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# Fischer-Tropsch to olefins over Co<sub>2</sub>C-based catalysts: Effect of thermal pretreatment of SiO<sub>2</sub> support



Liusha Li<sup>a,b</sup>, Fei Yu<sup>a</sup>, Xiao Li<sup>a,b</sup>, Tiejun Lin<sup>a</sup>, Yunlei An<sup>a</sup>, Liangshu Zhong<sup>a,c,\*</sup>, Yuhan Sun<sup>a,c,\*</sup>

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

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

<sup>c</sup> School of Physical Science and Technology, ShanghaiTech University, Shanghai, 201210, PR China

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### ABSTRACT

SiO<sub>2</sub> supported Co<sub>2</sub>C-based catalysts were used for Fischer-Tropsch to olefins (FTO), and the effect of thermal pretreatment of SiO<sub>2</sub> support under different temperatures on the Co<sub>2</sub>C morphology and catalytic performance was investigated. It was found that the interaction between cobalt and support was weakened when SiO<sub>2</sub> was pretreated at high temperature (990 °C) due to the decreased content of surface Si—OH groups. The relative weak interaction between cobalt and support benefited the formation of cobalt manganese composite oxide after calcination and reduction, and thus promoted the generation of Co<sub>2</sub>C nanoprisms with promising FTO performance. In contrast, for the SiO<sub>2</sub> support pretreated at 350 °C or 650 °C, the strong interaction between cobalt and support led to phase separation of cobalt and manganese. As a result, only Co<sub>2</sub>C nanospheres were generated which displayed low activity and high methane selectivity.

#### 1. Introduction

Olefins are well known as fundamental building blocks, and widely applied for the production of various polymers, cosmetics, drugs and detergents [1]. In general, olefins are produced by thermal or catalytic cracking of naphtha and dehydrogenation of alkanes. However, with the concern of exhausted petroleum resource, direct synthesis of olefins from syngas, which is derived from coal, natural gas, biomass and even  $CO_2$ , is becoming more attractive due to the abundant reserves [1–6]. Fischer-Tropsch to olefins (FTO) [1,5–11] and oxide-zeolite bifunctional catalytic process [2,3,12] are the reported routes for direct synthesis of olefins from syngas, and have been extensively studied in recent years. For instance, Torres Galvis et al. developed a supported Fe-based FTO catalyst with sodium and sulfur as promoters, and found that the selectivity to lower olefins  $(C_{2-4}^{=})$  reached 61 C% [1]. As for oxide-zeolite catalysts, Jiao et al. reported that the catalyst obtained from coupling ZnCrOx and mesoporous SAPO zeolite realized 80 C% selectivity for  $C_{2-4}^{=}$  with CO conversion of 17 % [2].

In our previous study,  $Co_2C$  nanoprisms were found to exhibit excellent FTO performance with a  $C_{2-4}^{=}$  selectivity of 60.8 C% and low methane selectivity of 5.0 C% at mild conditions [4,13–20]. The roles of

Na and Mn were investigated in details. It was found that the Na promoter acting as an electronic donor can promote the formation and stable existence of Co<sub>2</sub>C phase, while the Mn promoter as an electronic and structural additive exhibited a significant effect on the final morphology of  $Co_2C$  nanostructure during reaction process [19–22]. Before FTO reaction, catalyst activation was conducted for the formation and stabilization of Co<sub>2</sub>C nanoprisms using syngas [23-25]. Co<sub>2</sub>C nanoprisms were mainly generated from bulk CoMn oxides prepared via coprecipitation method. In general, the application of catalyst supports is expected to decrease active metal content and improve mechanical strength, and it remains great interest to fabricate supported Co<sub>2</sub>C nanoprisms by simple impregnation method. Previously, the effect of different supports including  $SiO_2$ ,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and carbon nanotubes (CNTs) on the FTO reaction was studied, and the results indicated that Co2C nanoprisms were formed for the inert CNT with high olefins selectivity and low methane selectivity [19]. However, Co<sub>2</sub>C nanospheres were observed for both SiO2 and Al2O3 supported CoMn catalyst due to the strong interaction between cobalt and supports. The formed Co<sub>2</sub>C nanospheres led to a relatively high methane selectivity. With the advantages of low price, oxygen resistance and strong mechanical strength, oxide supports are still the best potential choices for practical

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<sup>\*</sup> Corresponding authors at: CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai, 201203, PR China.

E-mail addresses: zhongls@sari.ac.cn (L. Zhong), sunyh@sari.ac.cn (Y. Sun).

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Catalytic performance	for various	CoMnNa/SiO <sub>2</sub>	catalysts <sup>a</sup> .

Catalyst	Temperature (°C)	CO Conv.(C%)	CO <sub>2</sub> Sele. (C%)	Product Selectivity (C%, CO <sub>2</sub> -free)			Olefin/Paraffin Ratio				
				Ole.	Oxy.	Para.	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	O/P
CoMnNa/SiO <sub>2</sub> -350	260	3.1	9.7	57.4	5.1	37.6	18.7	2.9	11.2	8.8	1.5
	265	4.4	10.5	51.4	4.7	43.9	25.7	1.9	10.8	8.0	1.2
	270	5.2	15.0	49.3	5.3	45.4	35.9	1.4	10.7	7.3	1.1
CoMnNa/SiO <sub>2</sub> -650	260	4.0	9.1	60.4	7.0	32.6	19.7	2.6	11.2	8.8	1.9
	265	4.3	12.3	57.1	4.6	38.2	26.1	1.9	11.2	8.6	1.5
	270	5.3	12.9	45.7	4.2	50.1	28.5	1.2	10.5	7.7	0.9
CoMnNa/SiO <sub>2</sub> -990	260	11.9	37.7	75.9	10.0	14.1	3.9	10.4	17.2	12.8	5.4
	265	19.0	42.8	78.5	10.7	10.8	3.8	8.5	17.5	12.1	7.2
	270	23.9	46.0	79.9	9.7	10.4	4.3	6.8	18.1	12.5	7.6

<sup>a</sup> Reaction condition: 5 bar,  $H_2/CO = 0.5$  and WHSV = 2000 mL g<sup>-1</sup> h<sup>-1</sup>. Ole.: olefins; Oxy.: oxygenates; Para.: paraffins.

industrial application of supported catalysts. And we wonder whether it is possible to weaken the interaction between oxide supports and cobalt for better FTO performance over supported CoMn catalysts.

Much efforts have been made to tune the interactions between oxide supports (such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub>) and cobalt, which have a significant influence for the reducibility and catalytic performance [26–28]. Generally, the modification methods includes precoating with carbon interlayer, introducing reactive inorganic oxide, surface hydrophobic treatment and modifying with surface silanol groups [27,29-39]. For instance, Vissers and co-workers reported that carbon-covered Al<sub>2</sub>O<sub>3</sub> via pyrolysis organic molecules (cyclohexene or ethylene) on the surface of Al<sub>2</sub>O<sub>3</sub> reduced the strong interaction between cobalt and Al<sub>2</sub>O<sub>3</sub>, which displayed higher catalytic activity [29]. Feller et al. discovered that the interaction between cobalt and SiO2 decreased while the reduction degree of catalysts increased via introducing zirconium into the Co/SiO<sub>2</sub> catalysts, resulting from the formation of a weaker cobalt-zirconium interaction [27]. Besides, Rytter et al. modified Al<sub>2</sub>O<sub>3</sub> with chloro or methoxy active ligands, and found that the interaction was prevented and the reduction of catalysts was easier due to hydrophobicity of Al<sub>2</sub>O<sub>3</sub> surface [38]. Recently, Okoye Chine et al. pretreated SiO<sub>2</sub> with ethylene glycol and thermal method, and discovered that the increased proportion of isolated silanol groups with ethylene glycol treatment enhanced the strong interaction, resulting in low activity for FTS [39]. In contrast, the proportion of isolated silanol groups did not increase for thermal method pretreatment.

Herein, we prepared  $SiO_2$  supported catalysts for FTO reaction, and found that the thermal treatment of  $SiO_2$  can effectively tune the metalsupport interaction, which greatly affect the formation of CoMn composite oxides and the final morphology of  $Co_2C$  nanostructures. Various characterization techniques were used to trace the phase and structure evolution of catalysts, and the structure-performance relationship was also investigated.

#### 2. Experimental section

#### 2.1. Catalyst preparation

CoMnNa/SiO<sub>2</sub> supported catalysts were prepared by incipient wetness impregnation method. Before preparation, SiO<sub>2</sub> support (480 m<sup>2</sup>/g, Aladdin) was firstly pretreated under different temperatures (350 °C, 650 °C and 990 °C) for 5 h in maffle furnace, and named as SiO<sub>2</sub>-350, SiO<sub>2</sub>-650, SiO<sub>2</sub>-990, respectively. Typically, 6.61 g SiO<sub>2</sub> support was impregnated with mixture liquid of 7.41 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sinopharm Chemical Reagent Co., Ltd.), 5.21 g aqueous of 50 wt% Mn(NO<sub>3</sub>)<sub>2</sub> (Sinopharm Chemical Reagent Co., Ltd.), 0.22 g NaNO<sub>3</sub> (Sinopharm Chemical Reagent Co., Ltd.) and suitable deionized water. The content of Co, Mn, Na was fixed at 20 wt%, 10 wt%, and 0.6 wt%, respectively, with respect to the sum of samples. The samples were then dried under room temperature for 24 h, and dried at 120 °C for 12 h. At last, the CoMnNa/SiO<sub>2</sub> samples were calcined at 350 °C in maffle furnace for 4 h.

# 2.2. Characterization

 $N_2$  adsorption experiments were conducted on a Micromeritics 2420 instrument for the textural properties of CoMnNa/SiO<sub>2</sub> catalysts. Before measurements, the samples were degassed at 200  $^\circ C$  for 5 h. The specific surface area (S\_{BET}) was calculated through BET method, and the pore volume (V\_{BJH}) and pore size distribution were determined by BJH method.

X-ray diffraction (XRD) patterns were obtained by a Rigaku Ultima IV X-ray powder diffractometer at a range of 20–80  $^\circ$  with a speed of 4 $^\circ/$ min. JCPDS standard cards were employed for the identification of characteristic peaks.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM 2011 electron microscope operated at 200 kV.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) measurements were carried out on Micromeritics Autochem-II 2920 instruments equipped with a thermal conductivity detector (TCD). Typically, 50 mg fresh sample was loaded into a quartz tube. Before reduction, the sample was pretreated with a He flow at 200 °C for 2 h, and then the temperature cooled down to 60 °C in He flow until the baseline was stable. At last, the samples were heated to 800 °C in a flow of 10 % H<sub>2</sub>/Ar, and the H<sub>2</sub> consumption was collected by TCD.

Fourier transform infrared spectrum (FTIR) experiments were carried out, and recorded by the Nicolet iN10 (Thermo Scientific) infrared spectrophotometer at a range of  $400-4000 \text{ cm}^{-1}$ . After the background was collected, the spectrum of sample was collected with transmission mode.

# 2.3. Catalytic evaluation

The CoMnNa/SiO<sub>2</sub> catalysts were evaluated in fixed-bed reactor constructed with 8 mm inner diameter. Typically, 1.0 g of 40-60 mesh fresh catalysts mixed with 3.0 g silica of same mesh. Prior to reaction, the catalyst was in-situ reduced at 300 °C for 5 h under a 10 % H<sub>2</sub>/N<sub>2</sub> flow with WHSV of 8000 mL  $g^{-1}$  h<sup>-1</sup>. After reduction, the temperature was cooled to 250 °C. Before feeding, the reactor was swept in a He flow for 30 min. Then the feed gas (syngas,  $H_2/CO = 0.5$ , v/v) with a WHSV of 2000 mL  $g^{-1}$  h<sup>-1</sup> was introduced into the system, and the pressure was increased to 5 bar (gauge pressure). After activation for 24 h, the temperature was raised to desired reaction temperature for CO hydrogenation tests. The gas phase products were analyzed online by gas chromatograph (Agilent 7890B) equipped with thermal conductivity (TCD) detector and flame ionization (FID) detectors after transiting the hot trap (120 °C) and cold trap (0 °C). The liquid products were collected in the hot trap and cold trap, and analyzed off-line by Shimadzu GC2010 plus. In addition, there may be some deviations resulting in the lower C8 and C<sub>9</sub> products, which was also reported by other researchers in FT study [40,41]. The data were taken when the performance kept in relatively stable states after reaction for 24 h. And each FTO testing held for 48 h under the desired temperature. The mass balance, oxygen



Fig. 1. ASF distributions and chain growth probability calculated by fitting curve from C3 to C7 using ASF model for CoMnNa/SiO<sub>2</sub>-350 (a), CoMnNa/SiO<sub>2</sub>-650 (b), CoMnNa/SiO<sub>2</sub>-990 (c) at the reaction condition of 5 bar,  $H_2/CO = 0.5$  and WHSV = 2000 mL g<sup>-1</sup> h<sup>-1</sup>.

balance, and carbon balance were calculated, and all higher than 95 %.

The catalytic activity for CoMnNa/SiO<sub>2</sub> catalysts was determined by Eq. (1) as follows, where the  $n_{CO,inlet}$  means the moles of CO at the inlet while the  $n_{CO,outlet}$  means the moles of CO at the outlet.

$$CO \text{ conversion} = \frac{n_{CO,inlet} - n_{CO,outlet}}{n_{CO,inlet}} \times 100\%$$
(1)





Fig. 2. Detailed hydrocarbon distributions for CoMnNa/SiO<sub>2</sub>-350 (a), CoMnNa/SiO<sub>2</sub>-650 (b), CoMnNa/SiO<sub>2</sub>-990 (c) at the reaction condition of 5 bar,  $H_2/CO = 0.5$  and WHSV = 2000 mL g<sup>-1</sup> h<sup>-1</sup>.



Fig. 3. Stability test for CoMnNa/SiO<sub>2</sub>-990 catalyst at 265 °C.

number of product *i*, respectively.

$$S_{CO_2} = \frac{n_{CO_2}}{n_{CO,inlet} - n_{CO,outlet}} \times 100\%$$
 (2)

$$\mathbf{S}_{i} = \frac{\mathbf{N}_{i} \times \mathbf{n}_{i}}{\sum \left(\mathbf{N}_{i} \times \mathbf{n}_{i}\right)} \times 100\%$$
(3)

#### 3. Results and discussion

#### 3.1. Catalytic performance

The CoMnNa/SiO<sub>2</sub> catalysts were evaluated under 5 bar syngas at several temperatures (260 °C, 265 °C and 270 °C) after in-situ reduction, and the results were summarized in Tables 1 and S1. CO conversions of CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts were quite low with less than 5 C% at 265 °C. However, CO conversion was up to 19.0 C% for CoMnNa/SiO<sub>2</sub>-990. As for the product selectivity, the olefins selectivity and the ratio of olefin to paraffin (O/P) for the catalyst with the support of SiO<sub>2</sub> pretreatment at 990 °C were the highest among all of the studied catalysts. However, methane selectivity for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 was almost up to 26 C%, which was much higher than that obtained by CoMnNa/SiO<sub>2</sub>-990 (3.8 C%). In addition, methane selectivity increased with the reaction temperature for all catalysts, especially for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650. Paraffins selectivity for CoMnNa/SiO<sub>2</sub>-990 (10.8 C%) was much lower than that obtained by CoMnNa/SiO<sub>2</sub>-350 (43.9 C%) and CoMnNa/SiO<sub>2</sub>-650 (38.2 C%). Moreover, oxygenates selectivity for all the catalysts was lower than 11.0 C%. Obviously, the CoMnNa/SiO<sub>2</sub>-990 catalyst exhibited high activity, high olefins selectivity and very low methane selectivity, which was much better than that obtained by CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts. In addition, the high CO<sub>2</sub> selectivity for CoMnNa/SiO<sub>2</sub>-990 suggested syngas derived from coal or biomass with low H<sub>2</sub>/CO ratio was more suitable for Co<sub>2</sub>C-based FTO reaction.

As shown in Fig. 1, the hydrocarbon distribution for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 followed the classical ASF distribution under different reaction temperatures. However, the hydrocarbon distribution significantly deviated from the ASF model for CoMnNa/SiO<sub>2</sub>-990, consistent with the considerably low methane selectivity. As for the chain growth probabilities, the  $\alpha$  values for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 were both around 0.58, and basically not affected by reaction temperature. On the other hand, the  $\alpha$  value was relatively low for CoMnNa/SiO<sub>2</sub>-990, indicating that the produced hydrocarbons were more concentrated in low-carbon numbers. The detailed hydrocarbon distribution was also summarized as shown in Fig. 2. It was clear that the hydrocarbon distribution was concentrated in the range of  $C_{1-12}$  for all of the catalysts, and olefins were the main products in hydrocarbons. However, a narrower hydrocarbon distribution was observed for CoMnNa/SiO<sub>2</sub>-990. Moreover, the methane proportion in hydrocarbons for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 was much higher than that of CoMnNa/SiO<sub>2</sub>-990. In addition, it is hard to collect the liquid product over CoMnNa/SiO<sub>2</sub>-350 catalyst under 270 °C as the light products with carbon number in the range of 1~7 dominated the products. The stability for CoMnNa/SiO<sub>2</sub>-990 catalyst was also tested at 265 °C as shown in Fig. 3. Both the activity and products selectivity almost remained unchanged during 100 h test, indicating promising stability.

### 3.2. Structure characterization

The distinguished difference for catalytic performance suggested there should exist great difference for the structure of various CoMnNa/ SiO<sub>2</sub> catalysts. Therefore, the structure of various catalysts was investigated in detail by a series of techniques. The composition of calcined catalysts was firstly tested by XRF and listed in Table S2. For all the calcined catalysts, the content of Co, Mn and Na was approximately 18.7 wt%, 10.0 wt% and 0.6 wt%, respectively, basically consistent with the theoretical loading amount. Compared with the unsupported CoMn catalysts without SiO<sub>2</sub>, the supported CoMnNa/SiO<sub>2</sub> catalysts exhibited a similar catalyst activity with reduced cobalt content [4]. In addition, the specific surface area and pore structure properties of various samples were showed in Fig. S1 and Table S2. The SBET for CoMnNa/SiO2-350, CoMnNa/SiO<sub>2</sub>-650 and CoMnNa/SiO<sub>2</sub>-990 was 260.6  $m^2/g$ , 246.9  $m^2/g$ and 45.8 m<sup>2</sup>/g, respectively. Meanwhile, type IV isothermal curve and type H<sub>2</sub> hysteresis loop were observed for all the samples, revealing similar mesoporous structure [42].

Fig. 4 showed the XRD patterns of CoMnNa/SiO<sub>2</sub> catalysts at different stages. After calcination,  $Co_3O_4$  (PDF #74-2120) and  $MnO_2$  (PDF #42-1169) were observed for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts. However, CoMnNa/SiO<sub>2</sub>-990 displayed diffraction peaks of  $MnCo_2O_{4.5}$  (PDF #32-0297) and  $Co_3O_4$  (PDF #74-2120). Herein, we noticed that CoMn composite oxide was formed only for the calcined CoMnNa/SiO<sub>2</sub>-990. In addition, according to the elemental mapping of the calcined catalysts in Fig. 5, obvious elemental separation



Fig. 4. XRD patterns of the calcined (a), reduced (b) and spent (c) CoMnNa/SiO<sub>2</sub> catalysts with rough scan and fine scan.

of cobalt and manganese appeared for CoMnNa/SiO<sub>2</sub>-350 while cobalt and manganese were highly overlapped for CoMnNa/SiO<sub>2</sub>-990. Furthermore,  $Co_xMn_{1-x}O$  was observed for the reduced CoMnNa/SiO<sub>2</sub>-990 (Fig. 4b). However, the diffraction peaks of CoO (PDF #71-1178) and MnO (PDF #75-0257) were identified for the reduced CoMnNa/ SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 samples, which further revealed the phase separation of Co and Mn. #65-1457) was the main phase of Co species for all spent CoMnNa/SiO<sub>2</sub> catalysts. Moreover, CoO, as another form of Co species, as well as MnO were all observed for CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts. In addition, a small amount of  $Co_xMn_{1-x}O$  and MnO was detected for CoMnNa/SiO<sub>2</sub>-990 catalyst. Moreover, no peaks associated with Co<sup>0</sup> were observed in XPS study (Fig. S2), indicating that Co species existed in an oxidized state at the surface. Besides, previous studies also revealed that no metallic Co was observed after activation process using

The XRD patterns of spent catalysts (Fig. 4c) showed that Co<sub>2</sub>C (PDF



Fig. 5. X-ray energy dispersive spectroscopy (EDS) mapping of the fresh calcined CoMnNa/SiO<sub>2</sub>-350 (a) and CoMnNa/SiO<sub>2</sub>-990 (b).



Fig. 6. (HR)TEM images of various spent catalysts for CoMnNa/SiO<sub>2</sub>-350 (a), CoMnNa/SiO<sub>2</sub>-650 (b) and CoMnNa/SiO<sub>2</sub>-990 (c).



Fig. 7.  $\rm H_2\text{-}TPR$  profiles of various fresh  $\rm CoMnNa/SiO_2$  catalysts after calcination.

in situ XAFS characterization [43,44]. Although Co<sub>2</sub>C was the main phase for all of the spent catalysts, the morphology of Co<sub>2</sub>C for various samples exhibited significant difference as shown in Fig. 6. A number of Co<sub>2</sub>C nanospheres were discovered from randomly selected HRTEM images for both CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts. In contrast, a large amount of Co<sub>2</sub>C nanoprisms with exposed (020) and (101) facets were observed for CoMnNa/SiO<sub>2</sub>-990 catalyst. According to the previous study [45,46], the spherical Co<sub>2</sub>C nanoparticles usually displayed low activity and high methane selectivity, consistent with the relatively poor FTO performance for CoMnNa/SiO<sub>2</sub>-350 and CoMn-Na/SiO<sub>2</sub>-650 catalysts. In contrast, the Co<sub>2</sub>C nanoprisms always exhibited high activity, low methane selectivity and high olefins selectivity, and was in good agreement with the catalytic results for CoMn-Na/SiO<sub>2</sub>-990 catalysts [4]. Combined with the ASF distribution (Fig. 1), it was clear that the hydrocarbon distribution for the catalysts with Co<sub>2</sub>C nanospheres followed the typical ASF model while dramatically deviated ASF distribution for the catalysts with Co<sub>2</sub>C nanoprisms. Based on the above results, we can draw the conclusion that the diverse morphology of Co2C is the main underlying reason for the striking difference of FTO performance.

Based on our previous study, the precursor of cobalt manganese composite oxide was beneficial to the formation of Co2C nanoprisms with exposed (020) and (101) facets [4,13,20]. For both CoMnNa/-SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 samples, phase separation of Co and Mn was observed without the formation of CoMn composite oxide. Correspondingly, Co<sub>2</sub>C nanospheres were formed under reaction conditions conducted in the current work. Therefore, we speculated that stronger interaction between cobalt and SiO<sub>2</sub> hindered the formation of cobalt manganese composite oxide for the CoMnNa/SiO<sub>2</sub>-350 and CoMnNa/SiO<sub>2</sub>-650 catalysts. The average crystallite sizes of cobalt-containing phases at different stages were calculated by Scherrer's equation, and summarized in Table S3. The crystallite sizes for CoMnNa/SiO<sub>2</sub>-990 were larger than the others at all stages especially after reaction, which implying the weaker interaction between cobalt and SiO<sub>2</sub> support. Moreover, H<sub>2</sub>-TPR profiles of fresh CoMnNa/SiO<sub>2</sub> catalysts were investigated as shown in Fig. 7. The curve of CoMnNa/-SiO<sub>2</sub>-350 was similar to that of CoMnNa/SiO<sub>2</sub>-650, and both showed three main peaks at 225.7 °C, 287.0 °C and 566.8 °C, respectively. The first two peaks were ascribed to reduction of Co<sub>3</sub>O<sub>4</sub> to CoO and CoO to  $Co^0$ , respectively [47,48]. Notably, the intense peak around 566.8 °C was attributed to the signal of strong interaction between highly dispersed Co species and SiO<sub>2</sub> support [37,49]. On the other hand, CoMnNa/SiO<sub>2</sub>-990 exhibited three obviously different peaks around 246.8 °C, 343.4 °C and 426.8 °C. The first peak at 246.8 °C was ascribed to the reduction of MnCo<sub>2</sub>O<sub>4.5</sub> and Co<sub>3</sub>O<sub>4</sub>, while the second peak was attributed to reduction of the rest MnCo<sub>2</sub>O<sub>4.5</sub> to Co<sub>x</sub>Mn<sub>1-x</sub>O [18]. Besides, the broad peak around 426.8 °C was assigned to the further reduction of Co<sub>x</sub>Mn<sub>1-x</sub>O [18,19]. Specially, the peak around 566.8 °C was absent for CoMnNa/SiO<sub>2</sub>-990 catalyst, indicating that interaction between Co species and SiO2 support was relative weak for CoMnNa/SiO<sub>2</sub>-990.

It was well known that the strong interaction was usually derived from the interaction between Si—OH groups and cobalt [37]. Therefore, the content of Si—OH groups should possess a significant impact on the interaction. FTIR spectra of SiO<sub>2</sub> with different pretreatment temperature was tested as shown in Fig. 8a. The absorption bands at 480 cm<sup>-1</sup>, 820 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> were all attributed to vibration of Si—O from Si—O—Si [39,50]. The intensity of these absorption bands was similar for different SiO<sub>2</sub>. The absorption bands at 1631 cm<sup>-1</sup> and 3444 cm<sup>-1</sup> were both ascribed to the —OH vibration from H<sub>2</sub>O [39]. Specially, the absorption bands at 965 cm<sup>-1</sup> was assigned to the —OH vibration of Si—OH groups [39]. It is noteworthy that the absorption bands of Si—OH groups for SiO<sub>2</sub>-990 was significantly weakened compared with SiO<sub>2</sub>-350 and SiO<sub>2</sub>-650. Peak fitting from 1400 cm<sup>-1</sup> to 600 cm<sup>-1</sup> and



Fig. 8. (a) FTIR spectra of SiO<sub>2</sub> with different pretreatment temperature; (b) Peak fitting of FTIR spectra from 1400 cm<sup>-1</sup> to 600 cm<sup>-1</sup> for SiO<sub>2</sub> supports.

the corresponding semi-quantitative results were also shown in Fig. 8b and Table S4. With a benchmark of the peak area at 1050 cm<sup>-1</sup> (Si—O—Si), the relative peak area (A1/A2) at 965 cm<sup>-1</sup> (Si—OH groups) was in the order of SiO<sub>2</sub>-fresh > SiO<sub>2</sub>-350  $\approx$  SiO<sub>2</sub>-650 > SiO<sub>2</sub>-990. Especially, the relative peak area drastically decreased when the pretreatment temperature increased up to 990 °C, indicating the decrease of the content of Si—OH groups. Moreover, the IR mapping images at 965 cm<sup>-1</sup> with a randomly selected area for SiO<sub>2</sub> supports were shown in Fig. S2, which also indicated a decrease trend for the content of Si—OH groups with the increase of pretreatment temperature.

#### 3.3. Mechanism discussion

Generally, the surface silanol of SiO2 support would be deprotonated when contacting with impregnation liquid, as the point of zero charge (PZC) for SiO<sub>2</sub> (around 2) was always smaller than the pH of impregnation liquid [51]. As a result, the surface of SiO<sub>2</sub> support was negatively charged and could anchor the cations in the impregnation solution via electrostatic adsorption. For SiO<sub>2</sub> via pretreatment at 350 °C and 650 °C, the rich surface silanol of SiO<sub>2</sub> support made it easy to anchor the hydrated cations including  $[Co (H_2O)_6]^{2+}$  and  $[Mn (H_2O)_6]^{2+}$  during impregnation process. As the ion radius for  $[Co (H_2O)_6]^{2+}$  was smaller than that of [Mn (H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, [Co (H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> would possess stronger electrostatic interaction with SiO<sub>2</sub> support than  $[Mn (H_2O)_6]^{2+}$ . As a result, cobalt was concentrated on the surface of SiO<sub>2</sub> and phase separation occurred between cobalt and manganese. In contrast, the sharply decreased surface silanol for SiO<sub>2</sub>-990 support made it difficult to anchor the hydrated cations including  $[Co (H_2O)_6]^{2+}$  and  $[Mn (H_2O)_6]^{2+}$ during impregnation process. On the other hand, as the hydrated cations of  $[Co (H_2O)_6]^{2+}$  and  $[Mn (H_2O)_6]^{2+}$  possess the same charge number and coordination structure (octahedral coordination), they are easily to mix together during the drying process. Finally, CoMn composite oxide was formed after calcination.

Prior work has demonstrated that the CoMn composite oxides precursors benefit for the formation of Co<sub>2</sub>C nanoprisms, while Co<sub>2</sub>C nanospheres were formed for the separated Co species [52]. For SiO<sub>2</sub> pretreated at 350 °C or 650 °C, the separated cobalt was transformed into Co<sub>2</sub>C nanospheres under reaction conditions. It is well known that Co<sub>2</sub>C nanospheres always display low activity and high methane selectivity [53,54]. For SiO<sub>2</sub> pretreated at 990 °C, Co<sub>2</sub>C nanoprisms could be easily formed from the CoMn composite precursors during FTO reaction and exhibited high activity, high olefin selectivity and low methane. This work provides an effective way to fabricate SiO<sub>2</sub>-suppored Co<sub>2</sub>C nanoprisms for FTO reaction with excellent performance via thermal treatment of the SiO<sub>2</sub> support.

# 4. Conclusions

In this work, the effect of support pretreatment on the Co<sub>2</sub>C morphology and catalytic performance was investigated for SiO<sub>2</sub> supported Co2C-based FTO catalysts. The SiO2 support was pretreated at different temperature before impregnation. For the SiO2 support pretreated at low temperature (350 °C and 650 °C), the interaction between cobalt and support was very strong and Co and Mn were separated after calcination. As a result, Co<sub>2</sub>C nanospheres were formed during reaction, which displayed low activity and high methane selectivity. However, for the SiO<sub>2</sub> support pretreated at 990 °C, the interaction between cobalt and SiO2 support was weakened due to the decreasing content of Si-OH groups. Consequently, cobalt manganese composite oxide was formed, and transformed into  $Co_2C$  nanoprisms with exposed (020) and (101) facets under reaction condition, exhibiting excellent FTO catalytic performance with high activity, high olefins selectivity, low methane selectivity and narrow product distribution. According to this study, the thermal pretreatment of support plays an important role on the structure-performance of the corresponding supported Co2C-based FTO

catalysts and optimization of pretreatment procedure is necessary to greatly improve catalytic performance.

# CRediT authorship contribution statement

Liusha Li: Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing - original draft. Fei Yu: Resources, Formal analysis, Writing - review & editing. Xiao Li: Formal analysis, Writing review & editing. Tiejun Lin: Validation, Formal analysis, Writing review & editing. Yunlei An: Writing - review & editing. Liangshu Zhong: Conceptualization, Validation, Supervision, Project administration, Funding acquisition, Writing - review & editing. Yuhan Sun: Supervision, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118283.

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