Mesoporous Carbon-supported Iron Catalyst for Fischer-Tropsch Synthesis

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Mesoporous carbon materials have been employed as supports of iron-carbon complex catalysts for slurry phase Fischer-Tropsch (FT) synthesis. The mesoporous carbon-supported iron catalysts were prepared through the co-precipitation from aqueous solutions of ferrous and copper sulfates in the presence of mesoporous carbon materials synthesized through the soft-template and hard-template methods. The iron catalyst supported by the soft-templated mesoporous carbon exhibited a sharp product distribution at C5-C9 fractions (62 % in hydrocarbons) in FT synthesis at 260 °C under 2 MPa-G. On the other hand, the catalyst supported by the hard-templated mesoporous carbon having far larger mesopore openings showed a high selectivity to higher hydrocarbons (69 % of C10 + in hydrocarbons) with a high hydrocarbon productivity (0.74 g/g-Fe h). This catalyst also showed high catalytic activity and long lifetime up to 30 h even at lower reaction pressure of 1 MPa-G. The very large inner space of mesopores that are not easily blocked through the wax formation would be responsible for such high catalytic activity.

Keywords
Mesoporous carbon, Iron catalyst, Fischer-Tropsch synthesis, Soft-template method, Hard-template method

1. Introduction

The Fischer-Tropsch (FT) synthesis is a catalytic process developed in 1920’s to produce synthetic hydrocarbons, mainly liquid hydrocarbons, from syngas (the mixture of CO and H₂)1,2). FT products have broad distributions and can be utilized as gasolines or diesel oils after the secondary reforming. Because FT process can utilize syngas produced by the gasification of biomass, it would be one of the most promising approaches to utilize hard biomass as a feedstock. However, the source of biomass tends to vary; therefore, the compositions of syngas and the amount of impurities also change, which strongly demands a FT catalyst resistant to the change of such reaction conditions. Iron catalysts are able to satisfy this demand due to their high resistivity to severe reaction conditions.

Iron-based catalysts have been developed and frequently employed in FT synthesis until 1980’s; however, because of their low activity, short life due to pulverization of the catalyst, and low product quality, presently cobalt catalysts are used instead. Recently, we have succeeded in improving the activity of iron catalysts by employing carbon materials as supports3-5). Although wax products deposited on the surface of carbon supports deactivated the activity in the long run, we have also demonstrated that the catalytic activities can be improved by treating microporous active carbon supports with ozone owing to the formation of small amount of mesopores5,6).

In this study, mesoporous carbon materials have been synthesized through the soft-template and hard-template methods and employed as supports of iron-carbon complex catalysts for slurry phase FT synthesis. Mesoporous carbon materials would offer higher potential as catalyst supports due to their wider pore openings and larger pore volumes7,8).

2. Experimental

2.1. Preparation of Mesoporous Carbons

Mesoporous carbon materials were synthesized through the soft-template and hard-template methods. These two different synthesis methods are schematically summarized in Fig. 1. The soft-template method using a costly nonionic surfactant PEO-PPO-PEO triblock copolymer as an organic template was performed according to the procedure reported by Liang and Dai9). This carbon material is denoted as Cm1. On the other
hand, the hard-templated mesoporous carbon material was synthesized by the procedure similar to that reported by Ryoo et al.\textsuperscript{10,11} In contrast to the original recipe that employs ordered mesoporous silica MCM-48\textsuperscript{12} or SBA-15\textsuperscript{13} as a hard template, we used less expensive silica gel Q-10 (Fuji Silysia Chemical Ltd.) having three-dimensional pore system with the diameter of 10 nm, surface area of 300 m\textsuperscript{2}/g and pore volume of 1.0 mL/g. For the preparation, Q-10 was impregnated with sucrose and sulfuric acid in aqueous solution. The impregnated material was dried at 373-423 K, then, the dried material was heated at 1173 K in an inert atmosphere. Finally, the silica template was removed by the treatment with sodium hydroxide aqueous solution. The resultant carbon material is denoted as $C_{m2}$. For comparison, microporous active carbon (Kanto Chemical Co., Inc.), denoted as $C_a$, was also employed as a catalyst support.

2.2. Preparation of Mesoporous Carbon-supported Iron Catalysts

The mesoporous carbon-supported iron catalyst was prepared through co-precipitation from aqueous solutions of ferrous and copper sulfates (Fe : Cu = 100 : 1 in weight ratio) in the presence of a mesoporous carbon material as a support (Fe : C = 1 : 1 in weight ratio) under pH 8.0-8.2 at 70 °C using sodium carbonate. Copper was added to promote the reduction of iron species\textsuperscript{14}. As-prepared sample was dried at 110 °C for 12 h and calcined at 400 °C for 3 h under nitrogen atmosphere. Then potassium carbonate as a promoter was impregnated on the iron catalyst at Fe : K = 100 : 5 in weight ratio. Obtained catalysts are denoted as Fe-Cu-K/C_{m1} (soft-templated mesoporous carbon), Fe-Cu-K/C_{m2} (hard-templated mesoporous carbon), and Fe-Cu-K/C_{a} (microporous active carbon). For comparison, non-supported iron catalyst was prepared in the same way but in the absence of carbon supports and denoted as Fe-Cu-K.

2.3. Characterization

Nitrogen adsorption measurements at 77 K were taken with a MicrotcracBEL Corp. BELSORP-mini instrument. Samples were degassed at 200 °C for 2 h before the measurement. Micropore volumes ($V_{\text{micro}}$) were calculated from their $t$-plots. Mesopore volumes ($V_{\text{meso}}$) and mesopore radii ($R_p$) of the parent supports and the supported iron catalysts were calculated by the Barrett-Joyner-Halenda (BJH) method\textsuperscript{14}. Powder X-ray diffraction (XRD) patterns were taken on a PANalytical X’Pert Alpha-1 instrument equipped with a Cu K\textalpha X-ray source.

2.4. Catalytic Activity Tests

For the FT synthesis, 3 g of a catalyst was dispersed in 50 mL of n-hexadecane as a solvent in a slurry-bed reactor. The catalyst was treated with a reaction gas (CO : H\textsubscript{2} = 1 : 1 in molar ratio) initially at 300 °C under 0.5 MPa-G for 4 h. Successively, the reaction gas was allowed to react at 260 °C under 2 MPa-G ($W/F = 8.15$). The obtained products were quantitatively analyzed by a gas-chromatograph equipped with thermal conductivity detector (TCD) and hydrogen-flame ionization detector (FID).

3. Results and Discussion

3.1. Nitrogen Adsorption Analysis

The nitrogen adsorption isotherms and their BJH plots of the supports $C_a$, $C_{m1}$, $C_{m2}$ and the supported catalysts Fe-Cu-K/C_{a}, Fe-Cu-K/C_{m1}, Fe-Cu-K/C_{m2} were shown in Fig. 2. The isotherm in Fig. 2(a) shows the IUPAC type I profile typical for microporous materials, while the isotherms in Figs. 2(b), 2(c) show the IUPAC type IV profiles. A large hysteresis loop observed in Fig. 2(c) for $C_{m2}$ templated by amorphous silica gel would suggest non-uniform and irregular sizes in each pore. This almost closed but open hysteresis loop indicates the presence of very small “bottle-neck” in
some pores of Cm2. The BET surface area of Cm2 was estimated at 1380 m²/g, which is much larger than that of Cm1 (388 m²/g).

The BJH plots from the adsorption branch in Figs. 2(e), 2(f), which would reflect the longest diameter of the pores, show the presence of mesopores in these two carbon materials and the supported catalysts. As clearly observed in Fig. 2(f), Cm2 had very wide bimodal pore distribution with the peak tops at pore radii of 4.6 nm and 16.3 nm in almost the full range of mesopore region (2-50 nm). The mesopore volume of Cm2 (2.41 mL/g) was also much larger than that of Cm1 (0.38 mL/g). Upon metal incorporation, the mesopore volumes of both Cm1 and Cm2 decreased by more than half amounts of the parent mesoporous carbons due to the deposition of metal species inside the mesopores. Although active carbon C2 had a pore volume in the mesopore region, the pore volume was very small compared to those of mesoporous carbon materials, so the contribution from mesopores should be minor. The results of nitrogen adsorption measurements are summarized in Table 1.

### 3.2 X-ray Diffraction Analysis of Fresh and Used Catalysts

XRD patterns of fresh and used catalysts are shown in Fig. 3. In Fig. 3(a), magnetite (Fe₃O₄) was mainly observed in all catalysts, while small peaks of hematite (Fe₂O₃) were present in Fe-Cu/K/Cm1 and Fe-Cu/K/Cm2. Fe⁺² species well dispersed on the large surface of mesoporous carbon supports would be more easily oxidized to Fe⁺³ species upon calcination at 400 °C to give a small amount of hematite. For the used catalysts in Fig. 3(b), iron carbide as the active species for the FT synthesis appeared. This active species would accept electrons from carbon supports to catalyze the dissociation of adsorbed carbon monoxide and the growth of methylene (CH₂) species. The peaks assignable to wax products, which usually cause catalyst deactivation by blocking the porous structure, were observed in used Fe-Cu/K/Ca, Fe-Cu/K/Cm1 and Fe-Cu/K/Cm2 catalysts (Fig. 3(b)).

### 3.3 Catalytic Application

The catalytic performances of iron catalysts are summarized in Table 2. As reported in the precedent work, the productivity of the potassium-promoted catalyst (Fe-Cu-K) was higher than that of unpromoted catalyst (Fe-Cu) due to the electron donation from potassium to the active species, so the potassium-promoted catalysts were employed in the following reaction experiments. The carbon-supported iron catalysts Fe-Cu-K/Ca, Fe-Cu-K/Cm1, and Fe-Cu-K/Cm2 were regarded as more active than non-supported catalyst Fe-Cu-K, considering that the actual iron weight in these supported catalysts was just the half of the total catalyst weight.

### Table 1: Surface Properties Determined by N₂ Adsorption for the Various Carbons and Carbon-supported Iron Catalysts

| Sample       | S_BET [m²/g] | V_microp | V_meso+p | V_meso⁻ | R_meso⁻ [nm] |
|--------------|--------------|----------|----------|---------|--------------|
| Ca           | 1170         | 0.30     | 0.19     | 0.9     |              |
| Cm1          | 388          | 0.05     | 0.38     | 3.8     |              |
| Cm2          | 1380         | 0        | 2.41     | 4.6/16.3|              |
| Fe-Cu-K/Ca   | 433          | 0.23     | 0        | -       |              |
| Fe-Cu-K/Cm1  | 168          | 0        | 0.15     | 3.6     |              |
| Fe-Cu-K/Cm2  | 448          | 0        | 0.77     | 4.1/16.3|              |

a) BET surface area.
b) Micropore volume based on t-plot.
c) Mesopore volume and mesopore radius based on BJH plot.
Although the mesoporous carbon $C_{m1}$ synthesized by the soft-template method has relatively small BET surface area compared to microporous active carbon $C_a$, the productivity of $Fe_{-}Cu/C_{m1}$ (0.66 g/g-Fe h) is higher than that of $Fe_{-}Cu/C_a$ (0.50 g/g-Fe h), suggesting that the presence of large mesopore is effective to promote the activity. Hydrocarbon products formed in the narrow space of micropore would grow the carbon chain to form wax products resulting in the pore blockage. In contrast, products formed on the surface of iron carbide supported on the wide opened mesopores would be released easily; thus, wax formation could be suppressed. The larger openings of mesopores seem also beneficial to improve the selectivity to gasoline fraction; the proportion of C5-C9 to total hydrocarbons of $Fe_{-}Cu_K/C_{m1}$ (62 %) is much higher than that of $Fe_{-}Cu_K/C_a$ (50 %).

(Fig. 4, Table 2).

Furthermore, $Fe_{-}Cu_K/C_{m2}$ showed remarkably high productivity (0.74 g/g-Fe h) compared to $Fe_{-}Cu_K/C_{m1}$, probably owing to its larger mesopore size and to the good metal dispersion on the far larger inner surface area of the hard-templated mesoporous carbon support (1380 m²/g). A smaller amount of wax products remaining on the catalyst was tentatively implied by the XRD pattern of used catalyst after 6 h of reaction (Fig. 3(b)). It seems that the large mesopore size and large mesopore volume (2.41 mL/g) also benefited the selectivities to larger hydrocarbon products, 84 % of C5 + and notably 69 % of C10 + in hydrocarbons (Fig. 4, Table 2). In addition, electron-rich Fe⁰ species derived from electron donation from potassium through the electron-conductive carbon support would promote the dissociation and the hydrogenation of CO under reductive conditions, resulting in the larger hydrocarbon products. This $Fe_{-}Cu_K/C_{m2}$ catalyst showed a high catalytic activity and a longer lifetime up to 30 h even at a lower reaction pressure of 1 MPa-G (Fig. 5), which is industrially more favorable condition, also implying the little pore blockage by the wax products.

4. Conclusions

Mesoporous carbon-supported iron catalysts have been developed for the FT synthesis, and the iron catalyst supported on the hard-templated mesoporous carbon

| Table 2  | Catalytic Activity Results of the Non-supported and Supported Iron Catalysts |
|----------|---------------------------------------------------------------------------------|
| Catalyst | CO conversion [%] | Selectivity [%] | C5-C9 in HC [ %] | C10 + in HC [ %] | Productivity [g/g-Fe h] |
| Fe-Cu    | 62 | 42 | 58 | 50 | 14 | 0.30 |
| Fe-Cu-K  | 83 | 46 | 54 | 19 | 59 | 0.37 |
| Fe-Cu-K/Ca | 75 | 44 | 56 | 50 | 26 | 0.69 |
| Fe-Cu-K/Cm1 | 74 | 44 | 56 | 62 | 19 | 0.69 |
| Fe-Cu-K/Cm2 | 80 | 45 | 55 | 15 | 69 | 0.74 |

a) The weight of hourly produced hydrocarbons divided by the weight of iron in the catalyst.
material (Fe-Cu/K/Cm2) particularly showed a high productivity (0.74 g/g-Fe h) and a high selectivity to higher hydrocarbons (84 % of C5_up to C10_up to) with avoiding the pore blockage by wax products, compared to unsupported and active carbon-supported catalysts. This catalyst exhibited a long catalyst lifetime up to 30 h.

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Fig. 5 The Catalytic Result over Fe-Cu-K/Cm2 at 290 °C, 1 MPa-G up to 30 h.

要 旨
メソポラスカーボンを担体にしたフィッシャー・トロプシュ合成用鉄触媒

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メソポラスカーボンを担体にした鉄系触媒を調製し、ラリー床フィッシャー・トロプシュ合成反応に用いた。ソフトプレート法を用いて合成したメソポラスカーボンに担持した触媒は、260 °C, 2 MPa-G の反応条件下において、炭化水素中のC5～C9選択率が62 % と非常に高い値を示した。一方、ハードプレート法を用いて合成したメソポラスカーボンは、非常に大きな細孔径を持ち、これを担体にした触媒を用いた場合、炭化水素中のC10選択率が69 %、炭化水素生成速度が0.74 g/g-Fe h という高い値を得ることができた。この触媒は1 MPa-G の低圧反応条件下においても同様の高い活性を示し、その活性を30時間以上維持することができた。この担体が持つメソ細孔が大きいため、ワックス生成物の細孔内滞留および活性点被覆による活性劣化が抑制されるためだと考えられる。