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Synthesis of SBA-15 with different pore sizes and the utilization as supports of high loading of cobalt catalysts

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Abstract

Several types of SBA-15 with pore diameters of 3.6–12 nm have been synthesized under different reaction conditions, followed by air calcination, and utilized as supports for loading 10–20 mass% Co catalysts. Post-synthesis heat treatment after reaction at 308 K is more effective for increasing the pore diameter and volume of SBA-15 than the addition of trimethylbenzene before reaction. The combination of the two results in the formation of SBA-15 with large pore diameter but broad size distribution and less organized structures. When an acetone, ethanol, or water solution of $Co(NO_3)_2$ is used as a precursor for impregnation with SBA-15 with pore diameter of 3.6 nm, the average crystalline size of Co_3O_4 observed at 10 mass% Co exceeds the pore diameter irrespective of the kind of the solvent. On the other hand, the use of an ethanol solution of $Co(CH_3COO)_2$ or an acetone solution of $(CH_3COCHCOCH_3)_2Co$ provides no X-ray diffraction peaks of Co_3O_4 even at loading as high as 20 mass% Co, and catalyst addition considerably decreases the pore volume of SBA-15 support regardless of the pore diameter. These observations strongly suggest that Co catalysts exist as nanosized clusters inside the mesopores. The SAXS measurements show that the hexagonal mesoscopic organization of the SBA-15 support with pore diameter of 5.5 nm is almost retained even after addition of 20 mass% Co. The 20 mass% Co/SBA catalysts are also tested preliminarily in Fischer–Tropsch synthesis under 503–523 K and 2.0 MPa. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: SBA-15; Catalyst support; Cobalt loading; FT synthesis

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1. Introduction

Mesoporous silica with narrow pore size distribution has attracted increasing attention as a novel material for separations and reactions involving large molecules. Since the discovery of MCM-41 [1] and FSM-16 [2], several types of mesoporous silica have been developed [3]. SBA-15 has recently been synthesized in an acidic medium with poly(alkylene oxide) triblock copolymers, such as poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) and found to have uniform and large tubular channels up to 30 nm in diameter [4,5]. Since SBA-15 also possesses thick pore walls, the hydrothermal stability is much higher than MCM-41 [4]. Such features may provide high potential as supports for catalytic applications. Although some studies on the incorporation of Al [6,7] and Ti [8,9] into SBA-15 as framework species have been carried out, however,

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there has been only quite limited information about the utilization of SBA-15 as a support for loading a catalytically active component [8].

In the present work, therefore, SBA-15 supports with pore diameters in the range of 3.6–12 nm are synthesized under different reaction conditions, and their performances for catalyst loading, in particular at large quantities, are examined by N_2 adsorption, X-ray diffraction (XRD), and small angle X-ray scattering (SAXS) measurements. Co catalyst is selected as an active component, since it has been used practically in hydrotreating reactions of residual oils with large molecules and in Fischer–Tropsch (FT) synthesis to produce higher hydrocarbons from syngas. Preliminary FT runs are also carried out with 20 mass% Co catalysts supported on SBA-15.

2. Experimental

2.1. Synthesis of SBA-15

SBA-15 was synthesized with several kinds of triblock PEO–PPO–PEO copolymers (denoted as TCP), which were commercially available from Aldrich, Asahi Denka, and Polyscience. Among them, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$; average molecular weight (M_{av}) = 5800) from Aldrich, was used, unless otherwise stated.

The synthesis was carried out in a similar manner as reported elsewhere [4]. In a typical run, a homogeneous mixture, comprising 12.0 g of TCP, 60 cm^3 of hydrochloric acid (35–37%), and 312 g of distilled water, was first heated at 308 K during stirring, and then 25.6 g of tetraethyl orthosilicate (TEOS) was added to the mixture. The resulting gel was finally kept at 308 K for 24 h. As-synthesized SBA-15 was separated by filtration, followed by repeated washing with distilled water and subsequent dryness at room temperature under vacuum.

In order to increase the pore diameter of SBA-15, trimethylbenzene (TMB) was used as a swelling agent and a post-synthesis heat treatment (designated as PHT) was performed [4]. TMB was added to the homogeneous mixture before heating, and the weight ratio of TMB/TPC was changed in the range of 0.25–3. With PHT, the mixture after 24 h-reaction was subsequently heated at 370 K for 24 h.

In the calcination process to remove TCP, as-synthesized SBA-15 was heated at 1 K/min up to 773 K in a stream of air and soaked for 6 h at this temperature. The calcined SBA-15 was used as a support for Co catalyst.

2.2. Loading of Co^{2+} ions

The addition of Co^{2+} ions to SBA-15 was carried out by the impregnation method. Three kinds of Co compounds, such as $Co(NO_3)_2{\cdot}6H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, and $(CH_3COCHCOCH_3)_2Co{\cdot}2H_2O$, were used as the precursors of Co catalysts. Unless otherwise stated, $Co(CH_3COO)_2{\cdot}4H_2O$ was employed among them. In the impregnation process, these compounds were first dissolved into ethanol, acetone, or water, and a predetermined amount of SBA-15 was then added to the resulting solution, followed by heating for removal of the solvent. The nominal amount of the Co loaded ranged 5–20 mass% in the dried sample.

All Co catalysts supported on SBA-15 were calcined again under flowing air in the same manner as above. The resulting sample, denoted as Co/SBA-15, was subjected to N_2 adsorption, powder XRD, and SAXS measurements.

2.3. Characterization of SBA-15 supports and Co/SBA-15 catalysts

The measurements of N_2 adsorption for SBA-15 and Co/SBA-15 were carried out at 77 K, and their pore size distribution and surface areas were determined by the BJH and BET methods, respectively, the pore volumes being calculated by using the BJH desorption profile. Pore diameter described in the present paper means the peak of the BJH pore size distribution. The crystalline forms of Co catalysts were identified by the XRD analysis with Ni-filtered Cu Kα radiation (40 kV, 30 mA). The average crystalline size of Co species was determined by the Debye–Scherrer method. The crystalline structures of SiO_2 in SBA-15 and Co/SBA-15 were analyzed by the SAXS technique with Ni-filtered Cu Kα radiation (40 kV, 80 mA).

2.4. FT synthesis runs

Preliminary FT runs were carried out with a high-pressure gas-phase reaction system including a stainless flow reactor with a thermocouple well installed. About 0.5 g of 20 mass% Co/SBA catalyst was first charged into the reactor, then reduced in a flow of H_2 for 12 h at 673 K, and finally cooled down to 523 K, at which H_2/CO with a molar ratio of 2:1 was fed at 2.0 MPa. H_2, CO, CO_2, and CH_4 in the effluent were on-line analyzed with a high-speed micro-gaschromatograph.

3. Results and discussion

3.1. Properties of SBA-15 supports

The influence of the kind of TCP on the synthesis of SBA-15 was first examined. Almost no mesopores were developed with $EO_{26}PO_{39}EO_{26}$ ($M_{av} = 4600$) under the present conditions, even when the weight ratio of TEOS/TCP, the concentration of HCl, and reaction temperature (308–323 K) were varied. On the other hand, the use of $EO_{17}PO_{56}EO_{17}$ ($M_{av} =$ 4900) and $EO_{20}PO_{70}EO_{20}$ ($M_{av} = 5800$) lead to the development of mesoporous organization and provided the uniform pore size distribution. Thus, $EO_{20}PO_{70}EO_{20}$ was selected as TCP for the following experiments.

Pore properties and surface areas of SBA-15 materials as a function of weight ratio of TMB/TCP are shown in Fig. 1, where only the weight of TMB is changed keeping that of TCP constant. The pore diameter of SBA-15 was not sensitive to the ratio at 308 K and slightly increased to 3.9 nm at the values of 2–3. On the other hand, the effect of addition of TMB on the pore volume and surface area was evident; as the ratio of TMB/TCP increased, the former increased whereas the latter decreased. When reaction temperature was raised to 323 K, the addition of TMB lead to the formation of SBA-15 with slightly larger pore diameter, higher pore volume, and larger surface area.

Fig. 2 shows the pore size distribution of four kinds of SBA-15 prepared under different conditions. The distribution for SBA-15 without TMB addition was very sharp irrespective of PHT (Fig. 2A and B). The pore diameter increased from 3.6 to 5.5 nm by PHT. When PHT was combined with TMB addition, as

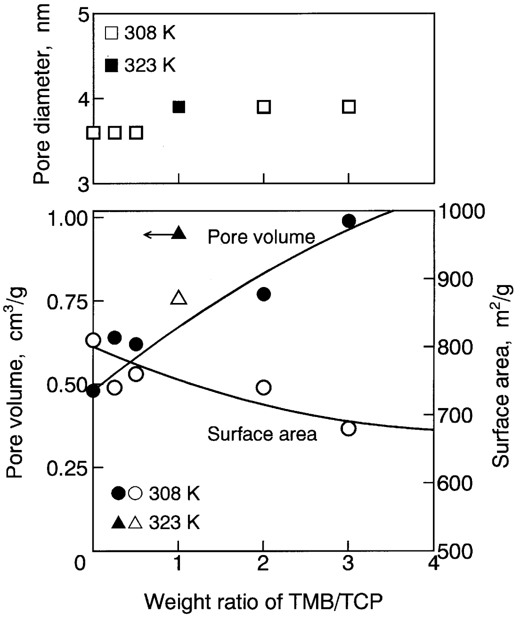

Fig. 1. Effect of weight ratio of TMB/TCP on pore properties and surface areas of SBA-15.

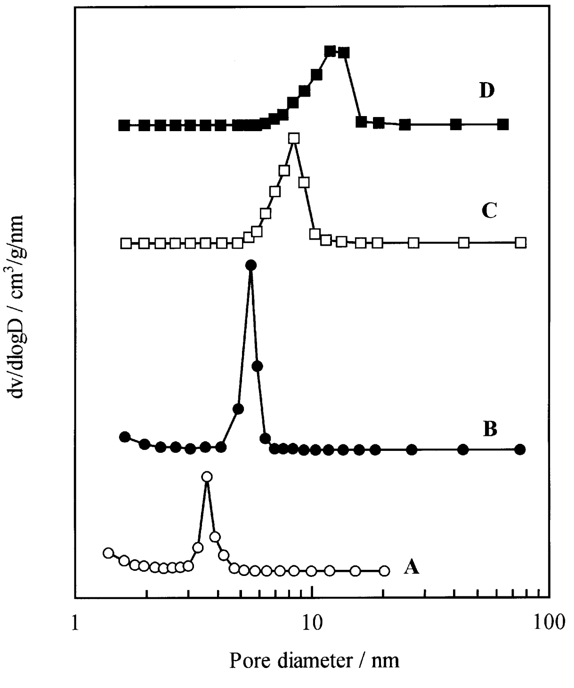

Fig. 2. Pore size distribution of SBA-15 synthesized under different conditions: (A) after reaction at 308 K; (B) with post-synthesis treatment (PST) at 380 K after reaction; (C) and (D) with PST after reaction in the presence of TMB at weight ratios of TMB/triblock copolymer of 0.50 and 1.0, respectively.

shown in Fig. 2C and D, the distribution was broad and the diameter was large, the degree of the two being higher at a larger weight ratio of TMB/TCP.

Pore properties and surface areas of SBA-15 materials are summarized in Table 1. PHT was more effective for increasing the pore diameter and volume than TMB addition. When PHT was carried out, the diameter and volume of SBA-15 increased with increasing weight of TMB added, and the largest values were 12 nm and 2.8 cm^3/g, respectively. Consequently, the SBA-15 with a larger pore diameter had a higher pore volume, whereas the SBA-15 with the diameter of 5.5 nm provided the highest surface area of 1000 m^2/g. As is seen in Table 1, five kinds of SBA-15 with pore diameters of 3.6–12 nm are denoted as SBA (3.6), SBA (5.5) and others.

The typical SAXS profiles for SBA-15 are illustrated in Fig. 3. The SBA (5.5) showed the strong (1 0 0) peak and very weak (1 1 0) and (2 0 0) signals, suggesting a high degree of hexagonal mesoscopic organization. On the other hand, only the weak shoulder peaks were observed at smaller scattering angles for the SBA (8.4), and no scattering signals were detectable for the SBA (12), though the latter is not given in Fig. 3. The observations show less organized pore structures of these samples. The $d(1\,0\,0)$ spacing for the SBA (5.5) was 9.9 nm. The wall thickness was calculated by $(\frac{2}{3}d(1\,0\,0)^{1/2}-$ average pore diameter) [4] to be 6.4 nm, which was similar to the values (3.4–6.4 nm) reported for SBA-15 samples with pore diameters of 5–6 nm [4].

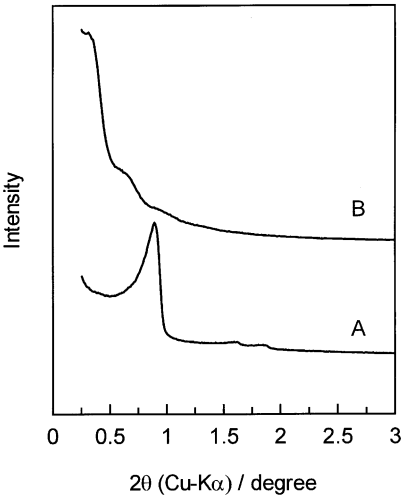

Fig. 3. SAXS profiles for SBA-15 with a pore diameter of 5.5 nm (A) or 8.4 nm (B).

3.2. Properties of SBA-15 supported Co catalysts

The XRD profiles after calcination at 773 K of Co catalysts supported on the SBA (3.6) are provided in Fig. 4, where a water, acetone, or ethanol solution of $Co(NO_3)_2$ is used for the impregnation method, the concentrations of Co^{2+} ions being 3–6 mg-Co/cm^3, unless otherwise described. At Co loading of 10 mass%, the XRD peaks of Co_3O_4 were detected for all the samples irrespective of the kind of the solution, and the highest diffraction intensity of the main peak was observed upon use of the water solution (Fig. 4A). When the concentration of Co^{2+} ions in water was doubled, the XRD pattern was almost unchanged. The average crystalline size of Co_3O_4 was dependent on the type of the solvent and calculated to be 20, 12 and 9.5 nm for water, acetone, and ethanol, respectively. The size with the acetone solution was slightly increased to 16 nm by using the SBA (3.9). Thus, all of the crystalline sizes estimated exceeded the pore diameter of SBA (3.6), which means that part of Co_3O_4 particles are formed on the external surface.

Since the use of ethanol as a solvent for $Co(NO_3)_2$ provided the relatively small size of Co_3O_4, ethanol was selected for impregnating $Co(CH_3COO)_2$ with

Table 1
Effects of both addition of TMB and PST on pore structures and surface areas of SBA-15

TMB/TCP (weight ratio)	PST	Pore diameter (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)	Name of SBA-15
0	No	3.6	0.48	810	SBA (3.6)
3.0	No	3.9	0.99	680	SBA (3.9)
0	Yes	5.5	1.1	1000	SBA (5.5)
0.5	Yes	8.4	1.8	830	SBA (8.4)
1.0	Yes	12	2.8	870	SBA (12)

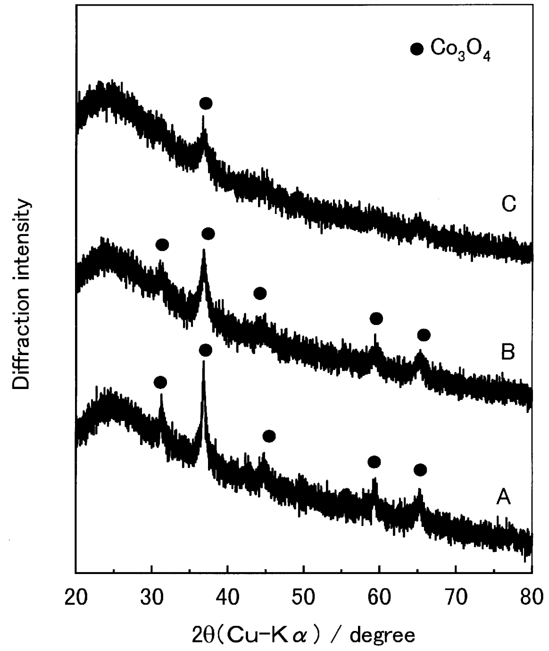

Fig. 4. XRD profiles after calcination at 773 K of Co catalysts loaded with different solutions of $Co(NO_3)_2$ on SBA-15 with a pore diameter of 3.6; Co loading, 10 mass%: (A) in water; (B) in acetone; (C) in ethanol.

SBA-15 supports, the concentration of Co^{2+} ions being 1–3 mg-Co/cm^3. Fig. 5 shows the XRD profiles after calcination at 773 K of Co catalysts loaded on SBA (3.6), SBA (5.5) and SBA (8.4). No diffraction lines attributable to Co_3O_4 were detectable for the SBA (3.6) with 10 mass% Co (Fig. 5A) and even for any supports with Co loading as high as 20 mass% (Fig. 5B–D). Further, when an acetone solution of $(CH_3COCHCOCH_3)_2Co$ was used in place of the acetate solution, no XRD peaks of any Co species were observed either. It has been reported that the use of metal acetylacetonates can retard crystallization reactions [10,11]. These observations strongly suggest that Co catalysts derived from $Co(CH_3COO)_2$ and $(CH_3COCHCOCH_3)_2Co$ exist as clusters inside the mesopores. The comparison of Figs. 4 and 5 shows that crystallization reactions of Co_3O_4 clusters and/or precursors proceed more readily with $Co(NO_3)_2$ than with $Co(CH_3COO)_2$ and $(CH_3COCHCOCH_3)_2Co$. Such the difference might be caused by the extent of interactions with a SiO_2 framework of SBA-15 support.

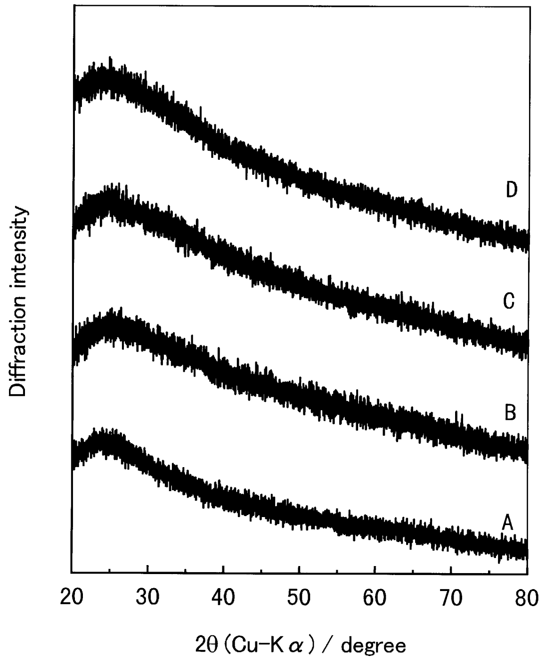

Fig. 5. XRD profiles after calcination at 773 K of Co catalysts loaded with an ethanol solution of $Co(CH_3COO)_2$ on SBA-15 supports with different pore diameters; Co loading, 10 mass% for A and 20 mass% for B–D; pore diameter, 3.6 nm for A and B, 5.5 nm for C, and 8.4 nm for D.

The 10 or 20 mass% Co/SBA-15 prepared with $Co(CH_3COO)_2$ had the same pore diameter as the corresponding SBA-15 support, except for the slightly increased diameter of the SBA (12) by catalyst addition. Pore volumes of Co/SBA-15 are summarized in Table 2. The comparison of Tables 1 and 2 indicates the remarkable decrease in pore volume by Co addition irrespective of the pore diameter of SBA-15 support. These observations support the above suggestion that Co catalysts derived from the acetate precursor are present as nanosized clusters inside the mesopores. The difference in the volume before and after Co loading, denoted as $(V_b - V_a)$, was approximately 0.08 cm^3/g at 10 mass% Co (Table 2). On the other hand, the 10 mass% Co/SBA-15 catalysts prepared from $Co(NO_3)_2$ tended to provide lower $(V_b - V_a)$ values. It is reasonable to understand that some of Co_3O_4 crystallites formed from the nitrate precursor are held on the outer surface of SBA-15, as indicated by the XRD measurements.

Table 2
Properties of SBA-15 supported Co catalysts prepared with an ethanol solution of $Co(CH_3COO)_2$ and the performances in FT synthesis

Support	Co loading (mass%)	Pore volume (cm^3/g)	$(V_b - V_a)$ (cm^3/g)[a]	Catalyst size (nm)[b]	CO conversion (mol.%)[c]
SBA (3.6)	10	0.35	0.082	0.54	–
SBA (3.6)	20	0.27	0.17	0.54	15[d]
SBA (3.6)	20[e]	0.29	0.14	0.51	6.7[f]
SBA (5.5)	20	0.68	0.43	0.74	–
SBA (8.4)	20	1.3	0.54	0.80	23
SBA (12)	20	1.8	0.94	0.96	–

[a] Difference in pore volume before and after Co loading.

[b] Calculated by using $(V_b - V_a)$ on the assumption that Co particles are spherical.

[c] After 2 h reaction at 523 K under 2.0 MPa.

[d] 11 mol.% at 503 K.

[e] Prepared with an acetone solution of $(CH_3COCHCOCH_3)_2Co$.

[f] At 503 K.

As is seen in Table 2, $(V_b - V_a)$ for 20 mass% Co/SBA-15 catalysts from $Co(CH_3COO)_2$ ranged 0.2–0.9 cm^3/g, and it was dependent on the pore diameter of SBA-15 and larger for the support with a larger pore diameter. This index for the SBA (3.6) support was almost the same with $Co(CH_3COO)_2$ and with $(CH_3COCHCOCH_3)_2Co$. When $(V_b - V_a)$ is assumed to be equal to total volume occupied by spherical Co clusters, one can calculate the average size, which is also provided in Table 2. The size estimated was <1 nm for all the catalysts and increased with increasing pore diameter of SBA-15 support.

When the SAXS measurement of the 20 mass% Co/SBA (5.5) catalyst was made, the intensities were almost unchanged, compared with those (Fig. 3A) before Co addition, but the $d(1\,0\,0)$ spacing was decreased slightly from 9.9 to 9.3 nm. The wall thickness estimated from the d value was 5.4 nm, which was lower than that (6.4 nm) before Co addition. These observations show that the hexagonal mesoscopic structure of the SBA support is almost remained even at Co loading as high as 20 mass%.

3.3. Performances of SBA-15 supported Co catalysts in FT synthesis

In preliminary runs, CO conversion over 20 mass% Co/SBA-15 increased with increasing time on stream up to approximately 1 h and appeared to be steady after 2 h. Table 2 thus shows CO conversion after 2 h over Co catalysts loaded on SBA (3.6) and SBA (8.4) supports. The catalyst with larger pore diameter and larger size of Co particles showed the slightly higher conversion at 523 K. Almost the same catalytic activity was observed at 503 K with $Co(CH_3COO)_2$ and with $(CH_3COCHCOCH_3)_2Co$ (Table 2). The main product was CH_4 in all cases. Since it is not clear whether the activity can correlate with the pore diameter or the particle size, to clarify this point should be the subject of future study.

CO conversions observed in the present work were lower than those (30–50 mol.%) reported with Co catalysts loaded on conventional supports [12,13], such as SiO_2, Al_2O_3, and TiO_2, under the similar reaction conditions as above. Lower activity of the present catalysts may be responsible for the small reducibility due to strong interactions with the framework of SBA-15. It can be expected that the reducibility, in other words, the catalytic activity, is improved by adding a small amount of a noble metal, such as Ir and Ru [13]. In FT synthesis where a wide variety of hydrocarbons is produced through propagation reactions of CH_2 chains, the use of SBA-15 supports with uniform pore size distribution might provide hydrocarbon products with narrow molecular weight distribution.

4. Conclusions

Several types of SBA-15 with different pore diameters of 3.6–12 nm have been synthesized under different reaction conditions, utilized as supports of high loading of Co catalysts derived from different precursors, and characterized by N_2 adsorption, XRD, and SAXS measurements. The conclusions are summarized as follows:

1. PHT after reaction of an acidic homogeneous mixture of a triblock copolymer and TEOS works more efficiently for increasing the pore diameter and volume of SBA-15 than the addition of TMB before reaction. When the two is combined, the pore diameter further increases from 3.6–5.5 to 8.4–12 nm, but the size distribution is rather broad and pore structures are less organized.
2. The use of an acetone, ethanol, or water solution of $Co(NO_3)_2$ during impregnation with the SBA-15 with a pore diameter of 3.6 nm provides larger Co_3O_4 crystallites than the pore size, regardless of the kind of the solvent, showing that part of Co_3O_4 is held on the external surface of the support.
3. When an ethanol solution of $Co(CH_3COO)_2$ or an acetone solution of $(CH_3COCHCOCH_3)_2Co$ is used in place of the above precursor, no XRD peaks of Co_3O_4 are detectable even at Co loading as high as 20 mass%. Further, Co addition markedly reduces the pore volume of SBA-15, irrespective of the pore diameter. It is evident that Co catalysts exist as clusters inside the mesopores.
4. The comparison of the SAXS profiles before and after Co addition reveal that the hexagonal structure of the SBA-15 support with pore diameter of 5.5 nm is almost retained in the presence of 20 mass% Co.
5. The 20 mass% Co/SBA catalysts are active in preliminary FT runs at 503–523 K under 2.0 MPa, though the activity is lower than those reported with conventional supports because possibly of lower reducibility of the present catalysts.

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References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[2] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, Bull. Chem. Soc. Jpn. 63 (1990) 988.
[3] A. Corma, Chem. Rev. 97 (1997) 2373.
[4] E. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[5] E. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[6] M. Cheng, Z. Wang, K. Sakurai, F. Kumat, T. Saito, T. Komatsu, T. Yashima, Chem. Lett. (1999) 131.
[7] Z. Luan, M. Hartmann, D. Zhao, W. Zhou, L. Kevan, Chem. Mater. 11 (1999) 1621.
[8] Z. Luan, E.M. Maes, P.A.W. van der Heide, D. Zhao, R.S. Czernuszewicz, L. Kevan, Chem. Mater. 11 (1999) 3680.
[9] M.S. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, Chem. Mater. 12 (2000) 898.
[10] M.G. White, M.B. Mitchell, V.R. Chakravarthy, Langmuir 10 (1994) 4523.
[11] P. van der Voort, E.F. Vansant, Micropor. Mesopor. Mater. 38 (2000) 385.
[12] S. Bessell, Appl. Catal. A 96 (1993) 253.
[13] E. Iglesia, S.L. Soled, R.A. Fiato, G.H. Via, J. Catal. 143 (1993) 345.