Hydrocracking of Fischer–Tropsch Wax to Diesel-range Hydrocarbons over Bifunctional Catalysts Containing Pt and Polyoxocation-pillared Montmorillonite

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(Received September 27, 2007; CL-071066; E-mail: yy.ryuu@aist.go.jp)

Bifunctional catalysts containing Pt and polyoxocation-pillared montmorillonite showed high yields of diesel-range hydrocarbons (>70%) in the hydrocracking of Fischer–Tropsch wax due to their weak acid strength, high thermal stability, large surface area, and large pore size.

Fischer–Tropsch (F-T) synthesis produces sulphur-free *n*-alkanes (>90%) from syngas, while the latter is easy to be obtained from biomass, coal, and natural gas. As consequence of the chain growth mechanism, a large fraction of F-T product has a boiling point higher than 643 K (C_{21+}, i.e. F-T wax).[1] The hydrocracking of F-T wax is a necessary stage to improve the yield of liquid fuel from the F-T synthesis procedure. The hydrocracking of F-T wax to diesel-range hydrocarbons (C_{11}–C_{20}) is very attractive because the normal alkanes produced from the F-T synthesis are very suitable to be used as high quality diesel fuel. $Pt/WO_3/ZrO_2$ and Pt/Al_2O_3–SiO_2 have been reported as the effective catalysts for the hydrocracking of F-T waxes to diesel-range hydrocarbons.[2,3]

Montmorillonite (denoted by Mont) is a kind of acidic clay which possesses an ability of cation exchange. Introduction of large cations into the interlayer region of Mont can greatly extend the surface area and the interlayer distances. Polyoxocation-pillared Mont is a kind of unique solid acid catalyst with large pores and high surface area.[4,5]

In the present study, we report on the high performance of the catalysts containing Pt and polyoxocation-pillared Mont for the hydrocracking of F-T wax to diesel-range hydrocarbons.

Na–mont was supplied by Kunimine Industrial Co. $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ pillared Monts (Al_{13}–Mont and Zr_4–Mont) were prepared by an ion-exchange of Na–Mont and the correspondent polyoxocation solution at 333 K.[6] The chemical compositions and physical properties of the samples are summarized in Table S1.[7] WO_3/ZrO_2 (12.5 wt % W) and Al_2O_3–SiO_2 (Si/Al = 100) were prepared using the methods in literature.[2,3]

Bifunctional catalysts Pt/Al_{13}–Mont, Pt/Zr_4–Mont, Pt/Al_2O_3–SiO_2, and $Pt/WO_3/ZrO_2$ (with 0.5 wt % Pt in each sample) were prepared by an impregnation of correspondent solid acid in $Pt(NH_3)_4Cl_2$ solution. Then, the samples were dried at 383 K overnight and calcined at 673 K for 2 h.

n-$C_{36}H_{74}$ (Aldrich) was used as a model wax. The F-T wax used in this study is a distilled residue (average molecular formula: $C_{37}H_{76}$) of an F-T product ($\alpha = 0.82$) over Co/SiO_2.

The catalysts were reduced in a flowing H_2 at 623 K for 2 h before reaction. The reaction was carried out using a 50-mL stainless steel autoclave reactor. In a typical run, 0.2 g of catalyst and 5-g wax was added to the autoclave. Then, 5 MPa H_2 was charged to the autoclave at 298 K. After reacting with vigorous stirring at 623 K for 1 h, both the gas and the liquid were sampled and analyzed. C_1–C_4 hydrocarbons were analyzed by a Shimadzu 8A GC equipped with a Porapak Q column, and C_{5+} hydrocarbons were analyzed by an Agilent Tech. 6890N GC equipped with a UA-DX30 capillary column.

The XRD patterns of various Mont compounds are shown in Figure 1. For a layered compound, the basal d_{001} spacing at the lowest angle in the XRD pattern includes the thickness of the host layer and the gallery height. Na–Mont showed a d_{001} diffraction peak at 12.4 Å. After subtracting the thickness of the host layer (9.3 Å) from the d_{001} spacing (12.4 Å), Na–Mont gives a gallery height of 3.1 Å. Al_{13}–Mont and Zr_4–Mont showed their d_{001} spacing at 19.2 and 19.0 Å, implying that their gallery heights are 9.9 and 9.7 Å, respectively. These gallery heights coincide with the sizes of polyoxocations $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$. After calcination at 673 K for 2 h, the d_{001} diffraction peak of Na–Mont shifted to higher degree and became weak greatly. This indicates that the layered structure of Na–Mont was severely collapsed after calcination. On the other hand, the values of d_{001} spacing in Al_{13}–Mont and Zr_4–Mont did not obviously change after calcination, indicating that Al_{13}–Mont and Zr_4–Mont remained their layered structures after calcination at 673 K owing to the robust polyoxocation pillars.

From N_2 absorption–desorption isotherms, the pore size of Al_{13}–Mont and Zr_4–Mont distributed in a range from about 10 Å to over 20 Å because their micropores are defined not only by the interlayer distance (between two clay layers) but also by the lateral distance (between two metal oxide pillars). After

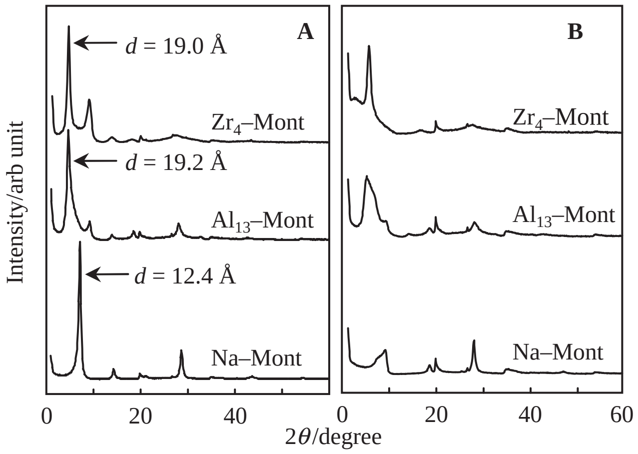

Figure 1. XRD patterns of various samples. A: before calcination; B: after calcination at 673 K for 2 h.

Table 1. Hydrocracking of n-$C_{36}H_{74}$ at 623 K for 1 h[a]

Catalysts	Conv./%[b]	Selectivity/%				
		C_1–C_4	C_5–C_{10}	C_{11}–C_{18}	C_{19}–C_{35}	C_{36+}
Pt/Na–Mont	21.2	3.8	22.3	59.5	11.9	1.9
Pt/Al_{13}–Mont	71.9	0.9	13.5	74.2	10.2	0.8
Pt/Zr_4–Mont	73.3	1.5	16.3	70.6	9.3	1.3
Pt/WO_3/ZrO_2	88.4	9.8	31.5	48.7	8.2	0.6
Pt/Al_2O_3–SiO_2	78.7	6.9	22.4	60.3	9.1	0.8
Pt/SiO_2	0.5	0	69.8	30.2	0	0

[a]Catalyst: 0.2 g; n-$C_{36}H_{74}$: 5 g; $P_{H2} = 5$ MPa (at 298 K). [b]Not include the isomerization of n-$C_{36}H_{74}$ to iso-$C_{36}H_{74}$.

calcination Al_{13}–Mont and Zr_4–Mont possess much higher BET surface areas ($>200\,m^2\,g^{-1}$) than Na–Mont ($<40\,m^2\,g^{-1}$) because of partial collapse of the layered structure of the last compound. From NH_3–TPD, the acid strength of the samples used in this study is in the order of $WO_3/ZrO_2 > Al_2O_3$–$SiO_2 > Zr_4$–Mont $\approx Al_{13}$–Mont $> SiO_2$ (no acidity), coinciding with the results reported in literature.[8]

The results of the hydrocracking of n-$C_{36}H_{74}$ (model wax) over various catalysts are shown in Table 1. Solid acid is indispensable to the hydrocracking of n-$C_{36}H_{74}$ because Pt/SiO_2 (no acidity) showed a very low activity. Pt/Na–Mont showed a much lower conversion (21.2%) than those of Pt/Al_{13}–Mont (71.9%) and Pt/Zr_4–Mont (73.3%) for the hydrocracking of n-$C_{36}H_{74}$. This indicates that the physical properties of the solid acid (such as surface area, micropore size, thermal stability, and so on) greatly influence the catalytic ability of a bifunctional catalyst for the hydrocracking of n-$C_{36}H_{74}$.

As shown in Table 1, although Pt/WO_3/ZrO_2 showed the highest conversion (88.4%) in this study, it formed a large fraction of light hydrocarbons (9.8% of C_1–C_4 and 31.5% of C_5–C_{10}). On the other hand, Pt/Al_{13}–Mont formed a large fraction of heavy hydrocarbons (74.2% of C_{11}–C_{18} and 10.2% of C_{19}–C_{35}) at a conversion of 71.9%. The hydrocracking of alkane undergoes via a bifunctional mechanism, in which Pt site achieves the function of dehydrogenation and hydrogenation, and acid site achieves the function of forming carbenium intermediate.[4,9] The balance of Pt site and acid site is crucial for the catalytic activity and the product distribution of a bifunctional catalyst. From the data in Table 1, the catalyst containing a strong solid acid possesses high activity but the catalyst containing a weak solid acid possesses high selectivity for heavy hydrocarbons in the hydrocracking of n-$C_{36}H_{74}$.

The carbenium intermediate formed on the acid site undergoes β-scission to achieve cracking. However, carbenium intermediate also undergoes polymerization and isomerization at the same time.[4,9] As shown in Table 1, C_{36+} hydrocarbons formed in the hydrocracking of n-$C_{36}H_{74}$ over each catalyst, which implies that the alkylation of the olefins, formed by β-scission of $C_{36}H_{73}{}^+$ cation, with another $C_{36}H_{73}{}^+$ cation takes place. Isomerization is a competitive reaction for cracking due to the common carbenium intermediate. All n-alkanes in the catalytic system (including reactants and products) undergo isomerization in parallel with cracking. The products over Pt/WO_3/ZrO_2 showed a higher ratio of iso-alkane/n-alkane (0.61 at a conversion of 88.4%) than that over Pt/Al_{13}–Mont (0.22 at a conversion of 71.9%) due to the strong acidity of WO_3/ZrO_2. Therefore, Pt/Al_{13}–Mont is more suitable to be used for producing high quality diesel fuel from the hydrocracking of n-$C_{36}H_{74}$ because its product contains a large fraction of heavy hydrocarbons (C_{11+}) with a low ratio of iso-alkane/n-alkane.

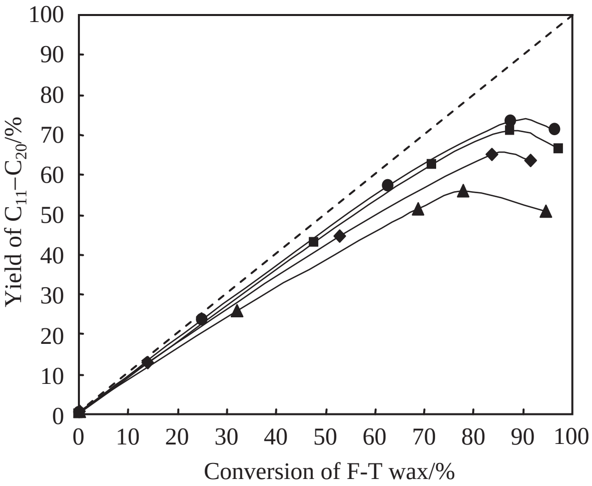

Figure 2. Plots of C_{11}–C_{20} yield vs. F-T wax conversion in an autoclave reactor at 623 K. ●: Pt/Al_{13}–Mont; ■: Pt/Zr_4–Mont; ◆: Pt/Al_2O_3–SiO_2; ▲: Pt/WO_3/ZrO_2. $P_{H2} = 5$ MPa (at 298 K).

The plots of the yield of diesel-range hydrocarbons (C_{11}–C_{20}) versus the conversion of F-T wax (for the hydrocracking of F-T wax over various catalysts at 623 K) are shown in Figure 2. Various yields and conversions were obtained by changing the reaction time and catalyst amount. With the increase of the conversion of F-T wax, the selectivity to diesel-range hydrocarbons decreases due to the further hydrocracking of the products. Thus, the yield of diesel-range hydrocarbons exhibits a maximum value for each catalyst. As shown in Figure 2, the maximum yield of each catalyst is in the order of Pt/Al_{13}–Mont > Pt/Zr_4–Mont > Pt/Al_2O_3–SiO_2 > Pt/WO_3/ZrO_2. This order implies that a bifunctional catalyst containing a weak solid acid could obtain a high maximum yield of diesel-range hydrocarbons in the hydrocracking of F-T wax. The further hydrocracking of the products has been suppressed in some degree on the weak acid sites, which improves the yield of diesel-range hydrocarbons. Both Pt/Al_{13}–Mont and Pt/Zr_4–Mont afforded high yields of diesel-range hydrocarbons over 70% in the hydrocracking of F-T wax.

In conclusion, polyoxocation pillared montmorillonite materials possess large BET surface area, large micropore size, high thermal stability, and weak solid surface acidity. These natures render the materials very effective for the hydrocracking of F-T wax to high quality diesel fuel.

References and Notes

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Published on the web (Advance View) November 10, 2007; doi:10.1246/cl.2007.1470