst. In addition, complete phase separation of CoO and MnO was observed in the reduced SiO₂-supported sample. In

the spent SiO₂-supported catalyst, Co₂C nanospheres were detected and Co₂C nanoprisms were not observed. Although the olefin selectivity is as high as 68.5 C%, the paraffin fraction increases to 19.6 C%, with methane selectivity as high as 12.0 C%. The product distribution follows the classical ASF distribution. These results suggest that the support material has a great influence on the Co₂C morphology and the weak cobalt-support interaction benefits the formation of Co₂C nanoprisms with promising catalytic performance with respect to the sustainable production of olefins via syngas.

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Graphical Abstract

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Effect of the support on cobalt carbide catalysts for sustainable production of olefins from syngas

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The cobalt-support interaction has a great impact on the Co₂C morphology and catalytic performance of the Fischer-Tropsch to olefin reaction.

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合成气直接制烯烃碳化钴基催化剂的载体效应

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摘要: 烯烃是重要的化工原料, 一般采用石油热裂解和催化裂解制备. 随着石油资源的枯竭, 以煤、天然气和生物质等含碳资源经合成气制取烯烃的工艺路线备受关注. 其中, 合成气经由甲醇或二甲醚间接制取烯烃技术(MTO)已实现工业化应用. 与之相比, 费托合成直接生产烯烃(FTO)工艺具有流程短、投资和运行费用低等优势, 具有良好的工业发展前景. 最近我们发现, 暴露特定晶面的棱柱状碳化钴表现出很好的合成气制烯烃催化性能, 但载体对催化剂结构和催化性能的影响尚不清晰.

本文采用浸渍法制备了一系列负载型钴基催化剂, 系统考察了SiO₂、γ-Al₂O₃和碳纳米管(CNT)对催化剂结构及合成气直接制烯烃催化性能的影响. 结果表明, SiO₂及γ-Al₂O₃负载的催化剂较强的钴-载体相互作用抑制了钴基复合氧化物的形成, 而相对惰性的CNT载体则有利于钴基复合氧化物的生成. 通过对反应后催化剂的结构表征, 发现SiO₂和γ-Al₂O₃负载的催化剂中出现大量球状的碳化钴颗粒, 而CNT负载催化剂中的碳化钴则呈现出具有(101)和(020)暴露晶面的纳米棱柱状结构. 将所制备的催化剂用于FTO反应, 在265 °C, 5 bar, 空速2000 mL h⁻¹ g_{cat}⁻¹和H₂/CO = 0.5的反应条件下, CNT负载的催化剂表现出最佳的催化性能, 烯烃和含氧化物的选择性分别为66.7 %和25.4 %, 甲烷的选择性仅为2.4 %, 总的烯烃/烷烃比达到8.4, 同时烃类产物分布极大地偏离传统ASF线性分布. 而对于SiO₂和γ-Al₂O₃负载的催化剂, 虽然烯烃的选择性也分别达到68.5 %和64.7 %, 但甲烷的选择性却升至12.0 %和5.8 %, 总的烯烃/烷烃比仅为3.5和5.1, 烃类产物分布基本符合传统的ASF分布. 在150 h的催化剂测试中, CNT负载催化剂表现出很好的催化性能稳定性, 甲烷的选择性稳定在2.2 %, C₂–C₄烯烃的选择性约为30 %, C₂, C₃和C₄烯烃烷烃比分别稳定在15, 19和13.

本研究表明, 钴-载体相互作用对碳化钴活性相结构及催化性能具有很大影响, 惰性的催化剂载体有利于钴基复合氧化物的生成, 进而促进碳化钴纳米棱柱状结构的形成, 从而表现出优异的合成气直接制烯烃催化性能.

关键词: 费托合成制烯烃; 碳化钴; 负载型催化剂; 烯烃; 合成气

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