Bio-syngas Converting to Liquid Fuels over Co Modified Fe$_3$O$_4$-MnO$_2$ Catalysts

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A bifunctional Co modified Fe$_3$O$_4$-Mn catalyst was prepared for Fischer-Tropsch synthesis (FTS). The influence of Co loading on the synergistic effect of Fe-Co as well as FTS performance over Fe$_3$Co$_x$Mn$_{1-x}$ catalysts was studied. Incorporation of Co species into the Fe$_3$O$_4$-Mn catalyst promoted the reduction of iron oxides, increasing iron active sites during FTS. Moreover, the adding of Co species enhanced the electron transfer from Fe to Co metal, which strengthened the synergistic effect of Fe-Co, improving the catalytic performance. The Fe$_1$Co$_x$Mn$_1$ catalyst with higher Co loading promoted further the hydrogenation ability, favoring the shifting of the product distribution towards shorter hydrocarbons. Under optimized conditions of 280 °C, 2.0 MPa and 3000 h$^{-1}$, the highest yield of liquid fuels was obtained for the Fe$_1$Co$_1$Mn$_1$ catalyst.

**Key words:** Fischer-Tropsch, Fe$_3$O$_4$-Mn, Co loading, Synergistic effect

I. INTRODUCTION

Fischer-Tropsch synthesis (FTS) process, converting syngas derived from coal, biomass to various alcohol, oil and high value-added hydrocarbon products, has received an increasing concern with the rapid development of economy and gradual depletion of crude oil in recent years [1–5]. The hydrocarbons product of FTS generally follows the Anderson-Schulz-Flory (ASF) model, with a distribution ranging from C$_1$ to C$_{50}$, which results in the difficulty for controlling selectively special hydrocarbons [6]. Designing of catalysts with high selectivity for special hydrocarbons is very important for industrial applications of FTS.

Fe, Co, Ni, and Ru are the conventional active metals for FTS [7], in which only Fe and Co are used for the production of liquid fuels in industry. Generally, less activity and producing long chain hydrocarbons are found over iron-based catalysts, whereas high activity and more expensiveness are displayed for cobalt-based catalysts. Thus, novel FTS catalyst is designed, combining with high activity of iron metal and heavy hydrocarbons selectivity of cobalt species. Actually,umerous attentions have been paid to preparing Fe-Co bifunctional catalysts [8–10]. Bragana et al. [11] found that Co-Fe bimetal supported on the HMS mesoporous material exhibited the highest activity and C$_5^+$ hydrocarbon selectivity. The results of Tavasoli et al. [12] showed that the single Co-based catalyst facilitated the formation of C$_5^+$ liquid hydrocarbons, whereas incorporation of iron into the Fe-Co catalyst did not change significantly the product distribution. In addition, Constant et al. [13] found that the formation of mixed Co-Fe bimetal species promoted the selectivity to light olefins while decreased catalytic activity compared to the Co-based catalyst. In addition, Lögberg et al. [14] found that the combination of cobalt and iron improved the FTS catalytic activity in comparison to the monometallic Fe catalyst. Recently, Rothenberg et al. [3] considered that the interaction between Fe and Co species was of vital importance to the enhancement of activity and stability in FTS. Though abundant studies have been conducted on the Co-Fe bimetallic FTS catalyst, there exists the controversy on the FTS performance due to different conditions and/or different catalyst systems. Therefore, the intrinsic relationship between Co and Fe species is necessary to be further illustrated.

In our previous work, a Fe$_3$O$_4$-Mn catalyst was synthesized by hydrothermal method, which exhibited a high olefins selectivity of about 80% [15]. It is expected that incorporation of cobalt species into Fe$_3$O$_4$-
Mn might further optimize catalytic activity and product distribution, whereas the synergy between Fe₃O₄ and Co is not understood clearly. Herein, a Co modified Fe₃O₄-Mn catalyst was prepared and applied in the FTS field. The synergistic effect of Fe₃O₄-Co was investigated in detail by the combination of several techniques including N₂ adsorption-desorption analysis, powder X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), and laser Raman spectroscopy (LRS).

II. EXPERIMENTS, RESULTS AND DISCUSSION

A. BET and SEM analysis

The N₂ adsorption-desorption isotherms of all the prepared catalysts are shown in FIG. 1. Obvious hysteresis loops can be found in isotherms of all catalysts, which can be identified as IV type isotherm [16]. The type H1 hysteresis loop can be observed while the ratio of $P/P_0$ is over 0.9, ascribed to a wide macroporous size distribution [17], revealing the shaggy structure of prepared Fe₃CoₓMn₁ catalysts. Similar macroporous structures are observed for all the Fe₁CoₓMn₁ catalysts, indicating that addition of Co to the Fe₃O₄-Mn catalyst does not destroy the intrinsic structures. The BET surface area of Fe₃O₄-Mn is 90 m²/g (Table S1 in supplementary materials), which decreases slightly with the adding of Co species, probably due to partial incorporation of Co particles into the macroporous structures of Fe₃O₄-Mn, decreasing BET surface area. Moreover, the average pore volume increases with the increasing of cobalt concentration. The average pore volume of Fe₁Co₀Mn₁ is 0.80 cm³/g, which increases gradually to 1.40 cm³/g as the ratio of Co/Fe raises to 1:1, demonstrating that Co species incorporated into Fe₃O₄-Mn are well dispersed inside the macroporous structures. The morphological and structural characteristics of Fe₁CoₓMn₁ catalysts are demonstrated in SEM images in FIG. 2. All catalysts have a structure of nanoplates and the addition of Co has no effect on the structural characteristics.

B. H₂-TPR and XRD results

H₂-TPR is used to characterize the reduction behavior of Fe₁CoₓMn₁. Four peaks appear when temperature is around 200–500 °C or 600–800 °C for the single Fe₃O₄-Mn catalyst (FIG. 3). According to our previous study, the peaks at around 400 °C and 750 °C are due to continual reduction of Fe₃O₄→FeO→Fe, respectively [15]. And the shoulder peak at around 200–500 °C corresponds to the reduction of MnO₂ [18]. For the Fe₁CoₓMn₁ catalysts, new main peaks appear at around 200–320 °C and 400–500 °C, which is due to reduction of Co₃O₄→CoO→Co, respectively [19]. Different from monometallic catalysts, reduction pattern of multi-metallic catalysts is more difficult to analyze because metallic oxide reduction steps are easily overlapped [20, 21]. It is apparent that the adding of cobalt species into Fe₃O₄-Mn results in the reduction peaks of iron oxides shifting towards lower temperature in some extent, indicating that the addition of Co promotes the reduction of metallic oxide via weakening the Fe-Mn interaction. This is in agreement with Diaz et al. [22],

FIG. 1 N₂ adsorption-desorption isotherms of the fresh Fe₁CoₓMn₁ catalysts. (a) Fe₁Co₀Mn₁, (b) Fe₁Co₀.₂Mn₁, (c) Fe₁Co₀.₅Mn₁, (d) Fe₁Co₀.₈Mn₁, (e) Fe₁Co₁Mn₁.

FIG. 2 SEM image of fresh catalysts. (a) Fe₁Co₀Mn₁, (b) Fe₁Co₀.₂Mn₁, (c) Fe₁Co₀.₅Mn₁, (d) Fe₁Co₀.₈Mn₁, (e) Fe₁Co₁Mn₁.
who demonstrated that Co species promoted the reduction of iron oxides.

XRD measurements are carried out to investigate phase structures of our catalysts. From FIG. 4 it can be found that all catalysts exhibit the diffraction peaks at 2θ of 30.0°, 35.4°, 53.4°, 62.5°, which are ascribed to the typical Fe3O4 (JCPDS: 00-019-0629) [23]. In addition, an amorphous peak is observed at 2θ=40.5°, corresponding to the amorphous structure of MnO2. No diffraction peak of Co species appears for the Co-doped catalysts, implying that Co species is well dispersed in the Fe1Co2Mn1 catalysts. Notably, with the gradual adding of Co species into the catalysts, the diffraction peaks of Fe3O4 shifted slightly towards higher angles, which may be due to the combination of Fe and Co species. The results of Lögdberg et al. [14] demonstrated that addition of Co into the Fe2O3 resulted in diffraction peaks of Fe2O3 shifting towards higher 2θ. Therefore, it may be the Fe2O3-Co solid solution in the Fe1Co2Mn1 catalysts contracts the crystal lattice of Fe2+(0.78 Å) and Fe3+(0.61 Å) via the incorporation of Co2+(0.75 Å) and Co3+(0.61 Å) [24].

C. XPS and Raman results

Phase compositions and electronic state on the surface layers of Fe1Co2Mn1 with different Co contents are characterized by XPS. In FIG. 5(A), all the catalysts show two obvious Fe 2p peaks at around 723.5 and 710.8 eV that can be ascribed to Fe3O4, which is in agreement with the XRD results in FIG. 4. Particularly, with the addition of Co content, Fe 2p peaks marginally shift to a higher binding energy. Moreover, at around 781.2 and 795.6 eV, Co 2p3/2 and Co 2p1/2 peaks gradually appear, demonstrating the existence of Co3O4 (FIG. 5(B)). In addition, the peak intensity of Co has an increasing tendency when Co content increases, probably due to the accumulation of added cobalt in both the bulky and surface layers.

In order to have a better insight into surface structure and carbonaceous species of used Fe1Co2Mn1 catalysts, Raman analysis is carried out to identify the carbon species on the surface catalysts. As shown in FIG. 6, two main peaks observed at 1342 cm⁻¹ and 1607 cm⁻¹ are ascribed to the disordered and ordered carbonaceous species, respectively [27]. The intensity of surface carbonaceous species shows an apparent increase when Co content is higher, demonstrating that addition of more Co to Fe1Co2Mn1 catalysts facilitates the formation of carbonaceous species on the surface layers. Moreover, the G/D ratio (the ratio of ordered and disordered carbon species) shows an apparent decrease from 0.94 to 0.21 as the Co content increases from 0 to 33%. The disordered carbon species is related to the structural disorder at the surface while the ordered carbon species is connected with the vibration of the sp² bonded carbon atoms [28, 29]. It is clear that incorporation of Co species can decrease the graphitization degree and increase the defect sites in graphene lattice, which can weaken the mobility of catalyst and suppress catalysts tendency to agglomerate [26].
FIG. 5 XPS spectra of the as-synthesized catalysts. (A) Fe 2p, (B) Co 2p, and (C) Mn 2p. (a) Fe$_1$Co$_0$Mn$_1$, (b) Fe$_1$Co$_{0.2}$Mn$_1$, (c) Fe$_1$Co$_{0.5}$Mn$_1$, (d) Fe$_1$Co$_{0.8}$Mn$_1$, (e) Fe$_1$Co$_1$Mn$_1$.

FIG. 6 Raman spectrum profiles of the spent Fe$_1$Co$_x$Mn$_1$ catalysts. (a) Fe$_1$Co$_0$Mn$_1$, (b) Fe$_1$Co$_{0.2}$Mn$_1$, (c) Fe$_1$Co$_{0.5}$Mn$_1$, (d) Fe$_1$Co$_{0.8}$Mn$_1$, (e) Fe$_1$Co$_1$Mn$_1$.

D. Catalytic evaluation

Fischer-Tropsch performance of the catalysts is carried out at the conditions of 280 °C, 2.0 MPa, 3000 h$^{-1}$ and CO:H$_2$=1:1 for 30 h. CO conversion of the Fe$_3$O$_4$-Mn catalyst is 43.32%, which shows an increase as Co content increases. (Table I). When the ratio of Co/Fe reaches 1:1, CO conversion increases to 58.90%, demonstrating that the addition of Co species to the Fe$_3$O$_4$-Mn promotes catalytic activity. The results of Yang et al. [30] showed that tuning Fe/Co molar ratio in the Fe$_5$C$_2$/Co catalyst changed obviously the FTS performance. Incorporation of 0.6 wt% Co into the Fe$_5$C$_2$/Co catalyst improved the catalytic activity about 4 times compared to pure Fe$_5$C$_2$ catalyst. Constant et al. [13] found that increasing cobalt content in Co-Fe bimetallic catalysts facilitated the FTS rate increase. In the present study, the adding of Co species into the Fe$_3$O$_4$-Mn catalyst promotes the reduction of iron oxides, as confirmed by H$_2$-TPR, which facilitates the formation of iron active sites. Furthermore, cobalt metal is used widely as the active metal to optimize the FTS performance [31–33]. The incorporation of Fe and Co in Fe$_3$Co$_x$Mn$_1$ catalysts improves the electron migration from Fe into Co, which may enhance the synergistic effect of two metals, further increasing catalytic performance.

From Table I it can be found that the Fe$_3$O$_4$-Mn catalyst exhibits a low CH$_4$ selectivity (3.58%) with a high C$_5^+$ selectivity (74.72%). The ratio of C$_2$-$C_4$/$C_2$-$C_4^*$ is 4.43. With the adding of Co species into the Fe$_3$O$_4$-Mn catalyst, the hydrocarbons product shifts towards lighter hydrocarbons, and the alkenes selectivity decreases gradually, demonstrating that the combination of Co and Fe facilitates the formation of shorter hydrocarbons. The results of Bezemer et al. [34] demonstrated that smaller cobalt metal particles in the Fe-Co bimetallic catalyst had higher hydrogenation ability in FTS, promoting the formation of lower C$_5^+$ hydrocarbons. Díaz et al. [22] suggested that the combination of Co and Fe bimetallic active sites enhanced the activation of reactants and desorption of intermediate hydrocarbons, favoring the production of lighter hydrocarbons. Therefore, incorporation of Co metal into the Fe$_3$O$_4$-Mn catalyst in this study strengthens the synergistic effect between Fe and Co active sites, which promotes the activation of reactants and desorption of intermediate hydrocarbons, changing the product distribution to lighter hydrocarbons. Furthermore, Co species added in the Fe$_1$Co$_x$Mn$_1$ catalysts provides higher hydrogenation ability for olefins hydrogenation reaction at relatively high reaction temperature (260 °C), favoring the production of paraffins.

E. Reaction conditions

The reaction conditions (temperature, GHSV and pressure) have great influence on the performance of the catalyst. In this study, the optimal Fe$_1$Co$_0$Mn$_1$ catalyst is selected to carry out the optimization of reaction conditions. The effect of reaction temperature
is shown in FIG. S1 (supplementary materials). It can be found that CO conversion increases from 58.90% to 96.63% when reaction temperature raises from 260 °C to 340 °C. The selectivity of CH4 and C2–C4 raises from 11.01% and 24.60% to 30.11% and 38.90%, respectively while that of C5+ hydrocarbons shows a sharp drop from 64.39% to 30.99%. It may be attributed to that higher reaction temperature suppresses the carbon chain growth of hydrocarbons, resulting in the formation of light hydrocarbons, which is consistent with the previous study [35].

The influence of reaction pressure on the catalytic performance of Fe1Co1Mn1 catalyst at 280 °C and 3000 h⁻¹ is presented in FIG. S2 (supplementary materials). The CO conversion increases from 17.98% to 59.86% while the reaction pressure increase from 1.0 MPa to 4.0 MPa (FIG. S1), demonstrating that higher pressure promotes catalytic activity. Moreover, the selectivity of CH4 and C2–C4 increases from 5.75% and 13.55% to 11.83% and 21.25%, respectively while that of C5+ hydrocarbons has a slight decrease from 80.69% to 66.92% with the increasing pressure. This suggests that lower reaction pressure is propitious to the formation of C5+ hydrocarbons.

FIG. S3 in supplementary materials shows the impact of GHSV on catalytic performance of Fe1Co1Mn1 catalyst at 280 °C and 2.0 MPa. CO conversion has an obvious decrease from 50.10% to 16.32% with the continual increasing of GHSV, which may be attributed to the shortened contact time in higher GHSV. Interestingly, the higher GHSV has slight influence on the hydrocarbons selectivity. According to these results above, the optimized performance of syngas to liquid fuels is achieved on the Fe1Co1Mn1 catalyst, which displays the highest yield of liquid fuels of 36.65% at 280 °C, 2.0 MPa and 3000 h⁻¹.

**III. CONCLUSION**

Briefly, the influence of cobalt on the synergy of Fe–Co and FTS performances over the Fe1Co2Mn1 catalyst was studied. Introduction of Co into the Fe3O4–Mn catalyst did not damage the catalyst macroporous structures, and enlarged the average pore volume. The increasing addition of cobalt enhanced the reduction of Fe3O4, which facilitated the formation of iron carbide. In addition, the Fe1Co2Mn1 catalyst with higher Co loading enhanced the electron transfer from Fe3O4 to Co3O4, probably strengthening the synergistic effect of Fe–Co and improving the catalytic performance. Furthermore, incorporation of Co species increased the hydrogenation ability of intermediate hydrocarbons, resulting in the hydrocarbon distribution shifting to shorter carbon number. The optimized Fe1Co3Mn1 catalyst displayed the highest yield of liquid fuels of 36.65% at 280 °C, 2.0 MPa and 3000 h⁻¹.

**IV. ACKNOWLEDGMENTS**

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**TABLE I** The catalytic performance of various catalysts in the FTS reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv./%</th>
<th>CO2 sel./%</th>
<th>Hydrocarbon sel./%</th>
<th>C5+ yield/%</th>
<th>C2–C4 Alkenes</th>
<th>C5–C12 Alkenes</th>
<th>C5–C12 Alkenes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH4</td>
<td>C2–C4</td>
<td>C5+</td>
<td>o/p</td>
<td>sel./%</td>
</tr>
<tr>
<td>Fe1Mn1</td>
<td>43.32</td>
<td>47.11</td>
<td>3.58</td>
<td>21.70</td>
<td>74.72</td>
<td>17.12</td>
<td>7.45</td>
</tr>
<tr>
<td>Fe1Co0.2Mn1</td>
<td>47.72</td>
<td>48.72</td>
<td>5.97</td>
<td>25.14</td>
<td>68.89</td>
<td>16.95</td>
<td>4.68</td>
</tr>
<tr>
<td>Fe1Co0.5Mn1</td>
<td>50.67</td>
<td>49.56</td>
<td>8.86</td>
<td>28.02</td>
<td>63.12</td>
<td>16.13</td>
<td>4.12</td>
</tr>
<tr>
<td>Fe1Co0.8Mn1</td>
<td>55.44</td>
<td>48.06</td>
<td>10.29</td>
<td>29.02</td>
<td>60.69</td>
<td>17.47</td>
<td>3.95</td>
</tr>
<tr>
<td>Fe1CoMn1</td>
<td>58.90</td>
<td>46.00</td>
<td>11.01</td>
<td>24.60</td>
<td>64.39</td>
<td>20.48</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Note: Reaction conditions: catalyst (0.5 g), syngas (CO:H2=1:1; 3000 h⁻¹), 2.0 MPa, 260 °C. Pretreated with H2 at 350 °C for 10 h. The data are collected at 30 h.


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