A New Method of Bimodal Support Preparation and Its Application in Fischer-Tropsch Synthesis

Noritatsu Tsubaki[1], Yi Zhang[2], Shouli Sun[2], Yoshiharu Yoneyama[1], Xiaohong Li[3], Kaoru Fujimoto[3]*

**1. Department of Material System and Life Science, School of Engineering, Toyama University, Gofuku 3190, Toyama 930-8555, Japan*
2. Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan
3. School of Engineering, Kita-kyushu University, Kita-kyushu, Fukuoka, Japan

Introduction

The reaction performance of the supported metal catalysts was controlled by a number of factors, such as support property, metal precursor identity and calcination temperature. Among these factors, support pore size has great effect on the mass transfer of reactants and products. The catalyst pore size affected not only catalytic activity but also product selectivity. On the other hand, the supported metal particle size has close relationship with the surface area of support. Generally, the metal dispersion is enhanced with the increased surface area of the support. But, if the support has large surface area, it usually has small pore size. Undoubtedly, the intra-pellet diffusion efficiency is poor for small-pore catalyst, especially in the multi-phase reactor. The bimodal catalyst where both large pore and small pore coexist can guarantee high diffusion efficiency and large supported metal area meantime, as theoretically proved by Levenspiel [1].

Inui et al. developed a kind of bimodal Ni/SiO_2 catalyst utilizing very strong acidic corrosion function of *aqua regia*. This kind of catalyst showed high activity for methanation of CO_2 [2]. Inoue et al. found an alcohothermal treatment method of gibbsite to prepare bimodal alumina support, using various alcohols [3].

To find a simple preparation method and control pore size more easily, we here propose a new method, which made small pores formed on the inner walls of the support with large pores. Thus, this kind of support is estimated to realize not only higher diffusion efficiency of reactants and products by large pore, but also higher metal dispersion through the enlarged surface area; and can be expected to realize high catalytic activity. As an application of this kind of bimodal support, it was used for liquid-phase Fischer-Tropsch synthesis (FTS) where cobalt was supported.

Experimental

The bimodal support was prepared by incipient-wetness impregnation of commercially available silica gel (Cariact Q-50, Fuji Silysia Co., specific surface area: 70 m^2 g^{-1}, pore volume: 1 ml g^{-1}, pellet size: 74-590 μm and pore diameter: 50 nm) with silica sol (Snowtex XS, Nissan Chemicals Co.) of different concentration. After the impregnation, the support was dried in air at 393 K for 12 h, and then calcined in air at 673 K for 2 h. The properties of the silica sol were listed in Table 1.

Cobalt-supported catalyst with 10wt% metal loading was prepared by incipient-wetness impregnation of different supports, including the bimodal support, with cobalt nitrate aqueous solution. The catalyst precursors were dried in air at 393 K for 12 h, then calcined in air from room temperature to 673 K with a ramping rate of 2 K min^{-1} and kept at 673K for 2 h. After calcination, the catalysts were activated in flowing hydrogen at 673 K for 10 h and at last, passivated by 1 % oxygen in nitrogen.

FTS reaction was carried out in a semi-batch autoclave (slurry-phase reactor, perfectly mixed flow reactor due to continuous stirring) with the inner volume of 80 ml. The passivated catalyst (1.0g, under 149 μm) and 20 ml liquid medium (n-hexadecane) were loaded in the reactor. During the reaction, effluent gas released from the reactor was analyzed by on-line gas chromatography. CO and CO_2 were analyzed by using an active charcoal column equipped with a thermal conductivity detector (TCD). The hydrocarbons were also analyzed on-line using capillary columns for C_1-C_5 (Porapak Q) and for C_6-C_{20} (SE-30, uniport), respectively. The carbon balance was between 95% and 98% for all of reactions. Argon was employed as an internal standard with concentration of 3 % in the feed gas. The reaction conditions were P (total) = 1.0 MPa, CO/H_2 = 1/2, W/F (CO + H_2 + Ar) = 10 g h mol^{-1}, T = 513 K.

Pore size distribution, BET surface area and pore volume were determined by the measuring instrument for surface area and pore size of porous materials (Shimadzu ASAP 2000) where nitrogen was used as absorbent. Supported cobalt crystalline size was detected by TEM (TOPCON EM-002B, Acc.Volt: 200kV, Point resolution: 0.18nm Line resolution: 0.14nm)

Results and Discussion

The pore distribution of the obtained bimodal support was shown in Fig. 1. It gave clear evidence that two kinds of pore existed. The two pore diameters of bimodal support prepared from Snowtex XS were 6 and 45 nm respectively. 45nm-pore was from the intrinsic pore of the used Cariact Q-50 pellet and 6nm-pore was the new pores formed from micro particle in silica sol Snowtex. Consequently, as compared in Table 2, BET surface area was enhanced from 70 m^2/g of Cariact Q-50 to 106m^2/g of the bimodal one, which was mainly the contribution from the newly-formed small pores. More importantly, the pore volume of the obtained bimodal support decreased from 1.0 ml/g of Cariact Q-50 to 0.4ml/g, indicating that silica sol indeed entered the uniformly distributed large pores of Cariact Q-50 as shown also in Fig. 1. If the silica sol did not enter the large pore, the observed pore volume would not change. Small silica particles from sol deposited onto inner walls of the large pore, via calcination and bond formation between surface silanol groups, to form small pores. If the large pore was blocked by the sol-derived silica structure, the BET surface area should be lowered remarkably. Considering the increased BET area and slightly decreased size of the large pore from original 50nm to 45nm, it is able to conclude that the obtained bimodal support formed according to the designed route.

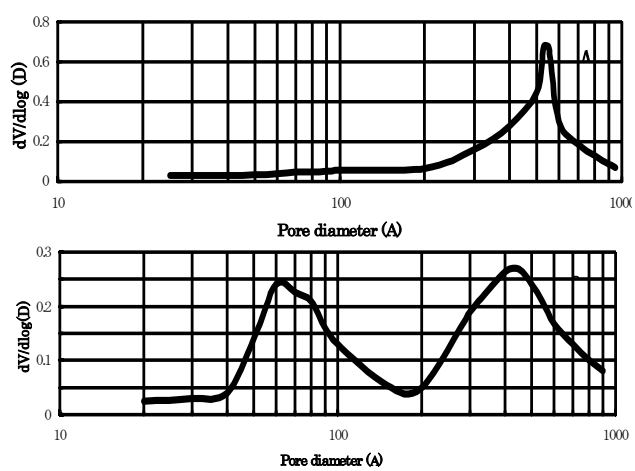

Figure 1. The pore size distributions of Q-50 and bimodal support A: Q-50. B: bimodal support.

Table 1 The properties of silica sol

Sol	pH	Content (wt%)	Solvent	Particle size nm
Silica	9.0-10.0	SiO_2 20%	Water	5.0

Table 2 The properties of various supports

Support	Surface area m^2/g	Pore Volume ml/g	Pore size nm
Q-50	70	1.0	50
Bimodal	106	0.4	6.0, 45
Q-3	546	0.3	3.0

To investigate the promotional role of the bimodal catalyst, it was applied to liquid-phase Fischer-Tropsch synthesis reaction. Liquid-phase Fischer-Tropsch synthesis reaction has advantages in temperature control, wax extraction and catalyst lifetime extension, compared to the common gas-phase reaction [4]. But the main drawback of the liquid-phase FTS reaction was the slow diffusion rate of the syngas as well as the formed hydrocarbons. To release the overall reaction from possible diffusion-controlled regime and obtain maximum hydrocarbon yield, bimodal Co/SiO_2 catalysts were tested.

The reaction performance of the catalysts prepared from the bimodal support or Cariact Q-50, Q-3 was compared in Fig. 3. The reaction rate of all of catalysts reached steady state from reaction running 1hr. Cariact Q-3 was an analogy to Q-50 but with average pore size of 3nm. Their property was shown in Table 2. Catalyst prepared from Q-3 support had the largest surface area but the smallest pore diameter. It exhibited low catalytic activity and the highest methane selectivity. For the catalyst prepared from Q-50 support, which had the lowest surface area and the largest pore size, the CO conversion, CH_4 and CO_2 selectivity were the lowest. For the catalyst prepared from bimodal support, the CO conversion was the highest, and meanwhile selectivities of CH_4 and CO_2 were as low as to those of the catalyst prepared from Q-50. Bimodal catalyst showed the best performances here.

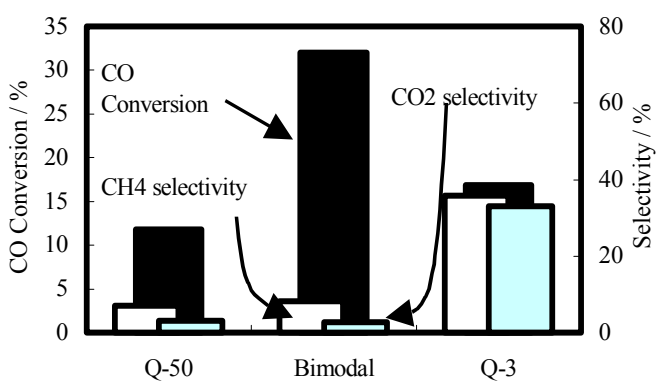

Figure 2. The reaction performance of cobalt catalysts prepared from different support
Reaction conditions: 513 K, 1.0MPa, W/F = 10 g h mol^{-1}, $H_2/CO = 2$, cobalt loading: 10wt%

The activities and selectivities of the FTS catalysts are markedly depending on their pore structure. The catalyst having a small pore size tended to produce lighter hydrocarbons. On the other hand, the product distribution of large-pore catalyst was wider and the proportion of the heavy hydrocarbon was high [5]. It has been already pointed out that the propagation of the carbon-carbon chain occurred more easily on the catalyst with lower specific surface area where metallic particle size was larger [6, 7], which naturally decreased methane formation. Furthermore, 1-olefins are generally produced as primary products in FTS and are successively hydrogenated to paraffins [8]. But they can re-adsorb onto metallic sites to receive secondary hydrocracking, breaking the terminal double bond and releasing methane, especially in the liquid-phase FTS reaction [4]. When the pore size was larger, the transportation of the primary product was more effective and relevantly methane formation rate from secondary hydrocracking of olefins was lower. Also lower BET surface area of large-pore support determined larger metallic size and suppressed methane formation. Based on these reasons, the methane selectivity was the lowest for the catalyst prepared from Q-50. Due to the larger pore existing in the catalyst prepared from bimodal support, the CH_4 selectivity was also low. On the other hand, FT synthesis rates on cobalt catalyst can be improved by increasing the dispersion of supported cobalt crystalline. Generally, the metal dispersion is increased with the increased surface area and the decreased pore size of support. And the TEM data in Table 3 showed the supported cobalt crystalline size as 37nm for Q-50 catalyst, 22.6nm for bimodal catalyst and 1.4nm for Q-3 catalyst. For Q-3 derived catalyst, its small pore and slow diffusion efficiency determined high methane selectivity. But its CO conversion was not the highest, regardless of its highest metal dispersion in this study.

Table 3 The properties of Co/SiO_2 catalyst derived from various supports

Catalyst	BET m^2/g	Pore vol. ml/g	Pore size nm	TEM crystal size nm
Q-50 catalyst	52	0.82	54	37
Bimodal catalyst	82	0.28	8.0 47	22.6
Q-3 catalyst	513	0.16	3.7	1.4

Cobalt loading: 10%

The BET surface and pore volume decreased and average pore size increased very slightly for various Co/SiO_2 catalysts, since the supported cobalt crystalline blocked some smaller pore of support, but the bimodal catalyst still kept bimodal structure with two kinds of pore size of 8nm and 47nm, as in Table 3. Bimodal catalyst, having higher metal dispersion due to its larger BET surface area, and accelerated diffusion rate derived from the bimodal structure, exhibited the highest CO conversion and low methane selectivity.

The preparation method of introducing oxide sols other than silica into large-pore silica pellet is being developed.

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