Conversion of Bio-syngas to Liquid Hydrocarbon over CuCoMn-Zeolite Bifunctional Catalysts

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A series of bifunctional catalysts composed of a component for higher alcohol synthesis (Cu-CoMn oxides, CCM) and an acidic zeolite (SAPO-34, ZSM-5, Y, MCM-41) were prepared for production of liquid hydrocarbon directly from a bio-syngas through a one-stage process. The effects of zeolite type, zeolite content, Si/Al ratio and preparation method on catalyst texture and its reaction performance were investigated. Higher selectivities and yields of liquid products were obtained by using bifunctional catalysts. The yields of liquid hydrocarbons decreased in the order CCM-ZSM-5 > CCM-SAPO-34 > CCM-Y > CCM-MCM-41. CCM-ZSM-5 (20wt%, Si/Al=100) prepared by coprecipitation method displayed the optimal catalytic performance with the highest CO conversion (76%) and yield of liquid products (30%). The catalysts were characterized by N2 adsorption/desorption, NH3-TPD, XRD, and H2-TPR analysis. The results showed that higher specific surface areas and pore volumes of bifunctional catalysts were achieved by adding zeolites into CuCoMn precursors. Medium pore dimension and moderate acidity in CCM-ZSM-5 were observed, which probably resulted in its excellent reaction performance. Additionally, a higher number of weaker acid sites (weak and/or medium acid sites) were formed by increasing ZSM-5 content in CCM-ZSM-5 or decreasing Si/Al ratio in ZSM-5. It was also seen that metal dispersion was higher and reducibility of metal ions was easier on the CCM-ZSM-5 catalyst prepared by coprecipitation. The higher alcohols-to-hydrocarbon process provides a promising route to hydrocarbon fuels via higher alcohols from syngas or biobased feedstocks.

Key words: Bifunctional, CuCoMn-zeolite, Higher alcohols-to-hydrocarbon process, Bio-syngas conversion, Liquid hydrocarbon synthesis

I. INTRODUCTION

With the gradual depletion of fossil fuel resources and environmental constraint, the production of clean fuels from syngas (CO and H2) has attracted renewed attention [1–3]. Syngas is an important industrial feedstock which can be produced from coal, natural gas and biomass [4, 5]. Especially, as an abundant and renewable resource, biomass can contribute to a sustainable nonfossil-based raw material for energy sources or chemicals [6, 7]. Two major routes of liquid hydrocarbon production from syngas have been widely reported [8–12]. One was Fischer-Tropsch (FT) synthesis which was an important technology for conversion of syngas to liquid hydrocarbons and high value-added chemicals [9]. However, the FT process had two unfavorable disadvantages, namely nonselective product distribution controlled by Anderson-Schulz-Flory (ASF) polymerization kinetics and mainly linear hydrocarbons with low octane value as gasoline [10]. The other route was methanol-to-gasoline (MTG) process which first converted syngas to methanol and then transformed methanol to hydrocarbons [11]. In recent decades, a number of researches have confirmed that the one-stage processes over bifunctional catalysts were more favourable for syngas conversion to gasoline than the two-stage and three-stage processes [9, 12]. With bifunctional catalyst, the synthesis of methanol from syngas on metallic sites and the transformation of methanol to hydrocarbons on acidic sites were allowed to occur simultaneously, which consequently thermodynamically enhanced methanol synthesis from syngas [9]. Moreover, the shape-selective properties of acidic function (e.g., zeolites) limited the generation of large molecules. Therefore, bifunctional catalysts have been verified to show good performance companied with high conversion and product selectivity for syngas to liquid hydrocarbons in the MTG process.

Very recently, higher alcohols have also been reported to produce gasoline-range hydrocarbons, and showed higher yields of gasoline compared to methanol [13, 14]. Mentzel et al. [15] studied i-propanol which was used...
as a reactant for conversion to gasoline over H-ZSM-5 zeolite. The results suggested that the total conversion capacity was more than 25 times higher for i-propanol than those for methanol and ethanol. Besides, the catalyst lifetime increased dramatically using i-propanol as the reactant. Thus, production of liquid hydrocarbons from syngas by the higher alcohols-to-hydrocarbon (HTH) route under MTG-like conditions has received great interest [9, 16]. Yan et al. have reported CuO-CoO-Cr$_2$O$_3$/H$^+$/ZSM-5 (C3Z) bifunctional catalysts prepared by physical mixing for CO hydrogenation to hydrocarbons [9]. Their results suggested that CO conversion and hydrocarbon yield increased when temperature and pressure increased. And hydrocarbon selectivity increased when H$_2$/CO ratio and space velocity of the feed gas decreased. Mohanty et al. have also synthesized (CuO-CoO-Cr$_2$O$_3$+MFI Zeolite) bifunctional catalysts for syngas conversion to liquid fuel [16]. Nevertheless, the HTH process for syngas to hydrocarbon via higher alcohols over bifunctional catalysts of higher alcohol synthesis catalyst and acidic zeolite has not been studied as extensively as that via methanol.

Several heterogeneous catalysts for higher alcohol synthesis from syngas have been explored and well reviewed [17]. Briefly, these catalysts can be classified into four types: (i) modified methanol synthesis catalysts [18, 19], (ii) modified Fischer-Tropsch synthesis catalysts [20–25], (iii) noble metals-based synthesis catalysts [26], and (iv) Mo-based synthesis catalysts [27, 28]. Among them, CuCo-based modified Fischer-Tropsch catalysts developed by Institut Francais du Petrole (IFP) have been regarded as one of the most promising catalysts for higher alcohol synthesis due to their relatively favorable reaction performance under mild operating conditions [9, 16]. In addition, migration of acid sites on different zeolites was also concerned for the bifunctional process [10]. Different zeolites (or more broadly molecular sieves) have clearly distinct properties in acidic nature and textural structure (e.g., pore size, shape-selectivity) [29].

Our previous work mainly focused on bio-syngas production [30–32] and higher alcohol synthesis from bio-syngas over Na-promoted CuCoMn catalyst [33]. In this work, we study the influence of zeolite topology (SAPO-34, ZSM-5, Y, MCM-41) on the reaction performance of CuCoMn-zeolite bifunctional catalysts in producing liquid hydrocarbon directly from a bio-syngas. The selected zeolites possess small pore (SAPO-34, 0.43 nm), medium pore (ZSM-5, 0.54 nm×0.56 nm, 0.51 nm×0.54 nm), large pore (Y zeolite, 0.74 nm) of micropores and mesopore (MCM-41, 3.3 nm) respectively [34]. Furthermore, a comparison of two preparation methods for zeolite addition to CuCoMn precursor is conducted.

II. EXPERIMENTS

A. Catalyst preparation

Four types of zeolites (SAPO-34, ZSM-5, Y, MCM-41) supplied from Nankai University catalyst Co., Ltd. (Tianjin, China) were applied to prepare CuCoMn-zeolite bifunctional catalysts. ZSM-5 was pretreated by conversion of sodium form to protonated form [35]. The molar composition of the CuCoMn oxides was constant (Cu/Co/Mn=1/1/0.8) with a desired proportion of zeolite. The preparation process of CuCoMn-zeolite bifunctional catalysts is detailed as follows. A specific zeolite was blended with sodium carbonate (AR grade) solution (so-called co-precipitation method). Subsequently, the mixed solution of metal nitrate (AR grade) was quickly added into the alkali solution. The precipitate was aged in the mother liquor for 1 h, and then washed. After being dried at 393 K for 12 h, the solid was impregnated with appropriate amounts of Na$_2$CO$_3$ and kept at 343 K for 2 h, and then calcined in air at 723 K for 4 h. The obtained CuCoMn-zeolite sample was further pressed, crushed and sieved. The particles of 40–60 mesh were used for kinetic tests. Accordingly, the finally obtained CuCoMn-zeolite catalysts were designated as CCM-SAPO-34, CCM-ZSM-5, CCM-Y, and CCM-MCM-41, respectively. The catalyst without adding any zeolite was marked as CCM. In addition, for comparison of the influence of different preparation method on CuCoMn-zeolite bifunctional catalyst, ZSM-5 and calcined CuCoMn oxides were homogenized in a mortar (so-called physically mixing method). The mixture was then pelletized to tablets and broken into 40–60 mesh particles.

B. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on an X’pert Pro Philips diffractometer (Philips, Netherlands), using a Cu Kα radiation (λ=0.15418 nm). The N$_2$ adsorption/desorption isotherms were performed at 77 K using the Micromeritics ASAP 2020 V3.00 analyzer. Brunauer-Emmett-Teller surface areas ($S_{\text{BET}}$) were evaluated from the linear part of the BET plots. Volumes ($V$) and average pore diameters ($d$) of mesopores were calculated using the Barrett-Joyner-Halenda (BJH) model on the desorption branch. The surface areas of micropores ($S_{\text{micro}}$) were measured by t-plot method. The volumes ($V_{\text{micro}}$) and median widths ($d_{\text{micro}}$) of micropores were determined by Horvath-Kawazoe method. H$_2$ temperature-programmed reduction (H$_2$-TPR) tests were carried out to study the reduction features of the catalysts in a home-built equipment. Prior to TPR experiments, the catalyst was treated in flowing Ar (30 mL/min) for 1 h. Subsequently, H$_2$ (5vol%, balance Ar) was switched on under argon flow (40 mL/min),

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solid and liquid products, increased from 10% on CuCoMnx zeolites to 18%, 30%, 14%, and 13% corresponding to CCM-ZSM-5, CCM-MCM-41, CCM-Y, and CCM-ZSM-5, respectively. CCM-ZSM-5 showed the optimal catalytic activity and yield of desired products. With regard to liquid products (\(S_{\text{liquid}}\), mainly including hydrocarbon and/or alcohols) increased over all CuCoMnx-zeolite bifunctional catalysts with just a little increment from 28% to 29% over CCM-MCM-41, \(Y_{\text{liquid}}\), a parameter combined with CO conversion and selectivity of liquid products, increased from 10% on CuCoMnx oxides to 18%, 30%, 14%, and 13% corresponding to CCM-SAPO-34, CCM-ZSM-5, CCM-Y, and CCM-MCM-41, respectively. CCM-ZSM-5 showed the optimal catalytic activity and yield of desired products. With regard to the by-products, CO\(_2\) was the primary product over zeolite-free CuCoMnx catalyst and remarkably decreased over zeolite-containing bifunctional catalysts. By contrast, the selectivities of methane and C\(_2\)-C\(_4\) gaseous hydrocarbons were enhanced with the addition of the zeolites.

Figure 2(b) shows the changes of liquid hydrocarbon distribution over CuCoMnx-based bifunctional catalysts with different zeolites. The contents of products decreased as their carbon numbers increased over the
The results of hydrocarbon synthesis reactions over bifunctional catalysts with CuCoMn oxide and 20wt% different zeolites prepared by coprecipitation. (a) Conversion of CO ($C_{CO}$), carbon selectivity of products ($S_X$) and carbon yield of liquid products ($Y_{\text{liquid}}$). (b) The carbon number distribution of hydrocarbon products. (c) The fraction distribution of hydrocarbon products. 0, means the CuCoMn oxide without adding zeolite; C17+, suggests the total content of C17 and larger than C17. The constant conditions: GHSV=4000 h$^{-1}$, $T=563$ K, $P=5$ MPa. The reaction conditions unless specifically stated otherwise are the same as those described here.

2. Effect of ZSM-5 content

Figure 3 shows the influence of different ZSM-5 contents (20% and 50%) on hydrocarbon synthesis over CuCoMn-ZSM-5 bifunctional catalysts prepared by coprecipitation method. When the content of ZSM-5 in bifunctional catalyst increased from 20% to 50%, CO conversion decreased from 76% to 51% while the changes of product selectivities were not obvious. This can be explained that much more metal active sites are covered by zeolite accompanying with the decrease in the metal number when ZSM-5 content increased. Thus, the yield of liquid products was higher on CuCoMn-ZSM-5 (20%) catalyst due to its higher CO conversion. From Fig.3(b), the carbon numbers...
were mainly concentrated in the range of C₅ to C₁₂. The C₅-C₁₂ fraction increased from 85% to 89% and accordingly the heavier fractions (C₁₃-C₁₆, and C₁₇+) decreased on CuCoMn-ZSM-5 (50%) catalyst. The results indicate that cracking reactions are more favorable to occur but the changes fluctuate within a narrow range with the increment of ZSM-5 content.

3. Effect of Si/Al ratio of ZSM-5

The Si/Al ratio of ZSM-5 used above was 100 and the ZSM-5 (Si/Al ratio 25) was employed for comparison. Figure 4 shows the effect of different Si/Al ratio of ZSM-5 on hydrocarbon synthesis over CuCoMn-ZSM-5 (20%) bifunctional catalysts prepared by coprecipitation method. CO conversions were 53% and 76% corresponding to the ZSM-5 with Si/Al ratio of 25 and 100 respectively. The selectivity of liquid product was higher on ZSM-5 (Si/Al=100) than that on ZSM-5 (Si/Al=25), and thereby with significantly higher yield. On the other hand, CO₂ selectivity was obviously lower on ZSM-5 (Si/Al=100) than that on ZSM-5 (Si/Al=25) and C₁-C₄ hydrocarbons were slightly higher correspondingly. Moreover, the fraction distributions were similar to each other. Combined with the reaction performance on zeolite-free CuCoMn catalyst, it is concluded that the improvement by adding ZSM-5 (Si/Al=25) to CuCoMn is not adequate, which can be ascribed to the acidic nature owing to the Si/Al ratio (detailed discussions will be given below in NH₃-TPD analysis).

4. Effect of catalyst preparation method

Figure 5 shows the influence of different preparation methods of CuCoMn-ZSM-5 (20wt%, Si/Al=100) bifunctional catalysts on hydrocarbon synthesis. CO conversion, selectivity, and yield of liquid products were 49%, 30%, and 15% respectively by physically mixing method, all of which were lower than those by coprecipitation method. The selectivity of C₁-C₄ hydrocarbons followed similar trends. Oppositely, 42% of CO₂ selectivity corresponding to physically mixing method was much higher than that corresponding to coprecipitation method. The light fraction (C₅-C₁₂) was slightly lower and thereby with higher heavier fractions (C₁₃-C₁₆, and C₁₇+) by physically mixing method. The results show that coprecipitation method is more favorable to prepare CuCoMn-ZSM-5 bifunctional catalysts. Based on the results above, hybrid CuCoMn-ZSM-5 (20wt%, Si/Al=100) prepared by coprecipitation method is the optimal bifunctional catalyst having the ideal reaction performance for hydrocarbon synthesis from bio-syngas.
TABLE I Textural parameters of CuCoMn-zeolite catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$/(m$^2$/g)</th>
<th>$V$/(cm$^3$/g)</th>
<th>$d$/nm</th>
<th>$S_{\text{micro}}$/(m$^2$/g)</th>
<th>$V_{\text{micro}}$/(m$^3$/g)</th>
<th>$d_{\text{micro}}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCM</td>
<td>75</td>
<td>0.23</td>
<td>12.8</td>
<td>9</td>
<td>0.021</td>
<td>0.96</td>
</tr>
<tr>
<td>CCM-SAPO-34</td>
<td>94</td>
<td>0.31</td>
<td>9.5</td>
<td>17</td>
<td>0.029</td>
<td>0.60</td>
</tr>
<tr>
<td>CCM-ZSM-5*</td>
<td>117</td>
<td>0.25</td>
<td>8.4</td>
<td>39</td>
<td>0.041</td>
<td>0.50, 0.52c</td>
</tr>
<tr>
<td>CCM-Y</td>
<td>139</td>
<td>0.30</td>
<td>9.8</td>
<td>58</td>
<td>0.050</td>
<td>0.60</td>
</tr>
<tr>
<td>CCM-MCM-41</td>
<td>173</td>
<td>0.27</td>
<td>3.0, 7.4b</td>
<td>9</td>
<td>0.042</td>
<td>0.64</td>
</tr>
<tr>
<td>Pure ZSM-5</td>
<td>233</td>
<td>0.22</td>
<td>5.8</td>
<td>80</td>
<td>0.106</td>
<td>0.54, 0.56c</td>
</tr>
<tr>
<td>CCM+ZSM-5</td>
<td>107</td>
<td>0.23</td>
<td>23</td>
<td></td>
<td>0.038</td>
<td></td>
</tr>
</tbody>
</table>

* CCM-ZSM-5 was prepared by coprecipitation method with 20% ZSM-5 and Si/Al ratio of 100.

b There are two obvious peaks.

c The calculated value is the simple sum of 80% CuCoMn oxide and 20% ZSM-5 (Si/Al=100).

B. Characterization of catalysts

1. Textural and acid properties of CuCoMn-zeolite bifunctional catalysts

Textural properties were obtained from $N_2$ adsorption/desorption analysis. Table I lists the surface areas, pore volumes, and average pore diameters $d$ of CuCoMn oxide, pure ZSM-5, and bifunctional catalysts with different zeolites (SAPO-34, ZSM-5, Y, MCM-41). When zeolites were added into CuCoMn precursor, $S_{\text{BET}}$, $V$, $S_{\text{micro}}$ and $V_{\text{micro}}$ of obtained bifunctional catalysts all increased except for $S_{\text{micro}}$ of MCM-41 as MCM-41 is a mesoporous material with minute quantities of micropores. These results can be explained that zeolites are porous materials with large surface areas and volumes. With respect to the average diameters, pore sizes of bifunctional catalysts in the mesopore range were smaller than that of CuCoMn catalyst which is expected that added zeolites occupy part of channels. $d$ of 3.0 nm in CCM-MCM-41 catalyst was identified as the long-range ordered mesopores from MCM-41. On the other hand, $d_{\text{micro}}$ exhibited interesting tendencies. $d_{\text{micro}}$ of CCM-ZSM-5 and CCM-Y catalysts were smaller than those of ZSM-5 and Y zeolites, which are attributed to the occupation of metal oxides. However, $d_{\text{micro}}$ of 0.60 nm in CCM-SAPO-34 catalyst was larger than that of 0.43 nm in SAPO-34 zeolite. This can be inferred that the micropores are formed mainly from metal oxides and metal oxides may block access to the micropores of SAPO-34 zeolite. The similar result was presumed in CCM-MCM-41 catalyst because mesoporous MCM-41 possesses small amount of micropore. These results shown above suggest that pore dimensions of the bifunctional catalysts are determined by the interaction of metal oxides and zeolites. In addition, the calculated values of (CCM+ZSM-5) by simply summing 80% CuCoMn oxide and 20% ZSM-5 were lower than those of CCM-ZSM-5 bifunctional catalyst prepared by coprecipitation, implying that incremental improvements in textural properties are achieved during the preparation process.

The surface acid properties of zeolite-containing samples were investigated by $NH_3$-TPD. The density of total acid sites and their distribution derived from $NH_3$-TPD profiles are summarized in Table II. The acid density of bifunctional catalysts containing 20% different zeolites decreased in the order CCM-Y > CCM-SAPO-34 > CCM-ZSM-5 (Si/Al=100) > CCM-MCM-41, which did not follow the trends of liquid product yields (Fig.2(a), CCM-ZSM-5 > CCM-SAPO-34 > CCM-Y > CCM-MCM-41). The relatively low yield obtained from CCM-Y is particularly surprising, because CCM-Y had the highest density of acid sites. With respect to the strength

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of acid sites, CCM-SAPO-34 and CCM-ZSM-5 had similar distributions, in other words, they had around 55%–56% weak acid sites, 36%–40% medium acid sites and 5%–7% strong acid sites. CCM-MCM-41 had fewer total acid sites, and contained mainly weak acid sites with a small amount of medium and strong acid sites (less than 10%). By contrast, CCM-Y contained much more medium and strong acid sites than the others.

By linking the results of hydrocarbon synthesis over these bifunctional catalysts with their textural and surface acid properties, it can be concluded that excellent reaction performance CCM-ZSM-5 displays is correlated with the medium micropore and moderate acidity of ZSM-5. SAPO-34 with small pore apertures (0.43 nm) is suitable for production of light olefins such as ethene and propene [36]. Y zeolite with large micropore favors the formation of (poly)aromatic-type coke which hinders the reactants from accessing the active sites. In addition, excessive medium and strong acid sites may be another reason in favor of coke deposition and thereby lower activity [37, 38]. MCM-41 containing only a few weak acid sites leads to the acidic function of bifunctional catalyst unconspicuous. In contrast, the medium-pore ZSM-5 produces low amounts of (poly)aromatic-type coke as coke precursors are hindered inside the relatively narrow channels, thus retaining a larger number of acid sites for further reactions of the primary long-chain n-paraffins such as isomerization and cracking [37].

Therefore, ZSM-5 having moderate acidic properties and an MFI pore topology with an intersecting 10-membered ring pore system composed of straight (0.54 nm×0.56 nm) and sinusoidal (0.51 nm×0.54 nm) channels is suitable to constitute the CuCoMn-zeolite bifunctional catalyst for production of gasoline-range hydrocarbons directly from syngas [34, 36].

2. Acid properties of CuCoMn-ZSM-5 with different contents and Si/Al ratios of ZSM-5

The acid densities and distributions of CCM-ZSM-5 (Si/Al=100) with 20% and 50% ZSM-5 are listed in Table II. CCM-ZSM-5 (50%) with a higher content of ZSM-5 contained about 2.5 times the number of acid sites than CCM-ZSM-5 (20%), in agreement with the increment of ZSM-5. However, the distributions of acid strength followed different trends. The percentage of weak acid sites in CCM-ZSM-5 (50%) catalyst increased while those of medium and strong acid sites decreased. Moreover, the absolute amounts of weak and medium acid sites increased compared to CCM-ZSM-5 (20%) catalyst, thus resulting in a slightly higher number of lighter compounds (C5-C12). From the NH3-TPD analysis and the reaction performance discussed above, it is seen that increasing ZSM-5 content in the CCM-ZSM-5 leads to the increment of weak acid sites at the expense of catalytic activity due to the loss of metal active sites.

The acid properties of CCM-ZSM-5 (20%) with Si/Al=25 are also listed in Table II. CCM-ZSM-5 (Si/Al=25) with a lower framework Si/Al ratio contained more than twice the amount of acid sites than CCM-ZSM-5 (Si/Al=100). The weak acid sites increased from 55.50% to 92.73%. Surprisingly, strong acid sites disappeared. Compared with pure ZSM-5, the medium and strong acid sites in CCM-ZSM-5 (Si/Al=25) catalyst dramatically decreased. This result indicates that stronger acid sites preferentially interact with metal precursors, as also seen in CCM-ZSM-5 (50%, Si/Al=100) catalyst. Further inference can be made that the strong interaction of metal with acid sites of zeolite may weaken the interaction of metal with reactants. On the other hand, despite a higher density of acid sites in CCM-ZSM-5 (Si/Al=25), CO conversion and selectivity of liquid products were lower than those on CCM-ZSM-5 (Si/Al=100). This may result from the fact that weak acid sites are catalytically inactive for alcohols-to-hydrocarbon reactions as the case of CCM-MCM-41 [36].

3. Crystalline phases and reducibility on CCM-ZSM-5 prepared by different methods

The crystalline phases of samples were identified using XRD analysis. Figure 6(A) shows the XRD pat-
The effects of preparation method on the properties of catalysts. (A) XRD patterns of (a) ZSM-5, (b) CuCoMn oxide, (c) CCM-ZSM-5 prepared by physically mixing, and (d) CCM-ZSM-5 prepared by coprecipitation, HZSM-5 (JCPDS 80-0922), CuCoMnO$_4$ (JCPDS 47-0324). (B) H$_2$-TPR profiles of (a) CuCoMn oxide, (b) CCM-ZSM-5 prepared by physically mixing, and (c) CCM-ZSM-5 prepared by coprecipitation.

IV. CONCLUSION

A series of bifunctional catalysts comprising a higher alcohol-synthesis component (CuCoMn oxides) and an acidic zeolite (SAPO-34, ZSM-5, Y, MCM-41) were successfully applied to enhance both the selectivity and yield of liquid hydrocarbon produced directly from a bio-syngas. The liquid product yields decreased in the order CCM-ZSM-5 > CCM-SAPO-34 > CCM-Y > CCM-MCM-41. The enhancement of reaction performance by using bifunctional catalysts can be attributed to the displacement of thermodynamic equilibrium of higher alcohol synthesis and the textural improvements (e.g., the increments of surface area and volume). ZSM-5 zeolite was preferred to be used as the acidic function in CuCoMn-zeolite bifunctional catalysts owing to its highest CO conversion (76%) and carbon yield of liquid product (30%) among four selected zeolites. The excellent reaction performance CCM-ZSM-5 exhibits is correlated with the moderate acidic properties and medium micropore of ZSM-5 with a particular topology. In addition, increasing ZSM-5 content in the CCM-ZSM-5 led to the increment of weak and medium acid sites at the expense of catalytic activity due to the loss of metal active sites. Decreasing Si/Al ratio in ZSM-5 induced the increase of weak acid sites and decrease of medium and strong acid sites. Accordingly, the CCM-ZSM-5 (Si/Al=25) with a lower Si/Al ratio showed lower CO conversion and product selectivity. Moreover, the CCM-ZSM-5 catalyst prepared by coprecipitation displayed higher metal dispersion and easier reducibility of metal ions. In the present study, the optimal bifunctional catalyst of CuCoMn-ZSM-5 (20wt%, Si/Al=100) prepared by coprecipitation method was obtained for transformation of bio-syngas into liquid hydrocarbon.

V. ACKNOWLEDGMENTS

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