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Effects of sodium on the catalytic performance of CoMn catalysts for Fischer-Tropsch to olefins

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ABSTRACT: The effects of the sodium (Na) promoter on the catalytic performance of Cobalt-Manganese (CoMn) catalysts for Fischer-Tropsch to olefins (FTO) reaction were investigated. For the sample without Na, Co⁰ was found to be the active phase for traditional Co-based Fischer-Tropsch reaction with low CO₂ selectivity. The Olefin/Paraffin (O/P) ratio was found to be low with a $C_{2.4}^{=}$ selectivity of only 15.4 C%. However, with the addition of Na, cobalt carbide (Co₂C) quadrangular nanoprisms with the (101) and (020) facets exposed were formed. The Co₂C nanoprisms displayed a high $C_{2.4}^{=}$ selectivity (54.2 C%) as well as a low methane selectivity (5.9 C%) under mild reaction conditions. The O/P ratio for C_{2.4} reached 23.9, and the product distribution deviated greatly from the classical Anderson-Schulz-Flory (ASF) distribution. Co₂C nanoprisms were considered to be an effective FTO active phase with strong facet effect. The Na promoter played a key role in the evolution of the FTO catalysts. The addition of Na, which acted as an electronic donor to cobalt, resulted in stronger CO adsorption and enhanced CO dissociation, which also benefited for the formation of the Co_2C phase, leading to highly stable and active catalysts. The effects of other alkali promoters were also studied, and only the K promoter had the similar effect as Na on the CoMn catalysts for promoting the FTO reaction.

KEYWORDS: Fischer-Tropsch to Olefins, Cobalt Carbide, Lower Olefins, Syngas, Nanocatalysis, Sodium

1. INTRODUCTION

Lower olefins ($C_{2.4}^{-}$) are extensively used in the chemical industry as building blocks to synthesize a wide range of products such as polymers, solvents, drugs, cosmetics, and detergents^{1.4}. They are traditionally produced by naphtha cracking or as byproducts in the oil refining process⁵. With the rapid depletion of the limited petroleum reserves, alternative production routes for these major commodity chemicals via non-oil-based processes have attracted increasing attention⁶. Fischer-Tropsch synthesis (FTS) is a surface-catalyzed polymerization process that uses the CH_x monomers formed by the hydrogenation of adsorbed CO, leading to hydrocarbons with a broad range of carbon chain length⁶. The direct conversion of syngas derived from coal, biomass, and natural gas into lower olefins via the Fischer-Tropsch to olefins (FTO) process is another attractive option due to its simplified operation and low energy consumption⁷. Fischer-Tropsch catalysts can be used for the selective formation of lower olefins by catalyst modification. Recently, promoted iron-based catalysts have been extensively studied for the FTO reaction^{1-2,}

⁸⁻¹². de Jong et al. found that Na and S-promoted iron catalysts using an inert support with weak interaction exhibited excellent selectivity to lower olefins $(61 \text{ C}\%)^8$. It was suggested that Na reduced methane selectivity by increasing the chain growth probability while sulfur reduced the hydrogen coverage on the catalyst resulting in an even lower methane selectivity and higher olefin selectivity in the products⁹. The size effect of iron carbide nanoparticles was also studied by de Jong et al. and it was found that smaller iron carbide particles display higher surface specific activities mainly due to higher methane production^{5, 13-14}. Ma et al. developed a Zn and Na-modulated Fe catalyst, in which Zn served as the structural promoter and Na altered the electronic structure. The modification of the electronic structure of the catalyst surface suppressed the hydrogenation of double bonds and promoted the desorption of products, which rendered the catalyst unexpectedly reactive toward olefins, especially C₅₊ olefins¹⁵. However, iron-based FTO catalysts always suffer from coke formation and sintering due to the high reaction temperature. In recent years, Cobalt-Manganese catalysts were also investigated for the FTO reaction¹⁶⁻¹⁷. However, the performance is not good enough for potential industrial applications.

Product selectivity can be improved by adjusting the process conditions, as well as by optimizing the catalyst composition and structure. The use of electronic

promoters to improve the catalytic performance is a well-investigated topic in the context of Co-based FTS catalysts¹⁸⁻²⁰. Mn has been described as a perspective promoter to enhance both the catalytic activity and hydrocarbon selectivity²¹. Bell et al. found that the Mn promoter led to higher CO surface coverage and facilitated CO dissociation, which resulted in a heavier hydrocarbon product distribution owing to less H availability as well as more rapid C_1 monomer generation¹⁸. Bezemer et al. also found the chain growth probability increased with the addition of Mn for Co-based catalysts supported on carbon nanofiber²⁰. The effect of alkali metals on the FTS reaction has been much studied for Fe-based catalysts, but much less for Co-based catalysts²². Previous studies of Co-based catalysts have shown that the addition of alkali elements to the supported Co catalysts resulted in a sharp decrease in the catalytic activity and an increase in the selectivity towards heavier hydrocarbons. The O/P ratio and the CO_2 selectivity also increased upon alkali addition²²⁻²³. Kruse et al. found that the K-promoted CoMn catalysts exhibited excellent oxygenates selectivity up to ~ 50.0 % with a CO conversion of more than 40 %, and the product distribution was tuned toward olefins by adjusting the reaction conditions, and the combined oxygenate/olefin selectivities of ~65 % at a CO conversion up to ~20 % were obtained for the Co₄Mn₁K_{0.1} and Co₂Mn₁K_{0.1} catalysts²⁴. However, there were no specific studies on the effect of Na promoter on the CoMn catalysts for syngas conversion.

Recently, we discovered Co₂C nanostructures to possess strong facet effects and Co₂C nanoprisms with specifically exposed facets of (101) and (020) as a new FTO active phase exhibited high $C_{2.4}^{=}$ selectivity, low methane selectivity and high activity under mild reaction conditions (250 °C and 1 bar)²⁵. The residual Na was suggested to play an important role in achieving such a promising catalytic performance. However, little information was available about the effect of Na on the CoMn catalyst for the FTO reaction. We reported here an investigation of the Na-promoted CoMn FTO catalysts, which combined detailed catalyst characterization and performance studies. These efforts were undertaken with the aim of clarifying the chemical basis for the observed effects of the Na promoter on the CoMn catalysts. In addition, connections were established between catalyst structure and performance, which explained the dependence of the activity and selectivity on the promoter. These findings strongly favored the hypothesis that the addition of the Na promoter to the CoMn catalysts promoted the formation and stabilization of the Co₂C nanoprisms and the transition of

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the catalytic performance from traditional FTS to FTO. In addition, the effects of other alkali promoters on the CoMn catalysts were also studied.

2. EXPERIMENTAL SECTION

2.1 Catalyst Preparation

The CoMn catalyst without Na was prepared by the co-precipitation method. Typically, an appropriate amount of cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O, Sinopharm Chemical Reagent Co., Ltd)$ and manganese nitrate (50 wt.% Mn(NO₃)₂, aq, Sinopharm Chemical Reagent Co., Ltd) were dissolved in deionized water to form a 2 mol/L mixed salt solution (Co/Mn (atomic ratio) = 2/1). Meanwhile, ammonium carbonate anhydrous ((NH₄)₂CO₃, Sinopharm Chemical Reagent Co., Ltd) was dissolved in deionized water to form a 2 mol/L alkali solution as the precipitant. The above-mentioned salt and alkali solutions were simultaneously added into a beaker with 100 ml deionized water under mechanical stirring. The pH value was maintained at 8.0 ± 0.1 and the temperature was kept at 30 ± 1 °C during the precipitation process. After aging for 2 hours at 60 °C, the obtained suspension was centrifuged and washed with deionized water for 8 times, dried at 80 °C for 12 hours. Then the samples were calcined in a furnace at 330 °C for 3 hours under static air.

Na-promoted catalysts with different Na loading (0.1, 0.2, 0.4 and 0.6 wt.% Na) were prepared by excessive impregnation of aqueous solution of sodium carbonate. Typically, an appropriate amount of sodium carbonate (Na₂CO₃, Sinopharm Chemical Reagent Co., Ltd) was dissolved in 21 ml deionized water. Then, the solution was mixed with 10 g of CoMn catalysts by magnetic stirring under room temperature for 1 hour. The mixtures were then dried at 110 °C for 12 hours. The samples were calcined in a furnace at 330 °C for 3 hours under static air. Other alkali metal-promoted catalysts were prepared with a similar procedure. The obtained samples were termed CoMn-xM, where x and M denoted the concentration (x=0, 0.1, 0.2, 0.4 and 0.6 wt.%) and identity of the promoter.

2.2 Catalyst Characterization

The concentration of Na was obtained with an Inductively Coupled Plasma

Optical Emission Spectrometer (ICP-OES, Optima 8000, Perkin Elmer).

X-ray diffraction (XRD) patterns of catalysts were recorded on a Rigaku Ultima IV X-ray powder diffractometer using Cu K α radiation with a wavelength of 1.54056 Å at 40 kV and 40 mA. For phase identification, the samples were scanned from 10° to 90° with a rate of 1°/min (1.2 s per 0.02°) in the continuous scanning mode. For semi-quantitative analysis, the samples were scanned from 40° to 48° in a step scanning mode with a rate of 0.24°/min (5 s per 0.02°). The content of the different phases was calculated by reference intensity ratios (RIR). Generally, the integrated intensity of the most intense peak of each phase was obtained from fitting and deconvolution of the XRD patterns. The mass fraction of x phase (w_x) was calculated from the following equation:

$$w_{\chi} = \frac{l_{\chi}}{RIR_{\chi} \sum_{i=1}^{N} \frac{l_{i}}{RIR_{i}}} \tag{1}$$

where I is the integrated intensity of the most intense peak, and the RIR values are available from the PDF cards.

TEM micrographs and particle size distribution of the catalysts were obtained with a JEOL JEM 2000FX microscope operating at 200 kV. For the TEM measurements, the solids were dispersed in ethanol and dropped on a copper microgrid covered by a holey carbon film. Nanoparticle size distribution for each sample was determined using samples of ~300 nanoparticles. The surface mean diameter of the nanoparticles in a catalyst sample was calculated from the following equation:

$$\bar{d} = \frac{\sum_{i}^{N} n_i d_i^3}{\sum_{i}^{N} n_i d_i^2} \tag{2}$$

where n_i is the number of particles with diameter d_i in a nanoparticle sample of size N. For the TEM characterization, the catalysts were reduced at 300 °C with a mixture of H₂ and Ar (10 % H₂ v/v, 12000 ml/(h·g_{cat})) for 5 hours at the atmospheric pressure with a heating ramp of 1 °C/min.

Temperature-programmed reduction (TPR) experiments were performed with Micromeritics Autochem-II 2920 instrument equipped with a thermal conductivity detector (TCD) and an MKS Cirrus 2 mass spectrometer. The samples were pretreated in a Helium flow at 200 °C for 120 min. Once the TCD signal was stable, the gas stream was switched to 5 % (v/v) H₂/Ar, and the temperature was then raised from 50 to 800 °C at a rate of 5 °C/min.

Nitrogen adsorption measurements were performed on a Micromeritics 2420

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instrument at -196 °C. ~150 mg sample was degassed at 300 °C in vacuum for 6 hours. The specific area was calculated by the Brunauer-Emmett-Teller (BET) equation. The total pore volume and the average pore size were determined with the Barrett–Joyner–Halenda (BJH) method.

The rate and extent of cobalt carbonization, where CO dissociates to form Co_2C and CO_2 , was assessed by a Micromeritics Autochem-II 2920 instrument equipped with a thermal conductivity detector (TCD) and an MKS Cirrus 2 mass spectrometer. The catalyst was reduced *in situ* and exposed to CO at 250 °C and 1 bar for a fixed amount of time ranging from 30 min to 120 min. Then, the tube was flushed with He for 30 min to remove the gas phase. The yield of Co_2C was then determined by flushing the tube with 5 % H₂/Ar and monitoring the effluent for methane using an MKS Cirrus 2 mass spectrometer.

Fourier transform infrared spectroscopy (FTIR) measurements were made using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a liquid N₂ cooled MCT detector. The spectra were collected in the diffuse reflectance mode from 650 to 3000 cm⁻¹ with a resolution of 4 cm⁻¹ and an accumulation of 64 scans. The high-purity carbon monoxide (>99.9 %) were used as the probe gas. Helium (>99.999 %) and hydrogen (>99.999 %) were used as the flushing gas and the reducing gas, respectively. The catalyst (~50 mg) was placed in an infrared cell with a ZnSe window and reduced *in situ* with a hydrogen flow of 40 ml/min for 5 hours under atmospheric pressure and 400 °C. Subsequently, the cell was flushed for 30 min with He with a flow rate of 40 ml/min. The cell was cooled down to 250 °C and the background spectra were recorded. CO was then fed to the cell and IR spectra were collected repeatedly until the spectra were no longer changing over 30 min.

2.3 Catalyst Evaluation

The FTS reaction was performed at 1 bar and 250 °C in a tubular quartz fixed-bed reactor (diameter, 8 mm). A moulding process was necessary to form large particles with sizes of 40~60 mesh (0.3~0.45 mm) prior to the reaction in order to avoid blockage and improve diffusion. The catalyst was diluted with 0.4 g SiC powder to remove any temperature gradient within the catalyst bed. The catalyst was reduced prior to the reaction at 300 °C with a mixture of H₂ and Ar (10 % H₂ v/v, 12000 ml/(h·g_{cat})) for 5 hours at atmosphere pressure, and the heating ramp was 1

^oC/min. The temperature was then dropped to 250 ^oC in He (99.999 %) flow for 30 min to purge the residual reducing gas. Subsequently, the feed flow was switched to a mixture of N₂, H₂ and CO (N₂/H₂/CO=3/64.6/32.3 v/v/v, 3000 ml/(h·g_{cat})). The reaction was carried out for 24 hours. During the reaction, the reactor effluent was analyzed on-line by an Aglient 7890A gas chromatograph equipped with two columns and two detectors. Analysis of N₂ (reference), H₂, CO, CH₄ and CO₂ was performed using a packed column (J&W Q&5A) and a thermal conductivity detector (TCD) using Helium as the carrier gas. Hydrocarbons from C₁ to C₆ were analyzed using a capillary column (Agilent 19095P-K25) and a flame ionization detector (FID). The selectivity was calculated as the percentage of equivalent carbons present in the hydrocarbon product (C%).

CO conversion was calculated on a carbon atom basis according to the following equation:

$$CO Conversion = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}} \times 100\%$$
(3)

where *CO_{inlet}* and *CO_{outlet}* represent moles of CO at the inlet and outlet, respectively.

CO₂ selectivity was calculated according to the following equation:

$$CO_2 Selectivity = \frac{CO_2 outlet}{CO_{inlet} - CO_{outlet}} \times 100\%$$
(4)

where $CO_{2 \text{ outlet}}$ denotes moles of CO_2 at the outlet.

The selectivity of the individual product C_nH_m based was obtained from the following equation:

$$C_n H_m Selectivity = \frac{nC_n H_m outlet}{CO_{inlet} - CO_{outlet} - CO_{2 outlet}} \times 100\%$$
(5)

where $C_n H_m$ outlet represents moles C of the product at the outlet.

The catalytic performance changed significantly at the initial stage. It was very difficult to perform a full analysis of all the products in the short time period at 1 bar. In this case, the method by difference was used to calculate the C_{5+} + Oxy. selectivity (CO converted to products other than CO₂ and the C₁-C₄ products), where C₅₊+Oxy. represented hydrocarbons with 5 or more carbons and Oxy. denoted oxygenate products.

3. RESULTS AND DISCUSSION

3.1 Composite and Textural Properties

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The concentrations of cobalt, manganese and sodium in the unpromoted and promoted catalysts are presented in Table S1. The concentrations determined with ICP were similar to the nominal concentrations. For all the CoMn catalysts, the Co/Mn atomic ratios are approximately 2. For the Na-promoted samples, the Na loading are 0.006, 0.09, 0.15, 0.37 and 0.60 wt.%, respectively.

Textural properties were acquired for the reduced and spent CoMn catalysts with different Na concentrations and presented in Table S2. The S_{BET}, V_{total} and D_{pore} values of the various reduced catalysts range from 45.3 to 61.2 m²/g, 0.19 to 0.23 cm³/g, and 11.1 to 14.9 nm, respectively, whereas the S_{BET}, V_{total} and D_{pore} values of spent catalysts range from 37.1 to 56.5 m²/g, 0.13 to 0.18 cm³/g, and 10.1 to 12.0 nm. The specific surface area decreased slightly for most samples after the reaction except for CoMn-0Na and CoMn-0.6Na. In addition, both the pore volume and pore diameter decreased after the reaction.

3.2 Reducibility, Morphology and Particle Size Distribution

The TPR results for all the samples are presented in Figure 1a. Two distinct peaks centered around 250 and 378 °C for the CoMn catalyst without the Na promoter and three distinct peaks centered around 168, 250 and 378 °C for the CoMn catalyst with the Na promoter were identified. The signals from the mass spectrometer revealed that all three peaks for the Na-promoted CoMn catalyst involved the consumption of hydrogen and the formation of water (Figure S1). In order to assign each peak in the TPR profiles, the CoMn-0.4Na sample after the reduction at different temperatures was investigated by XRD as shown in Figure 1b. Compared with the calcined CoMn-0.4Na sample, XRD patterns of the CoMn-0.4Na sample reduced for 12 hours at 150 °C showed an increase in the cell volume from 535.1 Å to 541.6 Å. In addition, the XRD result for the sample reduced for 12 hours at 250 °C indicated the presence of diffraction peaks corresponding to the CoMn composite oxide with lower valency. It was suggested that the first peak around 168 °C in the TPR profiles was caused by partial reduction of the CoMn composite oxide and the second peak around 250 °C was due to the further reduction. The XRD measurement of the CoMn-0.4Na catalyst reduced for 12 hours at 375 °C revealed the presence of diffraction peaks corresponding to metallic Co (fcc and hcp) and MnO, indicating the third peak around 378 °C originated from the reduction of the CoMn composite oxide to Co^0 and MnO.

For the CoMn-0.6Na catalyst, the third peak was split into two peaks as high Na loading would hamper the reduction of CoO to $\text{Co}^{0.26}$.

TEM images and particle size distributions for the reduced samples are shown in Figure S2. For all the reduced catalysts, sphere-like nanoparticles were observed with size distributions ranging from 5 to 30 nm. All the samples were in the $Co_xMn_{1-x}O$ phase, and the d-spacings of 2.13 Å and 2.48 Å represented the (200) and (111) facets, respectively. The surface mean diameters increased slightly with increasing Na concentration from 14.5 nm to 17.8 nm.



Figure 1. (a) TPR profiles of CoMn catalysts with different Na concentrations. (b) XRD patterns of calcined and reduced CoMn-0.4Na catalysts at different temperatures.

3.3 Effect of the Na Promoter on the Active Phase

X-ray powder diffraction was carried out to study the structure of the spent CoMn catalysts. The results showed the presence of diffraction peaks corresponding to a mixture of the CoMn composite oxide, MnO, fcc Co, and Co₂C as shown in Figure 2a. The step scanning patterns for 2 θ between 43° and 48° are shown in Figure 2b. With the increasing Na concentration, the intensity of fcc Co(111) facet decreased while the intensity of Co₂C(021) facet increased. To get semi-quantitative information of the Co₂C weight percentage in all the cobalt-containing phases, the peaks from the step scanning patterns of the spent catalysts with different Na concentrations after the reaction for 24 hours were fitted as shown in Figure S3. For CoMn-0Na, the peaks belonging to Co₂C were rather weak and the Co₂C content was only about 2.8 wt.% in

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all the cobalt species. With increasing Na concentration, the weight percentage of Co_2C increased and reached the highest for CoMn-0.4Na (33.2 wt.%). Thus, the Na promoter appears to facilitate the formation of Co_2C . However, further increasing the Na concentration slightly decreased the amount of Co_2C to about 31.1 wt.%.



Figure 2. XRD patterns of spent CoMn catalysts with different Na concentrations. (a) Continuous scanning with 2θ from 30° to 90° . (b) Step scanning with 2θ from 43° to 48° .

TEM images of the spent CoMn catalysts with different Na concentrations are shown in Figure 3. In the case of the spent CoMn-0Na sample, the FTS active phase (fcc Co^0) was observed with a spherical morphology without specific exposed facets. However, the FTO active phase, Co_2C nanoprisms with specific exposed facets of (101) and (020), were not detected. Recently, we discovered Co₂C nanostructures to possess strong facet effects and Co₂C nanoprisms with specifically exposed facets of (101) and (020) as a new FTO active phase exhibited high $C_{2.4}^{=}$ selectivity, low methane selectivity and high activity under mild reaction conditions (250 °C and 1 bar)²⁵. With the presence of Na promoter (CoMn-0.1Na and CoMn-0.2Na), fcc Co⁰ and Co₂C both in the shape of nanosphere and nanoprism were identified. For the unpromoted and promoted CoMn catalysts with low Na concentrations (CoMn-0Na, CoMn-0.1Na, and CoMn-0.2Na), the transition of the active phase from fcc Co^0 to Co₂C nanoprisms was observed. For the Na-promoted CoMn catalysts with high Na concentrations (CoMn-0.4Na and CoMn-0.6Na), Co₂C nanoprisms marked by red rectangle in Figure 3 were observed, while the FT active phase, fcc Co⁰, was undetected. This trend can be correlated with the XRD results (Figure S3). For the

spent CoMn catalysts with high Na concentration, such as CoMn-0.4Na and CoMn-0.6Na, only the Co₂C phase was observed, and no metallic Co⁰ was detected. These findings strongly support the hypothesis that the presence of the Na promoter could stimulate the formation of Co₂C nanoprisms. Davis and co-workers had studied the FTS reaction on Co₂C, and found that a fraction of the Co₂C was reduced to metallic Co⁰ during the FTS process²⁷. Bulk Co₂C appeared unstable under FTS conditions, especially at high reaction temperature. However, in the present study, the Co₂C nanoprisms were stable at the high reaction temperature of 250 °C for a much longer reaction time (>100 h) as shown in Figure S4, suggesting that the Na promoter also benefited the stabilization of Co₂C.



Figure 3. TEM images of spent CoMn catalysts with different Na concentrations. (a) CoMn-0Na, (b) CoMn-0.1Na, (c) CoMn-0.2Na, (d) CoMn-0.4Na, (e) CoMn-0.6Na. The nanoparticles marked by red circles and rectangles were in the shape of nanosphere and nanoprism, respectively.

3.4 Effects of the Na Promoter on Catalytic Performance

The CoMn catalysts were tested in the Fischer-Tropsch reaction at 250 °C, 1 bar and a H_2/CO ratio of 2 (v/v) to determine the influence of the Na promoter on the catalytic activity and product selectivity as shown in Figure 4. Each sample was tested twice at the same reaction conditions in order to understand the statistical significance of the measurement. As shown in Table S4, both CO conversion and products selectivities were similar for each test with low relative deviation (always less than 6 %), indicating that the catalytic results were reproducible and reliable. The sample without the Na promoter (CoMn-0Na) exhibited a high catalytic activity (72.0 C%), a high methane selectivity (24.4 C%), a low $C_{2-4}^{=}$ selectivity (14.3 C%), a low CO_2 selectivity (15.7 C%), and a low O/P ratio ($C_{2-4}^{=}/C_{2-4}^{0} = 0.9$). In the present study, the reaction temperature for all samples was 250 °C, while the normal reaction temperature for Co-based FT catalyst was below 220 °C with low CO₂ selectivity. At high reaction temperature, the high CO conversion for the CoMn-0Na sample resulted in high concentration of water. The high reaction temperature and high water partial pressure improved the activity of the water gas shift (WGS) reaction and led to high CO₂ selectivity. In order to prove the correlation between the reaction temperature and CO₂ selectivity, the CoMn-0Na catalyst was also tested at different reaction temperatures as shown in Table S3. The CO conversion, CO₂ selectivity, methane selectivity and selectivities to lower olefins increased with the reaction temperature, while the C_{5+} +Oxy. selectivity and O/P ratios decreased. Once Na was added as in the case of CoMn-0.1Na, methane selectivity decreased to 7.5 C% while C5+ selectivity increased to 69.6 C%. Previous studies of Co-based FT catalysts have also shown that the addition of alkali promoters to the supported Co catalysts resulted in an increase in the selectivity towards heavier hydrocarbons²³. Eri et al. reported that the chain growth probability of FTS on a cobalt/alumina catalyst was 0.75 in the absence of the alkali promoter, and increased up to 0.87 upon the addition of the alkali promoter²². Li et al. reported that Co₂C is highly efficient for CO nondissociative adsorption, whereas the Co metal is highly active for CO dissociative adsorption. The interface between the cobalt metal and its carbide phase benefited for CO insertion to form oxygenates²⁸. According to the XRD (Figure 2 and S3) and TEM (Figure 3) results of the spent CoMn-0.1Na sample, both metallic Co⁰ and Co₂C were identified. It is

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reasonable to speculate that the outlier of the CoMn-0.1Na sample was caused by the coexistence of metallic Co^0 and Co_2C . With the further increase in the Na concentration, the CO conversion decreased significantly from 72.0 C% to 5.4 C%. Davis et al. reported that the activity of cobalt carbide was very low, and the CO conversion under the similar reaction conditions to those in the present study was about 12.6 $C\%^{27}$. As Co₂C was generated for the samples with the Na addition, it was speculated that the decrease in the CO conversion was caused by the transition of the active phase from Co^0 to Co_2C nanoprisms. Compared with the sample without the Na promoter, the Na-promoted CoMn catalysts exhibited high CO₂ selectivity. Previous studies indicated that alkali promoted Co₂C catalysts exhibited high activity and stability for the low temperature WGS reaction²⁹. The presence of the Na promoter for the sample CoMn-0.6Na resulted in a decrease in methane selectivity from 24.4 C% to 9.1 C%, but an increase in $C_{2-4}^{=}$ selectivity from 14.3 C% to 56.3 C% and O/P ratios from 0.9 to 24.9. The product distributions of the CoMn catalysts with different Na concentrations are shown in Figure 4f, and the methane selectivity deviated gradually from the traditional ASF distribution with increasing Na concentration. The deviation in methane selectivity was caused by a strong facet effect of the Co₂C nanoprisms with the exposed facets of (101) and (020), which were found to suppress the formation of methane and benefit the selectivity to olefins²⁵. The products selectivities were also studied at comparable CO conversion (~ 20 C%) by changing the GHSV. As shown in Figure S5, the trend in the product selectivities at the CO conversion of about 20 C% was similar to that at other CO conversions (Figure 4). However, as the contact time of the CoMn-0.6Na sample increased significantly at the lower GHSV, the product selectivities shifted towards heavier hydrocarbons. Previous studies reported that the reinsertion of α -olefins into the growing chain is the main secondary reaction, causing an increase in the growth probability with increasing chain length and the dependency on the catalyst contact time 30 .



Figure 4. Catalytic performance of the CoMn catalysts with different Na concentrations at 250 °C, 1 bar, 3000 ml/($h \cdot g_{cat}$), H₂/CO=2. (a) CO conversion, (b) CO₂ selectivity, (c) Product selectivity, (d) Lower olefin selectivity, (e) O/P ratios of C₂₋₄, (f) product distributions.

For Fe-based FT catalysts, the Na promoter always led to a lower methane selectivity and a significant increase in the O/P ratio and the WGS activity³¹⁻³². The effect of the Na promoter is usually explained by a decrease in the strength of C-O bond in the adsorbed CO molecule, leading to a higher coverage of the dissociated CO on the surface⁹. We speculated that the addition of the Na promoter have the similar effect on the Co-based FT catalysts. Therefore, the addition of Na promoter to the CoMn catalysts could enhance the dissociation of CO and promoted the formation of Co₂C nanoprisms with FTO activity. The Na promoter can also have an electronic effect on the Co₂C nanoprisms and altered the electronic structure of Co₂C leading to low methane selectivity and high olefin selectivity. In the case of Fe-based FT catalysts, the maximum extent of iron carbonization was observed at the optimal Na concentration. However, higher concentrations of the Na promoter inhibited iron carbide formation and resulted in lower activity and higher rate of light hydrocarbon formation³². In our study, the presence of the Na promoter in the CoMn catalysts resulted in a sharp decrease in methane selectivity and a significant increase in $C_{2,4}^{=}$ selectivity and O/P ratios. The best catalytic performance was obtained with the CoMn-0.4Na catalyst, which had a high catalytic activity (20.4 C%), a low methane selectivity (5.9 C%), a high lower olefin selectivity (54.2 C%), and a high O/P ratio (O/P=23.9). However, further increase of Na concentration in the CoMn catalyst led to increase of methane selectivity and decrease of O/P ratio.

3.5 Origin of the Na Promoter Effects

The extent of Co₂C formation was assessed by the quantity of methanated carbon. The CO carbonization extent was normalized by the mass of the catalyst and the extent of CoMn-0Na. The CO carbonization rate was assessed by the CO carbonization extent as a function of the CO exposure time and normalized by the rate of CoMn-0Na exposed in CO at 30 minutes. The CO carbonization rate and extent of the CoMn catalyst with different Na concentrations are shown in Figure 5. The carbonization rate decreased with the CO exposure time. However, the rate and extent of carbonization increased sharply with Na promoter concentration. The carbonization rate of CoMn-0.4Na was almost six times than that of CoMn-0Na. A maximum rate and extent of carbonization were reached for CoMn-0.4Na, consistent with the catalytic performance, XRD and TEM.



Figure 5. Relative carbonization rate and extent of the CoMn catalysts with different Na concentrations. (a) Relative carbonization rate with exposure time, (b) Relative carbonization rate and extent of the CoMn catalysts with different Na concentrations at 30 min exposure time.

In situ IR spectra revealed the presence of CO adsorbates on the catalyst surface when the reduced catalysts were exposed to CO at the reaction temperature. Figure 6 shows the *in situ* IR spectra obtained after 30 minutes of CO adsorption on the different catalysts. Close to the rotational/vibrational transitions of CO in the gas phase around 2174 and 2114 cm⁻¹, the region between 2060 and 1990 cm⁻¹ reflected the stretching vibrations of CO linearly adsorbed to the surface of the metallic Co^0 phase³². The Na promoter induced a shift of this peak toward lower wavenumbers as presented in Figure 6b. The red shift of the linearly adsorbed CO peak was consistent with stronger binding of CO to the Co surface^{18, 33}. It has been reported that the probability of the C-O bond dissociation depended mainly on the strength of the metal-carbon (M-C) bond. Strong M-C bonds are favored by electron-rich metal centers due to π -backbonding, which at the same time weakens the CO triple bond leading to lower carbonyl stretching frequencies^{18, 33}. The Na promoter, which acts as an electronic donor to cobalt, would increase the π^* back-donation from Co to adsorbed CO and hence decrease the carbonyl stretching frequency³⁴. The spectral region, roughly between 1900 and 1700 cm⁻¹, was commonly assigned to the bridge-bonded CO on the metallic Co^0 surface. The relative peak area centered at 1413 cm⁻¹ increased with Na concentration and reached a maximum for the sample with 0.4 wt.% Na as shown in Figure 6c. The absence of the peak at 1413 cm⁻¹ for the

unpromoted catalyst suggested that this peak was attributed to the CO adsorbate species interacting with the Na promoter. Previous studies of the metal oxides-promoted Co-based catalysts by Bell et al. reported that cations within the metal oxide promoters serve as Lewis acids and speculated that CO may adsorb onto Co in a tilted configuration so as to interact with nearby metal oxides, thereby facilitating CO dissociation³⁵. The Na ions have empty orbital to accept electrons and act as Lewis acids with weak Lewis acidities³⁶. Therefore, it was suggested that the Na ions exposed at the edge of cobalt could act as Lewis acids enhancing the adsorption of CO. We note that this effect was sensitive to the fractional coverage of the metal by the Na promoter and reached a maximum at a coverage of 0.4 wt.%. The peak centered at 1587 cm⁻¹ was associated with adsorbates related to the interface of Co and MnO_x^{18} . The Na promoter induced a shift of this peak toward higher wavenumber as shown in Figure 6d. The blue shift of the adsorbed CO peak in the interface of Co and MnO_x - was consistent with weaker binding of CO. With the increasing Na concentration, part of Na promoter were interacted with MnO_x and changed its electronic structure, which would suppress the promotion effect of MnO_x promoter. Thus, we proposed that the addition of the Na promoter acted as an electronic donor to cobalt, as well as a Lewis acid exposed at the edge of cobalt, both resulting in stronger CO adsorption and enhanced CO dissociation, which attributed to the formation of Co₂C nanoprisms with the promising FTO performance.



Figure 6. IR study of adsorbed CO on the reduced CoMn catalysts with different Na concentrations. (a) In situ IR spectra measured at 250 °C and 1 bar. (b) Peak wavenumber of linearly adsorbed CO changing with Na concentrations. (c) Ratio of the area at 1413 cm⁻¹ of the CoMn-xNa (A_x) to that of the CoMn-0.4Na ($A_{0.4}$) changing with Na concentrations. (d) Peak wavenumber of adsorbed CO on Co-Mn interface changing with Na concentrations.

3.6 Effects of Other Alkali Promoters

The effects of other alkali promoters on the CoMn catalysts were also investigated. All catalysts with other alkali promoters were prepared with the same alkali concentration of 0.4 wt.%. As shown in Table S4, the activity decreased dramatically with the atomic number of the alkali promoter. The CO₂ selectivities of CoMn-0.4Li, CoMn-0.4Na, CoMn-0.4K and CoMn-0.4Rb were 28.9 C%, 46.5 C%, 39.7 C%, and 20.7 C%, respectively, whereas the C₂₋₄⁼ selectivities were 20.0 C%,

54.2 C%, 57.4 C%, and 45.8 C%. In addition, the O/P ratios for these four samples were 1.1, 23.9, 18.0, and 5.8, respectively. CoMn-0.4Na was found to be the best FTO catalyst with the lowest methane selectivity and the highest O/P ratio. The product distributions of the CoMn catalysts with different alkali promoters are presented in Figure S6. For CoMn-0Na, CoMn-0.4Li, and CoMn-0.4Rb, the deviation of methane selectivity in the ASF distribution was not observed. Methane selectivities for CoMn-0.4Na and CoMn-0.4K were much lower than those predicted from the ASF distribution. To uncover the active phase of the CoMn catalysts with different alkali promoters, XRD and TEM studies were carried out as shown in Figures S7 and S8. The active phases of CoMn-0.4Li were mixtures of fcc Co⁰ and spherical Co₂C. XRD results of CoMn-0.4Na, CoMn-0.4K and CoMn-0.4Rb revealed the existence of Co₂C. TEM images showed that the Co₂C in CoMn-0.4Na had the shape of nanoprisms, whereas the obtained Co₂C in CoMn-0.4K and CoMn-0.4Rb were mixtures of nanospheres and nanoprisms. The spherical Co₂C nanoparticles were considered as the reason of deactivation in Co-based FT reaction with low activity and high methane selectivity. As a result, the appearance of spherical Co_2C nanoparticles for CoMn-0.4K and CoMn-0.4Rb was corresponding to the worse FTO performance with higher methane selectivity compared with CoMn-0.4Na.

4. CONCLUSIONS

CoMn catalysts with different concentrations of the Na promoter were prepared and evaluated for the FTO reaction. Characterization of the catalysts by techniques such as ICP, XRD, N₂ adsorption, H₂-TPR, and TEM were performed to investigate the effect of the Na promoter on the formation of the active phase and reveal the relationship between catalyst structure and performance. The Na promoter was found to induce the formation of Co₂C with specifically exposed facets, which was responsible for the transition of the syngas reaction from traditional FTS to FTO. The maximum C₂₋₄⁼ selectivity (54.2 C%) with a low methane selectivity (5.9 C%) was obtained over the CoMn-0.4Na catalysts under mild reaction conditions, and the active phase was exclusively attributed to Co₂C nanoprisms. The O/P ratio for C₂₋₄ reached a very high value of 23.9, and the product distribution deviated greatly from the classical ASF distribution. Furthermore, the rate and extent of carbonization

increased with increasing Na concentration. In situ IR studies revealed that the Na promoter acted as an electronic donor to cobalt, leading to stronger CO adsorption and enhanced CO dissociation. Therefore, the addition of the Na promoter to the CoMn catalysts promoted the formation and stabilization of Co₂C nanoprisms with specifically exposed facets of (101) and (020), which displayed excellent FTO catalytic performance with low methane and high $C_{2-4}^{=}$ selectivity simultaneously. The effects of other alkali promoters were also examined to show that only the K promoter had the similar effect on the CoMn catalysts for the FTO reaction.

In addition to the study of the Na promoter effects on the CoMn catalysts, more efforts are still needed to reveal the role of Mn and the detailed formation mechanism of Co_2C . Obviously, the Co_2C -based FTO route would become more feasible with the further improvement in the activity, selectivity and stability. CO_2 selectivity could be decreased by hindering the WGS activity. In addition, the catalytic activity and stability could be substantially increased by the introduction of modifiers and/or the use of a suitable support (such as ZrO_2 and Al_2O_3).

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge.

Elemental analysis, textural properties, catalytic performance data, mass spectra, XRD patterns, TEM images and products distributions. (PDF)

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Table of Contents

Co

234567

-1

(n/"/u)u

40 ⊢300

-20Ratio

10

unpromoted

-0

Co₂C

1234567

-2

-5

-6-

(u)

/"-3)u

Na⁺

CoMn

-30_{0/P}

-20Rato

