Synthesis of Zr-grafted SBA-15 as an Effective Support for Cobalt Catalyst in Fischer–Tropsch Synthesis

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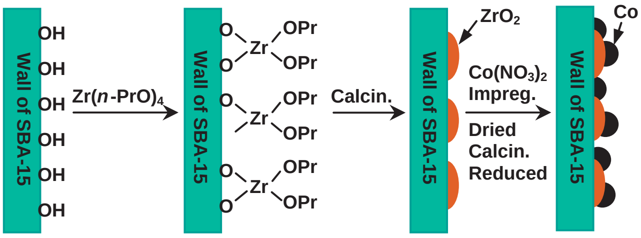
Zr-grafted SBA-15 is the most effective support among Zr-modified SBA-15 materials prepared by various methods for supporting Co catalyst in the Fischer–Tropsch synthesis due to the large BET surface area of the support and the strong interaction between Zr promoter and Co catalyst.

Fischer–Tropsch (F–T) synthesis produces sulphur-free *n*-alkanes from syngas, while the latter can be obtained from the gasification and/or reforming of biomass, coal, and natural gas. Co catalyst is very attractive for F–T synthesis owing to the high activity (compared to Fe catalyst) and the low price (compared to Ru catalyst). SiO_2 is an effective support for Co catalyst in F–T synthesis. The surface area and pore size determine the performance of SiO_2 support for F–T synthesis.[1] Mesoporous silicas have been reported as good supports for F–T synthesis due to the large surface area, uniform-sized pores, and high thermal stability.[2] SBA-15 is the most attractive among mesoporous silicas owing to the thick walls and large pores.[3]

Zr is an effective promoter for Co/SiO_2 catalyst in F–T synthesis because it increases the reduction degree of Co_3O_4 particles.[4] Co/Zr–MCM-41 and Co/Zr–FSM-16 have been reported as good catalysts for F–T synthesis.[5] Impregnation, precipitation, and isomorphous substitution are the methods that usually are used for introducing promoters. Chemical graft is a new method for introducing a promoter into a catalyst.[6] Ti-grafted MCM-41 is a good support for Au catalyst in the epoxidation of propene.[7] In the present study, we have reported that chemical graft is the best method for introducing Zr promoter into Co/SBA-15 catalyst for F–T synthesis.

SBA-15 was synthesized using TEOS as a silica source, using $EO_{20}PO_{70}EO_{20}$ as a template, and using trimethylbenzene as a swelling agent in a weak acidic aqueous solution.[2] The solution was heated at 308 K for 20 h and then heated at 353 K for 48 h. As-synthesized SBA-15 was obtained by filtrating out solvent and drying in air. SBA-15 support was obtained after removing the template by calcination at 773 K for 3 h.

Zr-SBA-15 (i) was prepared by a wet impregnation method using $ZrO(NO_3)_2$ aqueous solution. Zr-SBA-15 (p) was prepared by a precipitation method using $ZrO(NO_3)_2$ solution and Na_2CO_3 precipitant.[8] Zr-SBA-15 (s) was prepared by an isomorphous substitution method, through adding $ZrO(NO_3)_2$ in the initial solution before heat in the synthesis process, in order to introduce Zr^{4+} into Si^{4+} position in the SBA-15 framework.[9] Zr-SBA-15 (g) was prepared by a chemical graft method (Scheme 1). In the grafting procedure, calcined SBA-15 was dispersed in dry ethanol containing Zr(*n*-PrO)$_4$ for 8 h at room temperature. After filtering out solvent, the solid was washed with dry ethanol, dried in air, and calcined at 773 K for 3 h. The Zr amounts in various Zr-modified SBA-15 supports were controlled at about 10 wt %.



Scheme 1. Synthesis route of Co/Zr-SBA-15 (g) catalyst.

Co catalysts were prepared by a wet impregnation of $Co(NO_3)_2$ aqueous solution on various supports. After drying at 383 K for 24 h, the samples were calcined at 673 K for 3 h. The Co loading was 15 wt % in each catalyst.

The F–T synthesis reaction was carried out using a gas-flowed semibatch system equipped with a 500-mL autoclave. The catalysts were reduced in a H_2 flow at 673 K for 10 h before reaction. In a typical reaction, 10-g catalyst was suspended in 200-mL *n*-hexadecane in the autoclave reactor. The feed gas consisted of 60% H_2, 30% CO, 3% Ar, and 7% N_2. Ar, N_2, CO, H_2, and CO_2 were analyzed by an on-line TCD-GC and C_1–C_4 hydrocarbons were analyzed by an on-line FID-GC. Liquid C_{5+} hydrocarbons were analyzed by an Agilent 6890 N FID-GC equipped with a UA-DX30 capillary column.

The low-angle XRD patterns of various supports are shown in Figure 1. SBA-15 exhibited a very strong reflection corresponding to (100) plane and two weak reflections of (110) and (200) planes, implying a high degree of hexagonal mesoporous organization in the sample. Either Zr-SBA-15 (s) or Zr-SBA-

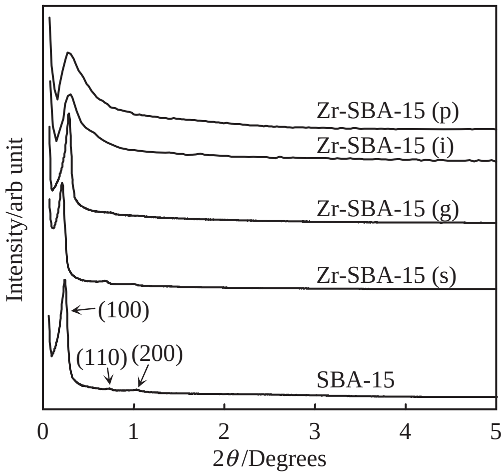


Figure 1. XRD patterns of various samples. The amount of Zr is about 10 wt % for each Zr-containing sample.

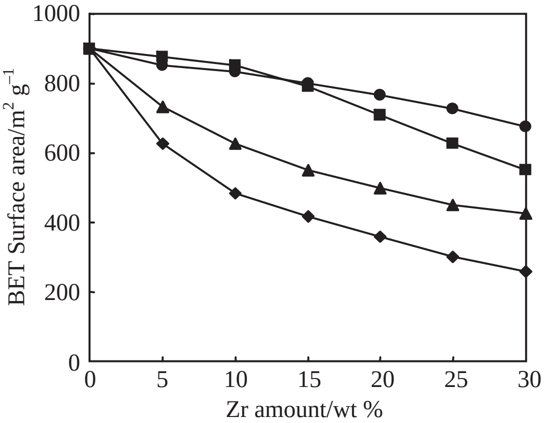


Figure 2. Dependence of Zr amount on BET surface area for various calcined supports. (●): Zr-SBA-15 (g), (■): Zr-SBA-15 (s), (▲): Zr-SBA-15 (i), (◆): Zr-SBA-15 (p).

15 (g) showed a very strong (100) reflection with a little shift in position compared to that of SBA-15. On the other hand, the (100) reflections became low and broad in the XRD patterns of Zr-SBA-15 (i) and Zr-SBA-15 (p), implying that the mesoporous organization greatly decreased in the samples.

The dependence of Zr amount on BET surface area for various supports (calcined at 773 K for 3 h) is shown in Figure 2. SBA-15 possesses a high BET surface area of 900 m^2 g^{-1}. The BET surface areas of Zr-SBA-15 (i) and Zr-SBA-15 (p) greatly decreased after introducing 5 wt % Zr in SBA-15, which implies that ZrO_2 particles were formed in SBA-15 pores and blocked the pores. The BET surface area of Zr-SBA-15 (s) was kept at a high value at Zr $<$ 15 wt % but rapidly decreased at Zr $>$ 15 wt %. Fifteen wt % is the maximum value for introducing Zr^{4+} ion into SBA-15 framework.[9] Zr-SBA-15 (g) has a high surface area ($>$700 m^2 g^{-1}) even the Zr amount up to 30 wt %. In Zr-SBA-15 (g), the Zr^{4+} ions were uniformly fixed on SBA-15 surface by chemical bond before calcination, and thus a high surface area could be kept upon calcination.

The results of the F–T synthesis over various catalysts are shown in Table 1. The catalytic activity of each catalyst did not decrease during reaction at 503 K for 8 h. Co/SBA-15 showed a CO conversion of 58.7%, which was much higher than that over Co/SiO_2 (36.5%) owing to the high surface area of SBA-15 (SBA-15: 900 m^2 g^{-1}; SiO_2 (Q-10 from Fuji Silysia Chemical Ltd.): 300 m^2 g^{-1}). Co/SBA-15 showed a selectivity for C_{5+} hydrocarbons (68.1%) similar to that over Co/SiO_2 (67.6%) due to their similar pore sizes (SBA-15: 11 nm; SiO_2: 10 nm). Co/ZrO_2 showed a high selectivity for C_{5+} hydrocarbons (78.3%) but it showed a very low CO conversion (20.3%) owing to the low surface area (120 m^2 g^{-1}). All Zr-modified Co/SBA-15 catalysts showed higher CO conversions than that over Co/SBA-15. The supported Co_3O_4 particles are difficult to be reduced to Co^0 active species even in a H_2 flow at 673 K for 10 h. The interaction between Zr promoter and Co_3O_4 particles favors the reduction of Co_3O_4 particles to active Co^0 species at low temperature and thus improves the catalytic avitivity.[4] The CO conversion followed the order Co/Zr-SBA-15 (g) $>$ Co/Zr-SBA-15 (s) $>$ Co/Zr-SBA-15 (i) $>$ Co/Zr-SBA-15 (p).

Table 1. F–T synthesis over various supported Co catalysts[a]

Catalyst[b]	CO conv./%	CH_4 select./%	C_{5+} select./%	α[d]
Co/SBA-15	58.7	16.3	68.1	0.80
Co/SiO_2	36.5	16.9	67.6	0.79
Co/ZrO_2	20.3	10.2	78.3	0.87
Co/Zr-SBA-15 (p)[c]	62.4	14.5	70.4	0.85
Co/Zr-SBA-15 (i)[c]	66.1	9.1	80.1	0.84
Co/Zr-SBA-15 (s)[c]	73.9	10.8	73.9	0.82
Co/Zr-SBA-15 (g)[c]	81.4	8.5	80.9	0.85

[a]Reaction conditions: 1.0 MPa, 503 K, $CO/H_2 = 1/2$, $W/F = 20$ g h mol^{-1}. [b]Co loading: 15 wt %. [c]Zr loading: 10 wt %. [d]α: chain growth probability, calculated from Schultz–Flory distribution.

Both physical interaction and chemical interaction exist between support and metal particles in a metal-supported catalyst. Introduction of Zr promoter into Co/SBA-15 catalyst increases the chemical interaction (by increasing the reduced degree of Co_3O_4 particles) but decreases the physical interaction (by decreasing the BET surface area of support). It is important to develop a method which can balance the two aspects. Co/Zr-SBA-15 (p) showed the lowest CO conversion among four Zr-modified Co/SBA-15 catalysts owing to the big fall in BET surface area. Isomorphous substitution could introduce Zr promoter into SBA-15 with keeping the BET surface area at a high level. However, although 10 wt % Zr-SBA-15 (s) possesses a larger BET surface area than that of 10 wt % Zr-SBA-15 (g) (Figure 2), Co/Zr-SBA-15 (s) showed a lower CO conversion than that over Co/Zr-SBA-15 (g) (Table 1). The Zr^{4+} ions were introduced into the SBA-15 framework in Zr-SBA-15 (s) (by isomorphous substitution) but the Zr^{4+} ions were distributed on the SBA-15 surface in Zr-SBA-15 (g) (by chemical graft). The Zr promoter on SBA-15 surface has more chance to sufficiently contact with the supported Co_3O_4 particles. From H_2 chemisorption, the Co particle sizes were 10.8, 7.5, 6.6, 8.7, and 8.9 nm for Co/SBA-15, Co/Zr-SBA-15 (s), Co/Zr-SBA-15 (g), Co/Zr-SBA-15 (i), and Co/Zr-SBA-15 (p), respectively. Therefore, we supposed that the interaction between Zr promoter and Co catalyst was stronger in Co/Zr-SBA-15 (g), which caused Co/Zr-SBA-15 (g) to catalyze the F–T synthesis more efficiently than Co/Zr-SBA-15 (s).

In conclusion, chemical graft is the most effective method for introducing Zr promoter into Co/SBA catalyst for the F–T synthesis because the method kept a large BET surface area of support as well as made the best use of Zr promoter.

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