Catalysis Letters Vol. 91, Nos. 3–4, February 2005 (© 2005)
DOI: 10.1007/s10562-005-2118-4

Preparation of alumina–silica bimodal pore catalysts for Fischer-Tropsch synthesis

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Received 15 October 2004; accepted 15 November 2004

The bimodal pore structure support has excellent advantages in solid catalysis reaction because the large pores provide pathways for rapid molecular transportation and small pores provide a large active surface, contributing to high diffusion efficiency and high dispersion of supported metal simultaneously. A multi-functional bimodal pore catalyst support, alumina–silica bimodal pore support, was prepared from polymer complex solution and silica gel. The obtained bimodal pore support had two kinds of main pores, decreased pore volume and enlarged specific surface area, comparing the original silica gel. This kind of bimodal pore support was applied in slurry phase Fischer-Tropsch synthesis, where cobalt was supported as active metal. Alumina–silica bimodal pore catalyst exhibited high catalytic activity and favorite selectivity, due to the spatial effects of bimodal pore structure and chemical effects of coexisting alumina, which formed the new small pores of bimodal pore support.

KEY WORDS: bimodal pore support; alumina; Fischer-Tropsch synthesis; cobalt catalyst; syngas.

1. Introduction

The production of fuels substituting the natural petroleum is an interesting way of the Fischer-Tropsch synthesis (FTS). Cobalt based catalysts attract most of current attention for the direct conversion of syngas in FTS because of its high activity, high selectivity for long chain paraffins, and low water gas shift activity [1]. Besides cobalt, the supports, such as SiO_2, Al_2O_3 and TiO_2, are indispensable. The chemical and texture properties of support influence the catalytic activity and product selectivity of Co catalysts, *via* their modification on the reducibility and dispersion of cobalt or the formation of well-fined phase. Synthesis of highly dispersed Co catalysts requires strong interaction between the support and the Co precursor, but in turn such strong interactions generally lower reducibility of such precursors [2]. Alumina is one of the most employed supports for cobalt FT catalysts due to its favorable mechanical properties and adjustable surface properties. The supports like Al_2O_3 have significant support interaction, contributing to formation of a smaller supported metal cluster; while supports such as silica always yield a large supported metal cluster size and high reduction degree. However, unlike the cobalt silica catalyst, Co/Al_2O_3 catalysts have limited reducibility because the support can interact with the active phase by the diffusion of cobalt ion into the structure of alumina to impede the reduction [3,4].

On the other hand, the activities and selectivities of the FTS catalysts are markedly depending on their pore structure. 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. A support with a distinct bimodal pore structure has excellent advantages in solid catalysis reaction because the large pores provide pathways for rapid molecular transportation and small pores serve a large area of active surface, contributing to high diffusion efficiency and enhanced dispersion of supported metal simultaneously, as theoretically proved by Levenspiel [5].

The present authors reported that silica–silica and silica–zirconia bimodal pore supports remarkably promoted the catalytic activity of cobalt catalysts in FTS reaction, due to their spatial and chemical effects [6]. The bimodal pore catalyst supports were obtained by building up nano-particles from silica or zirconia sol to form small pores, inside tailor-made large silica pores. In the present study, because the polymer complex solution can form a homogeneously distributed oxide particle and homogeneous packing of the particles, a multi-functional alumina–silica bimodal pore support was prepared by impregnating a polymer complex solution of aluminum into original silica gel. As an application of this kind of bimodal pore support, it was used for slurry-phase FTS reactions as the support of cobalt catalysts. This kind of support is estimated that it can not only realize higher supported cobalt dispersion by spatial effects of bimodal pore structure and chemical effects of alumina, but also obtain high reduction degree of supported cobolt by coexisting silica and alumina,

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and is also expected to realize high catalytic activity *via* higher diffusion efficiency of reactants and products by bimodal pore structure.

2. Experimental

The aluminum nitrate was dissolved in a 0.3 mol/L polyethylene glycol (PEG, average molecular weight of 200) aqueous solution to prepare polymer complex solution. After stirring at 353 K for 1 h, the solution was impregnated into original silica gel (Cariact Q-50, Fuji Silysia Chemical Ltd., specific surface area: 70 m^2 g^{-1}, pore volume: 1.2 ml g^{-1}, pellet size: 74–590 μm and mean pore diameter: 50 nm) by incipient-witness method. After the impregnation, the support was calcined in air at 673 K for 2 h. The alumina loading of the obtained bimodal pore support was 10 wt%. The preparation method of silica–silica bimodal pore support was reported elsewhere [6].

Cobalt-supported catalyst with 10 wt% metal loading was prepared by incipient-wetness impregnation of different supports, including the two bimodal pore supports with cobalt nitrate aqueous solution. The catalyst precursor were dried in air at 393 k for 12 h, and then were calcined in air from room temperature to 673 K with a ramping rate of 2 K $\min^{-1}$ and kept at 673 K 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. As comparison, a 10 wt% metal loading cobalt-supported alumina catalyst was prepared using JRC-ALO-5 alumina support (JRC-ALO-5, Reference catalyst, Catalysis Society of Japan, specific surface area: 233 m^2 g^{-1}, pore volume: 0.41 ml g^{-1}, pellet size: 74–590 μm mean pore diameter: 5.6 nm), in the same method.

FTS reaction was carried out in a flow type slurry-phase semi-batch autoclave, with the inner volume of 80 ml. The passivated catalyst (1.0 g, 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 anlyzed by on-line gas chromatography. CO and CO_2were analyzed by using an active charcoal column equipped with a thermal conductivity detector (TCD). The hydrocarbons were also analyzed using FID for C_1–C_5 (Porapak Q, on-line) and for C_6–C_{30+}(SE-30, uniport), respectively. Argon was employed as an internal standard with concentration of 3% in the feed gas. The reaction conditions were P (total) = 1.0 MPa, $CO/H_2 = 1/2$, $W/F(CO + H_2 + AR) = 5\,\text{g-cat. h mol}^{-1}$, $T = 513$ K.

Pore size distribution, BET surface area and pore volume were determined by absorption method (Quantachrome Autosorb-1, Yuasa Ionics), where nitrogen was used as adsorbent Supported cobalt crystalline size of the passivated catalysts was detected by XRD (Rigaku, RINT2000). The supported cobalt crystalline average size was calculated by $L = K\lambda/\Delta(2\theta)\cos\theta_0$ for XRD data, where L is the crystalline size, K is a constant ($K = 0.9 \sim 1.1$), λ is the wavelength of X-ray ($CUK_\alpha = 0.154$ nm), and $\Delta(2\theta)$ is the width of the peak at half height.

Temperature-programmed reduction (TPR) experiments were carried out in a quartz-made microreactor using 0.2 g calcined catalysts. The gas stream, 5% H_2 diluted by nitrogen as reducing gas, was fed *via* a mass flow controller. After the reactor, the effluent gas was, led *via* a 0.3 nm molecular sieve trap to remove the produced water, before reaching TCD.

Chemisorption experiments were carried out in a static volumetric glass high-vacuum system (Quantachrome Autosorb-1, Yuasa Ionics). Research grade gases (H_2: 99.9995%, Takachiho Co.) were used without further purification. Before absorption of H_2 the catalysts, previously reduced by H_2 and passivated, were treated in H_2 at 673 K for 1 h, followed by evacuation. H_2 adsorption isotherms were measured at 373 K. The calculation of chemisorption uptake (at 373 K), dispersion percentage and average crystalline diameter was described elsewhere [7].

The temperature-programmed surface reaction (TPSR) experiment was carried out in a quartz-made microreactor connected to thermal conductivity detector (TCD) equipped with active charcoal column using 0.2 g passivated catalysts. The passivated catalysts were reduced by hydrogen at 673 K for 1 h, and then the system was purged by helium stream for 1 h. After reduction of catalysts, the CO was introduced into microreactor at 15 ml/min for 5 min. After removing the physically adsorbed CO by helium stream, hydrogen of 30 ml/min was passed over the catalysts, which was heated at a rate of 3 K/min. The products, consisting CH_4, CO and CO_2, were analyzed.

3. Results and discussion

The pore distribution of the obtained bimodal alumina-silica bimodal pore support is shown in figure 1b. It gives clear evidence that two kinds of pore exist. The two pore diameters of bimodal support are 4.5 and 47 nm respectively. The intrinsic pore of the used Cariact Q-50 pellet, as shown in figure 1a, decreases from 50 to 47 nm and 4.5 nm pore is the new pore formed by alumina. Consequently, as compared in table 1, BET surface area is enhanced from 70 m^2/g of Cariact Q-50 to 101 m^2/g of the bimodal one, which is mainly the contribution from the newly-formed small pores. More importantly, the pore volume of the obtained bimodal support decreased from 1.20 ml/g of Cariact Q-50 to 0.78 ml/g, indicating that alumina indeed formed the new small pores inside the uniformly distributed large pores of Cariact Q-50. Small alumina particles deposited onto inner walls of the large pore, *via*

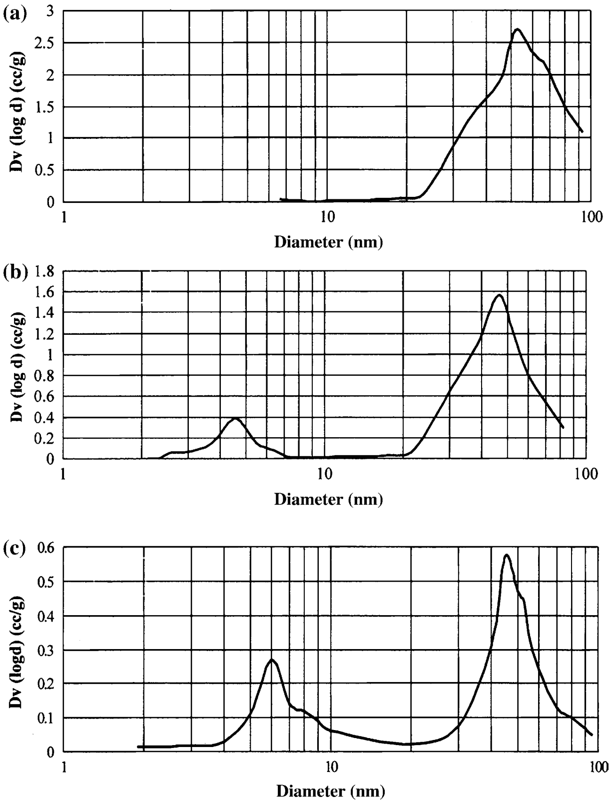


Figure 1. The pore distributions of alumina bimodal pore support. (a) Silica gel Q-50; (b) SiO_2-Al_2O_3 bimodal pore support; (c) SiO_2- SiO_2 bimodal pore support.

calcination and bond formation between surface Al-OH and Si-OH groups, to form small pores. If the large pore were blocked by the alumina structure, the BET surface area would be lowered remarkably. Considering the increased BET area and the decreased pore volume of obtained alumina–silica bimodal support comparing to silica gel Q-50, it is able to conclude that the obtained bimodal support formed according to the designed route.

To investigate the promotional role of the bimodal supports, 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 [8]. 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, alumina–silica bimodal support was used to prepare the 10 wt% cobalt supported catalysts, which were tested in liquid-phase FTS reaction.

Table 1
Properties of various supports

Support	BET of support (m^2/g)	SiO_2 or Al_2O_3 loading (wt%)	Pore diameter (nm)	Pore volume (ml/g)
Q-50	70	0	50.0	1.20
JRC-ALO-5	233	0	5.6	0.41
Q-3	546	0	3.0	0.30
Silica–Silica	108	12	6–45	0.46
Alumina–Silica	101	10	4.5–47	0.76

As shown in table 2, the alumina–silica bimodal catalyst shows the highest catalytic activity in FTS reaction, and lower selectivity of CH_4 and CO_2 as almost the same with that of Q-50 catalyst. Cariact Q-3 is an analogy to Q-50 but with average pore size of 3 nm, as compared in table 1. The catalyst prepared from Q-3 exhibits the lowest catalytic activity and the highest selectivity of CH_4 and CO_2. In addition the performance of cobalt-supported silica–silica bimodal catalyst is also compared in table 2, whose support was prepared by previously reported method [5]. This kind of catalyst shows higher CO conversion than that of Q-50 and Q-3 catalysts, and similar selectivity of CH_4 and CO_2 with Q-50 catalyst. The alumina–silica bimodal catalyst exhibits the best reaction performance in this study.

As compared in table 2, Q-3 silica supported catalyst showed the lowest CO conversion, indicating the diffusion-controlled regime due to its small pores. Furthermore, the methane selectivity and carbon dioxide selectivity of Q-3 silica supported catalyst were highest. As the byproduced water could not diffuse out of small catalyst pores quickly, water reacted with CO to form CO_2 *via* water gas shift reaction in large amount in Q-3 based catalyst. For high methane selectivity of Q-3 based catalyst, one reason was its small supported cobalt particle, which was not favorable to carbon chain growth [2]. As result, Q-3 exhibited the lowest chain growth probability, 0.82, in table 2, leading to the largest methane selectivity. As 1-olefins were intermediates of Fischer-Tropsch synthesis, they could readsorb onto cobalt metallic sites to be hydrocracked to form methane when transported to the outside of catalyst pellet. Small pores of Q-3 based catalyst made the transportation efficiency of 1-olefins lower, resulting in high methane selectivity as well. For the same reasons, Q-50 based catalyst and both bimodal catalysts in table 2 had low methane and low carbon dioxide selectivity because of large pores. As comparison, the cobalt-supported alumina catalyst (JRC-ALO-5) was also tested in liquid-phase FTS reaction under the same reaction conditions. This kind of catalyst presented CO conversion as low as 9.5% and CH_4 selectivity as high as 21.6%, which was similar with Q-3 catalyst.

The activities and selectivities of the FTS catalysts are markedly depended on their pore structure. The catalyst having a small pore size tends to produce lighter hydrocarbons. On the other hand, the Product distribution of large-pore catalyst is wider and the selectivity of the heavy hydrocarbon is high [9]. Larger pores would contribute to transport primary products, 1-olefins, more

Table 2

Reaction performance and properties of various catalysts

Catalyst	Co-Particle Size (nm)		Reduction degree^b (%)	Co Dispersion^c (%)	TOF^d (S^{-1})	CO Conv. (%)	Selectivity (%)		α
	XRD	H_2^a					CH_4	CO_2	
Q-50	35	41	98.5	2.5	0.061	13.5	7.1	2.1	0.86
Q-3	4.5	3.2	60.3	38.1	0.014	9.6	18.1	16.8	0.82
Silica–Silica	20.6	30.3	87.6	3.3	0.072	17.8	8.9	2.2	0.86
Alumina–Silica	15.3	23.2	90.2	4.3	0.121	38.9	10.2	1.3	0.87

Reaction conditions: $P = 1$ MPa; $T = 513$ K; $W/F = 5$ g-cat. h/mol; $H_2/CO = 2$; Weight of catalyst = 1 g; Cobalt loading: 10 wt%.

[a] Calculated from H_2 chemisorption at 373 K.

[b] Calculated by TPR from 373 K to 1073 K.

[c] Determined by H_2 chemisorption.

[d] Based on H_2 total uptake.

effectively and decrease methane formation rate from secondary hydrocracking of olefins. Also lower BET surface area of large-pore supports determine larger metallic size and suppresses methane formation. Based on these reasons, the methane selectivity was the lowest for the catalyst prepared from Q-50. Due to larger and smaller pores coexisting in the catalyst prepared from bimodal support, its CH_4 selectivity was remarkably lower than that of Q-3 catalyst and slightly higher than that Q-50 catalyst.

The activity of cobalt catalyst in FTS depends solely on the number of active sites located on the surface of crystalline metal formed by reduction. The number of active sites is determined by the Co particle size, loading amount, and reduction degree [10]. The supported cobalt particle size of various catalysts was determined by XRD and H_2 chemisorption. The XRD patterns of various reduced catalysts are shown in figure 2. The cobalt crystalline size of Q-50 was the largest, due the lowest specific surface area. Because of the enlarged specific surface area of bimodal supports, the supported cobalt particle size of bimodal catalysts was smaller than that of Q-50. However, the cobalt particle size of silica–silica bimodal catalyst was larger than that of alumina–silica catalyst, according to H_2 chemisorption data as compared in table 2. It was observed that support interactions on cobalt oxide species from alumina were stronger than that from silica [11], which could form smaller supported cobalt particles. Based on this, it is considered that as the chemical effects of alumina structure, the alumina bimodal catalyst formed smaller supported cobalt particle size than silica bimodal catalyst, resulting in higher supported cobalt dispersion as illustrated in table 2, even though their specific surface area was almost the same. Based on these findings, It is proved that the bimodal pore structure

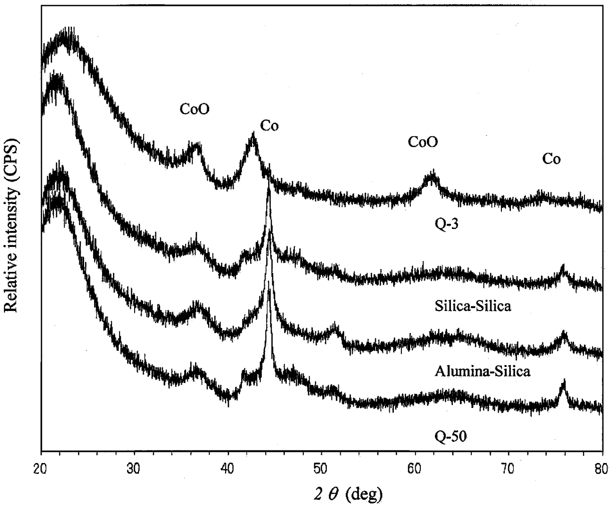


Figure 2. The XRD Patterns of various reduced catalysts.

and chemical effects of alumina improved the dispersion of the supported cobalt.

The reduction performance of various catalysts was determined by temperature-programmed reduction (TPR). In TPR spectra of various catalysts, as shown in figure 3, two peaks exist for the Q-50 catalyst, which locate at 612 and 673 K. The two peaks have been identified as conversion of Co^{3+} to Co^{2+} followed by the conversion of Co^{2+} to Co, and the broad region above 800 K indicate the existence of several species reduced at approximately the same temperature [12]. For the Q-3 catalyst, the first peak locates at 610 K and the second peak is rising from 700 K, while the H_2 consumption continuously increased until 1073 K indicating that some Co could not be reduced at lower temperatures. For silica–silica bimodal catalyst, there is only one wide peak from 500 to 820 K. For alumina–silica bimodal catalyst, a sharp low temperature peak locates at 609 K, and another broad peak distributes from 671 to 1000 K, which should be attributed to the reduction of various Co species, including the species with different particle size. Comparing the reduction degree of various catalysts, which were calculated by TPR data from 353 to 1073 K, the Q-50 catalyst showed the best reducibility as 98.5% due to its largest supported cobalt particle, which had lighter interaction with silica support. For Q-3 catalyst, due to its smallest supported cobalt particles, which had the strong interaction with silica support, the reducibility was the lowest as 60.3%. Both of two kinds of bimodal catalysts showed similar reducibility, as 87.6% for silica bimodal pore catalyst and 90.2% for alumina–silica bimodal pore catalysts. The large size cobalt particles or those located at silica surface cobalt particles were easier to be reduced, which can activate hydrogen after reduction, and the activated hydrogen can reduce the small cobalt particle by spill-over effect, contributing to high reducibility of supported cobalt [7]. On the other hand, it is considered that the coexisting silica could influence the reactivity of alumina surface, leading to improve the reducibility of supported cobalt on alumina surface. The TOF of various catalysts were calculated. As shown in table 2, the TOF of alumina-silica catalyst was higher than that of silica-silica catalyst, even though their reduction degree of supported cobalt was almost the same.

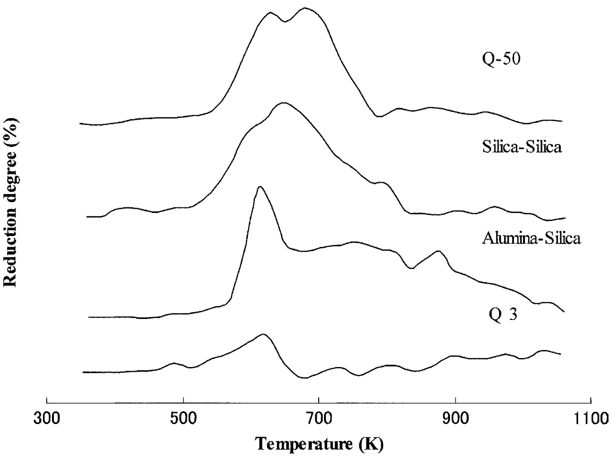
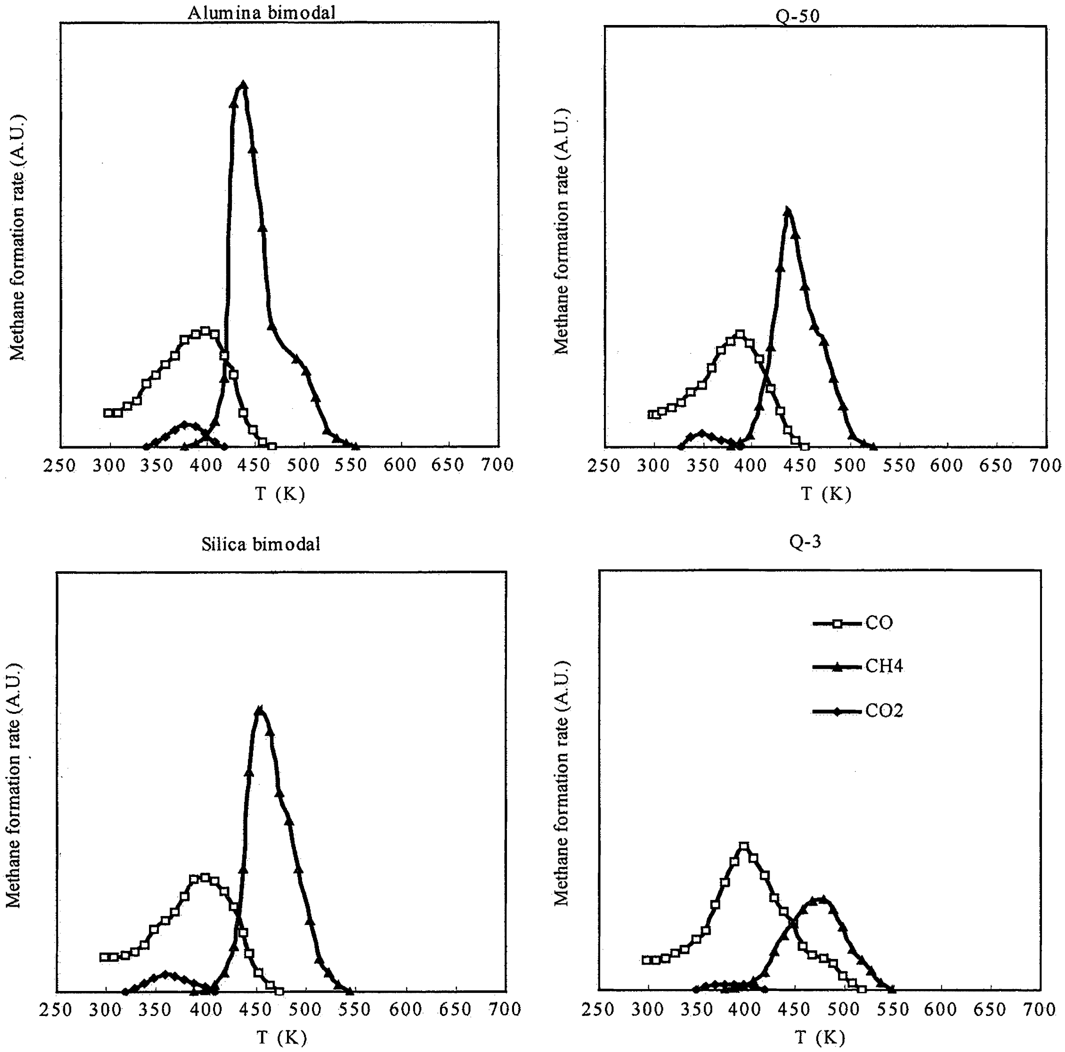


Figure 3. The TPR profile of various catalysts.

The peak temperature of CH_4 formation in CO TPSR was reported to closely relate to the catalytic activity of CO hydrogenation [13]. In figure 4, they are displayed the TPSR profiles of the various catalysts. The CH_4 peak temperatures of various catalysts were 436, 453, 476 and 438 K for Q-50, silica–silica bimodal, Q-3 and alumina–silica bimodal catalysts. Because of the smaller cobalt particle size of Q-3 and silica–silica bimodal pore catalyst as shown in table 2, the C═O bond is difficult to be cleaved, due to the geometric effect, resulting in higher temperature methane formation peak. However, the CH_4 peak temperature of alumina–silica bimodal pore catalyst was the lowest in this study, regardless of the smaller cobalt particle size than that of Q-50 and silica–silica bimodal pore catalyst. This fact suggested that CO was adsorbed in a more reactive state on the alumina–silica bimodal pore catalysts than on the others, resulting in the highest TOF in table 2.

A1umina–silica bimodal catalyst, having higher metal dispersion, reducibility of supported cobalt and accelerated diffusion rate derived from the bimodal structure, exhibited the highest CO conversion and low methane selectivity. The chain growth probability for Co/SiO_2 in liquid-phase FTS was influenced by a lot of factors, such as pore size of catalyst, supported metal crystalline size, and the secondary hydrocracking of products. In this study hydrocarbons from C_1 to C_{20} were analyzed, and the chain growth probability α was calculated by Anderson-Schulz-Flory equation to be 0.82 for Q-3 catalyst, lower than that of Q-50, silica and alumina bimodal pore catalysts, due to small pore size and small cobalt crystalline size of Q-3 catalyst.

Compared to silica–silica bimodal catalyst with similar pore structure, alumina–silica bimodal catalyst had larger pore volume, higher metal dispersion, higher reduction degree, and the highest TOF, as listed in tables 1 and 2. Mean while, alumina–silica bimodal catalyst had lower-temperature reduction peak, with the peak at 609 K, in TPR profile in figure 3, indicating that it was more reducible than silica–silica bimodal catalyst. On the other hand, the low temperature methane formation peak of alumina–silica bimodal catalyst in TPSR profile, as shown in figure 4, indicated that adsorbed CO on the alumina–silica bimodal pore catalysts was more reactive than on the others, resulting in the highest TOF in able 2. All of these factors are considered to be due to hetero-atom structure in alumina–silica bimodal structure, determining its higher activity than that of silica–silica bimodal analogy.


Alumina bimodal

Q-50

Silica bimodal

Q-3

Figure 4. The TPSR profiles of various catalysts CO adsorbed at room temperature.

4. Conclusions

As the summary, the multi-functional alumina–silica bimodal pore support was developed. The cobalt catalyst prepared by this kind of support exhibited the highest catalytic activity in liquid-phase FTS, due to the spatial and chemical effects of alumina–silica bimodal pore support. Due to larger and smaller pores coexisting in the catalyst prepared from alumina–silica bimodal pore support, where larger pores of bimodal pore catalysts provided pathways for rapid molecular transportation, namely high diffusion efficiency of reactants and products, the CH_4 selectivity was remarkably lower than that of Q-3 catalyst and slightly higher than that of Q-50 catalyst. The characterization details of this kind of catalyst are on the way.

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