FISCHER-TROPSCH SYNTHESIS OVER COBALT CATALYSTS SUPPORTED ON MESOPOROUS MATERIALS

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Introduction

Since the discovery of a series of mesoporous silicates (M41S), the materials have been used as the catalysts and support for many catalytic reactions, because of the uniform structure and the tunable mesopore diameters.[1-3] It is expected that the wide pores are advantageous to mass transfer of the products and to the chain growth in Fischer-Tropsch (F-T) synthesis. Several papers have been concerned with mesoporous materials as the support for F-T synthesis catalysts up to the present.[4-5] However, most of them are supported on mesoporous silica, and the effect of metals incorporated into the silica framework has not been reported. In the present paper, mesoporous alumino-silicate (MPAS) was prepared by the rapid-room temperature preparation method,[6] and Co-Ir catalysts supported on MPAS were used for F-T synthesis in slurry phase.

Experimental

Hexadecylpyridinium chloride (C_{16}-PyCl) was used as cationic surfactant in the preparation of mesoporous alumino-sililcate (MPAS). C_{16}-PyCl (3.0 mmol) was dissolved in 50 cm^3 of water. With vigorous stirring and optional heating, HCl was added to the surfactant solution in order to adjust the pH. The clear solutions of $Na_2O{\cdot}2SiO_2{\cdot}nH_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and NaOH were added dropwise to the surfactant solution, in the molar ratio of (Si+Al)/C_{16}-PyCl/NaOH/HCl/H_2O = 1/0.12/1.06-1.27/0.61/141, at room temperature with vigorous stirring. After further stirring for 3 h, the precipitated product was filtered, washed thoroughly with water, dried in an oven at 373 K for 6 h, and calcined in air at 873 K for 6 h to remove the template. Mesoporous silica (MPS) was similarly prepared without adding $Al(NO_3)_3$. The MPS and MPAS thus prepared were impregnated with aqueous solutions of $Co(NO_3)_2{\cdot}6H_2O$ and $IrCl_4{\cdot}H_2O$, dried and calcined at 573 K for 1 h, and then reduced in H_2 flow at 673 K for 15 h to form 20wt%Co-0.5wt%Ir/MPS and 20wt%Co-0.5wt%Ir/MPAS catalysts, respectively.

The catalyst powder (2 g) was slurried with 50 cm^3 of *n*-hexadecane under an inert atmosphere. The F-T reaction was carried out with the catalyst slurry in an autoclave-type semi-batch reactor (flow type for gas phase). The feed gas (H_2:CO:Ar = 60:30:10) was bubbled into the slurry, and the dissolution of the gas was promoted by a specially designed stirring rod.[7] The reaction conditions were as follows: T = 503 K, P = 1 MPa, W/F = 10 g-catal.h/mol. The effluent gas was periodically analyzed by on-line gas chromatography, and the contents of inorganic gases and C_{1-14} hydrocarbons were determined, with using Ar in the sample gas as the internal standard. The contents of C_{11+} hydrocarbons in the slurry were determined separately by gas chromatography after the reaction.

Results and Discussion

The XRD patterns of MPS and MP AS samples showed three peaks in the region 2θ = 2-6°, corresponding to the (100), (110), and (200) reflections of a typical hexagonal lattice, indicating that they were structurally analogous to MCM-4l. The N_2 adsorption measurements at 77 K, and the TEM images of MPS and MP AS confirmed the honeycomb structures with one-dimensional channels of ca, 3 *nmq}* in diameter. The pore size distribution of the catalysts demonstrated that the uniform mesopore structure was retained after metal loading, as illustrated in Fig. 1. The MAS-^{27}Al-NMR result indicated that most of Al of MPAS was incorporated into the silica framework, as shown in Fig. 2.

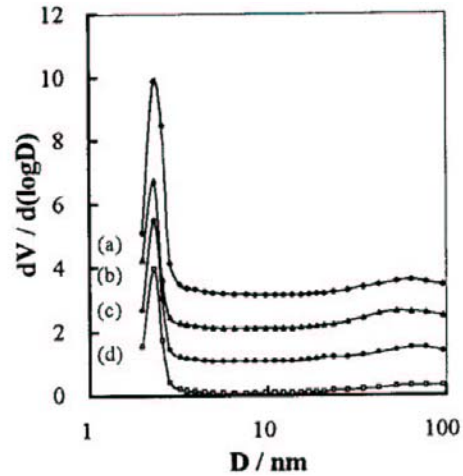

Figure 1. Pore size distribution of (a) MPAS (Si/AI = 29), (b) *5wt%CofMPAS,* (c) 10wt%CofMPAS, and (d) *15wt%CofMPAS.*

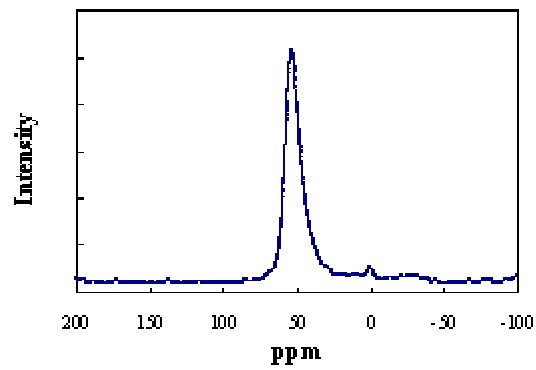

Figure 2. MAS-^{27}Al-NMR spectrum of MPAS (Si/Al = 19).

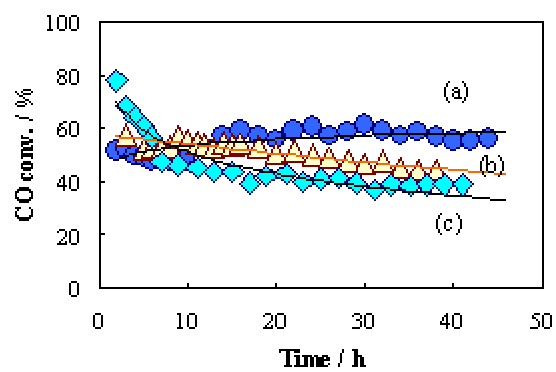

Figure 3. Time course of F-T reaction over (a) 20wt%Co-0.5wt%Ir/MPAS (Si/Al=19), (b) 20wt%Co-0.5wt%Ir/MPS, and (c) 20wt%Co-0.5wt%Ir-1.3wt%Al/MPS catalysts.

Figure 3 shows time course of F-T reaction over Co catalysts supported on MPAS (a), MPS (b), and MPS impregnated with Al (c).

The catalyst supported on MPAS (Si/Al = 19) was more stable than the catalyst supported on MPS, which was gradually deactivated during the reaction. The catalyst supported on MPS with Al-impregnation (Si/Al = 29) was also deactivated. The main difference between catalyst (a) and catalyst (c) is that Al of the former is incorporated into the silica framework, forming a tetrahedral coordination with O, while Al of the latter is in the form of Al_2O_3. Therefore, the framework Al is important for the stable activity of the catalyst.

Table 1. Effect of Catalyst Support on Fischer-Tropsch Reaction in Slurry Phase [a)]

Catalyst support	CO conv. / %	Selectivity / C-%			α [b)]
		CH_4	C_{2-4}	C_{10-20}	
MPAS [c)]	56.6	7.9	9.1	31.4	0.90
MPS	50.8	14.2	25.2	13.0	0.76
Al/MPS [d)]	42.0	13.0	18.9	20.5	0.77

a) Reaction results at the steady state (average values). b) Chain growth probability. c) Si/Al = 19. d) MPS impregnated with Al (Si/Al = 29).

Table 1 summarizes the F-T reaction results over the catalysts. The values listed are the average during 40 h of the reaction, since some of the catalysts were deactivated. Higher selectivity for C_{10-20} hydrocarbons (diesel fuel fraction) and higher α-value (chain propagation probability of the CH_x intermediates of F-T reaction) were obtained over the catalyst supported on MPAS than the catalysts supported on MPS and Al-added MPS, with suppressing CH_4 formation below 8%.

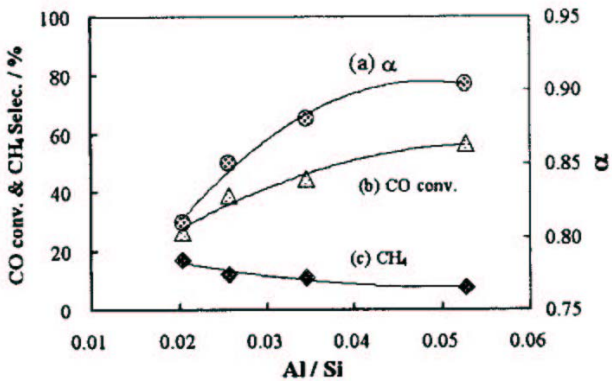

Figure 4. Effect of Al/Si ofMPAS on F-T reaction over 20wt%CoI wt%Ir/MP AS catalysts.

The effect of Al/Si ofMPAS on the reaction is depicted in Fig. 4. The a-value and CO conversion increased and C~ selectivity decreased with Al/Si ofMPAS. It is generally accepted that Al incorporated into silica framework gives rise to an acid site. If AI ofMPAS played an role of acidity in the F-T reaction, cracking of the products might take place, resulting in an increase of light hydrocarbon selectivity, as well as C~ formation, and a decrease in the a-value. However, the reaction results were contradictory to the case. And no Broensted acidity was detected by FT-IR measurement.

Since MPAS was prepared under basic conditions (pH = 10), it is possible that trace amount of Na may remain on the catalyst surface after washing, affecting the F-T reaction. However, neither catalytic activity nor selectivity were improved by adding trace amount ofNa to the 20wt%Co-O.5wt%Ir/MPAS catalysts. Therefore, the improved catalytic properties are not ascribed to the impurity which might remain on the surface. The reason for such high catalytic properties has not been elucidated yet, and is now under investigation.

It was previously reported that the pore size of the catalysts affected F-T reaction, and that wide pores were preferable to higher hydrocarbon production.8) In addition, the cost of MPAS is generally higher than the commercial silica. Thus, the surface of commercial wide pore silica (Fuji Silysia; Q-50, average pore diameter = 49 nm) was coated with MPAS, and utilized as the catalyst support, in order to reduce the cost of support and to improve the selectivity for higher hydrocarbons. The mixed support was prepared by adding Q-50 silica powder to the surfactant solution in the preparation step ofMPAS (SilAI = 19).

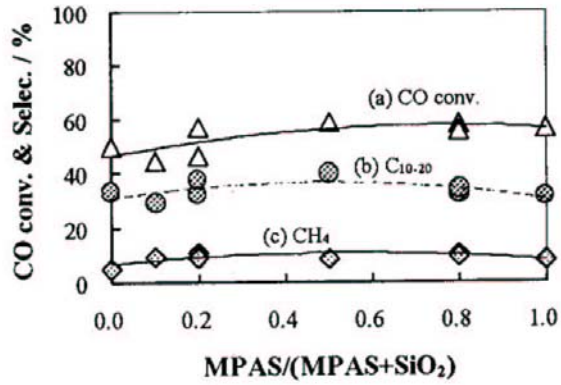

Figure 5. Effect of MPAS content in the support on F-T reaction.

When the mixed support MPAS-Si02 was used, a synergistic effect was observed, as illustrated in Fig. 5. The relatively low conversion over the catalyst supported on Q-50 silica was ascribed to the low surface area, although the a-value was high. Over the catalyst supported on MPAS alone, the pore size was so small that the chain growth of the reaction intermediates was limited in the catalyst pores, resulting in low CI0-20 selectivity. Consequently, the highest selectivity up to 40% was obtained over the catalyst supported on 1: 1 mixture of MP AS-SiOz, though the role of Al in the mixed support was not clear so far.

Conclusions

By using CJ6-PyCl as surfactant, mesoporous alumino-silicate (MPAS) was prepared under mild conditions. The Co-based catalyst supported on MPAS showed high and stable activity, and high selectivity for CIO-ZO hydrocarbons in F-T synthesis. By using the mixed support ofMPAS (SilAI = 19) and wide pore SiOz (Q-50), the selectivity was improved up to 40% at CO conversion of 58.8%.

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