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Simultaneous introduction of chemical and spatial effects *via* a new bimodal catalyst support preparation method

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Nano-sized zirconia–silica bimodal catalyst supports are prepared by direct introduction of zirconia sol into silica gel, which improved supported cobalt catalyst activity significantly *via* a spatial effect and a chemically promotional effect of zirconia in liquid-phase Fisher–Tropsch synthesis (FTS).

In general, the activity of a supported metal catalyst should be increased if the dispersion of supported metal is increased, which is mainly controlled by the surface area of the support. Of course, large specific surface area favors high metal dispersion, and small metal crystallite size. However the pore sizes of supports with large surface area are small, and therefore large surface area of the support results in poor diffusion efficiency of reactants and products in the intra-pellet structure. On the other hand, while showing improved inside-pore diffusion efficiency, a catalyst with large pore sizes has a small specific surface area and is not beneficial to disperse supported metal, leading to low metal dispersion and low catalytic activity. A support with a distinct bimodal structure has excellent advantages for solving this contradiction because the large pores provide rapid transportations of reactant and product molecules; while small pores simultaneously provide a large surface area, as theoretically expressed by Levenspiel.[1]

In order to develop a simple and general method for the preparation of functional bimodal supports with both large and micro-pores, and to control the pore sizes precisely, a new method using silica gel with large pores of desired size and zirconia sol for generating small pores is proposed. As a promoter of the Fisher–Tropsch synthesis (FTS) reaction, zirconia is expected to promote the catalytic activity of FTS. The SiO_2–ZrO_2 bimodal support has multiple functions for FTS reaction. In this study, a cobalt supported bimodal catalyst was examined for estimating the ability of the SiO_2–ZrO_2 bimodal support in the liquid-phase FTS reaction. This method can be expanded to prepare various bimodal structure catalyst supports with different chemical compositions as it is possible to change the combination of the large-pore gel and sol. For instance, Al_2O_3–SiO_2 (large pore: Al_2O_3, small pore: SiO_2), SiO_2–SiO_2 or SiO_2–Al_2O_3 (large pore: SiO_2, small pore: Al_2O_3) bimodal structures are also possible.

The bimodal support was prepared by incipient-wetness impregnation of silica gel (Cariact Q-50, Fuji Silisya Chemical) and zirconia sol (Seramica, Nippan, ZrO_2 particle size: 1.7–2.4 nm). After the impregnation, the support was dried in air at 393 K for 12 h, and then calcined at 673 K for 2 h. Cobalt-supported catalysts (10 wt%) were prepared by incipient-wetness impregnation of different supports using cobalt nitrate aqueous solution. The catalyst precursors were dried in air at 393 K for 12 h, and then calcined from room temperature to 673 K at 2 K min^{-1} and kept at 673 K for 2 h. Finally, the Co catalysts were reduced in H_2 at 673 K for 10 h.

The pore size distributions of silica gel Q-50, the bimodal support and Co supported bimodal support are shown in Fig. 1. The prepared bimodal support had both 3.2 and 45 nm pores, unlike silica gel Q-50 with 50 nm pores only. In the calcination step, the 3.2 nm pores were formed by the zirconia sol through dehydration of OH groups of the particles of the zirconia sol in the large pores of the silica gel. Therefore the large pore size of the bimodal support decreased from 50 nm of silica gel Q-50 to 45 nm. Concerning the pore size distributions, the obtained bimodal support distinctly exhibited two types of pores. The BET surface area of the bimodal support significantly increased from 70 m^2 g^{-1} (for silica gel Q-50) to 201 m^2 g^{-1}, due to the contribution from the newly formed small pores, as summarized in Table 1. As a porous zirconia structure was formed inside the large pores of silica gel Q-50, the pore volume of bimodal support decreased from 1.2 ml g^{-1} of Q-50 to 0.42 ml g^{-1}. The increased BET surface area and the decreased pore volume proved that the particles of zirconia entered the large pores of Q-50, and deposited on the inner walls of Q-50 to form the small pores, as illustrated in Fig. 2. If the zirconia particles were deposited at the entrance of large pores of Q-50, the large pores would be blocked, and the BET surface area of the bimodal support would decrease significantly. However, the above results clearly indicate that the bimodal support was formed according to the route in Fig. 2.

In order to investigate the properties of the bimodal support, the Co supported bimodal catalyst was applied to the liquid-phase FTS reaction. The disadvantage of the liquid-phase FTS reactions is the slow diffusion rate of syngas as well as of the produced hydrocarbons inside the pores of the catalyst. Slow diffusion efficiency of syngas inside the micropores will lead to hydrogen-rich reactant gas, stimulating CH_4 formation. Slow

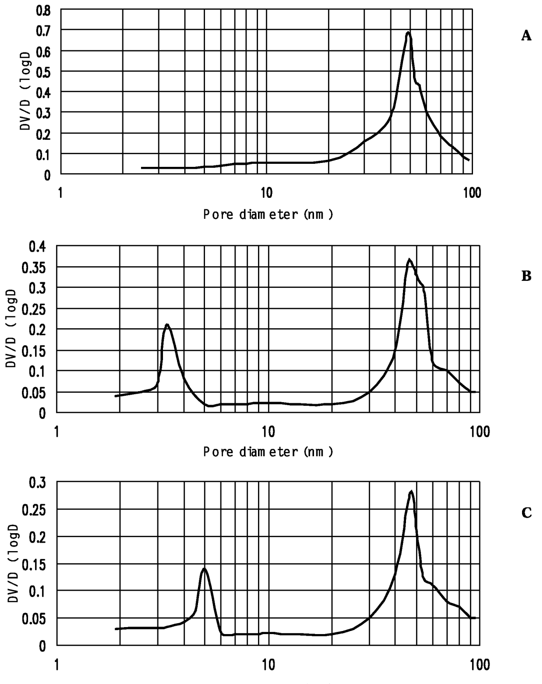

Fig. 1 Pore size distributions of (A) the Q-50 support, (B) the SiO_2–ZrO_2 bimodal support and (C) the SiO_2–ZrO_2 bimodal catalyst.

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Table 1 The properties of various Co/SiO_2 catalysts and corresponding supports

	Surface area/m^2 g^{-1}		Pore vol./ml g^{-1}		Pore size/nm		Co crystal size/nm	
Catalyst	Support	Catalyst	Support	Catalyst	Support	Catalyst	XRD	TEM
Q-50	70	52	1.2	0.82	50	54	35	37
Bimodal	201	171	0.42	0.28	3.2, 45	5.0, 47	23.6	21.6
Q-3	546	452	0.3	0.16	3.0	3.7	4.5	1.4

Cobalt loading: 10 wt%; zirconia loading of bimodal support: 16.8wt%.

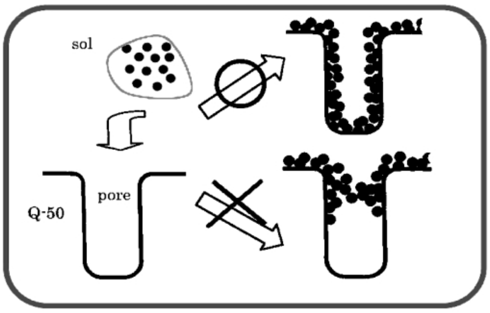

Fig. 2 Formation scheme of the bimodal support.

diffusion rates of the products inside the pores of the catalyst enhances methane production through the readsorption and decomposition of intermediate 1-alkenes.[2] The activity and the selectivity of the FTS catalyst are markedly controlled by the pore structure. Catalysts with a small pore size tend to produce lighter hydrocarbons while those with large pore sizes tend to produce heavy hydrocarbons.[3,4] It is expected that the bimodal catalysts can overcome the disadvantages of liquid phase FTS reactions and improve the overall conversion, since large pores can improve the diffusion rate of syngas and the products, and micropores can enhance the dispersion of the active metallic crystallites.

The reaction performances of the cobalt catalysts prepared from the SiO_2–ZrO_2 bimodal supports, Q-50 or Q-3 silica support are compared in Table 2. Silica support Q-3 was used for comparison, since it is analogous to Q-50, but with a much smaller pore size of 3 nm. In addition, the performance of a cobalt-supported SiO_2–SiO_2 bimodal catalyst was also compared, prepared by introducing silica sol (particle size: 5 nm) to Q-50 silica gel by the same method. Low diffusion rates of syngas and products inside pores of the Q-3 catalyst determined the largest CH_4 selectivity of this catalyst. The catalyst prepared from Q-50 had the lowest surface area and the largest pore size, and its CO conversion, byproduct CH_4 and CO_2 selectivity were the lowest. On the other hand, for the silica–zirconia bimodal catalyst, the CO conversion was the largest, while CH_4 and CO_2 selectivities were also the lowest. The CH_4 and CO_2 selectivity for the silica–silica bimodal catalyst were the lowest, similar to that of the silica–zirconia bimodal catalyst. These differences are due to the bimodal structure. The large pores in Q-50 and bimodal catalysts improved the mass transfer rate of syngas and 1-alkenes, and lowered the production of CH_4. Furthermore, as the byproduct H_2O could escape from large pores quickly, the formation rate of CO_2 was reduced since CO_2 arises from the water–gas shift reaction ($CO + H_2O = CO_2 + H_2$). However, the CO conversion for the silica–silica bimodal catalyst was not high, even though its bimodal structure was spatially similar to that of the silica–zirconia bimodal support. The silica–zirconia bimodal catalyst showed the best performance in liquid-phase FTS reaction.

Table 2 The reaction performances of various Co/SiO_2 catalysts

Catalyst	CO Conversion (%)	CH_4 Selectivity (%)	CO_2 Selectivity (%)
Silica bimodal	33	10	2.7
Q-3	26	22	20.5
Q-50	17	7.1	3.2
Zirconia bimodal	86	11	3.2

Reaction conditions: P (total) = 1.0 MPa, CO/H_2 = 1/2, W/F = 10 g h^{-1} mol^{-1}, $T = 513$ K.

Ali *et al*. reported that increasing the ratio of ZrO_2/SiO_2 in the support did not enhance Co dispersion or reduction degree.[5] Because both silica–silica and silica–zirconia bimodal catalysts had similar bimodal spatial structures, the dispersion of supported cobalt metal seemed to be similar to each other. It has been found that in FTS, addition of zirconia into the silica support enhanced C_{5+} selectivity, indicating that carbon chain growth probability was increased.[6] Withers *et al*. found an increase in activity for FTS reaction with increased ratio of ZrO_2/SiO_2 in the support for a Co supported catalyst.[7] Thus zirconia in the silica–zirconia bimodal catalyst promoted the liquid-phase FTS reaction here *via* not only a spatial effect of the bimodal structure but also *via* a chemical promotional effect. By comparison, the silica–silica bimodal catalyst showed only a spatial effect and exhibited lower activity than its silica–zirconia analogue.

From the above, it is clear that building up micropores using zirconia particles inside silica large pores realized both chemical and spatial promotion, enhancing the activity for liquid phase FTS reaction. The bimodal structure, with both large and small pores in the supports, improved the diffusion rate of syngas and products, and the dispersion of active metal particles, respectively. In addition, the presence of zirconia in the bimodal supports acted as a promoter for the FTS reaction. These results indicate that a new, simple and general method for preparing bimodal supports is developed by manipulation of zirconia nano-particles from its sol inside the pores of silica gel. By this method, multi-functional bimodal supports with both large pores of desired size and micropores can be easily prepared and the large pore size of the bimodal structure can be successfully controlled.

Furthermore, building small pores using oxide A as a ‘brick’ *via* its sol inside large pores of oxide B can be easily extended to prepare bimodal supports containing variable amounts of A and B. Besides the spatial effect of bimodal structure, new chemical effects might appear with hetero-atom formation between A and B.

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