# Enhancement in the reducibility of cobalt oxides on a mesoporous silica supported cobalt catalyst†

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**The silylation of SBA-15 enhances the reducibility of cobalt oxides on a SBA-15 supported cobalt catalyst, and consequently increases the catalytic activity for Fischer–Tropsch synthesis of hydrocarbons from syngas and selectivity for longer chain products.**

Fischer–Tropsch (FT) synthesis is well-known to produce very clean alternative fuels from coal derived CO and $H_2$. The FT synthesised fuels consist primarily of linear paraffins and are further characterized by low aromaticity and zero sulfur content. Cobalt catalysts have been widely investigated for the FT synthesis since they give high yields of long chain paraffins and have long active life times.[1,2] The activity of cobalt catalysts for the FT synthesis depends primarily on the overall amount of exposed metallic cobalt atoms. Thus, a highly active cobalt catalyst requires a high dispersion of cobalt metal. Very uniform mesoporous materials such as MCM-41 and SBA-15 have been recently used as supports for cobalt.[3,4] The high surface area (500–1500 $m^2\ g^{-1}$) of the mesoporous materials gives higher metal dispersions at higher cobalt loadings compared with conventional amorphous silicas. Furthermore, the uniform pore diameters (2–30 nm) permit better control of the cobalt particle size and the distribution of hydrocarbon products from the FT synthesis.[5,6]

The hydrocarbon yields from the FT synthesis should be significantly enhanced by greater reducibility of cobalt oxide species in silica supported catalysts. The formation of cobalt oxide species (crystalline $Co_3O_4$, amorphous cobalt oxides and cobalt silicates) depends on the surface nature of the support and the treatment conditions such as calcination temperature, pH of the precursor solution, *etc.*[7] After reduction at elevated temperatures, the cobalt oxides interact strongly with the support and cobalt silicates remain in an irreducible state. In particular, water vapor trapped in the mesoporous silica materials can increase the amount of irreducible cobalt oxides.[8]

In the present study, enhancement of the reducibility of cobalt oxides supported on SBA-15 has been investigated, and a new approach to achieving highly reducible cobalt oxides that promote cobalt activity for the FT synthesis is reported. The reducibility of the cobalt catalyst is greatly increased after the modification of SBA-15 *via* a hydrophobic silylation. Furthermore, methane formation is significantly decreased, and carbon monoxide conversion and yields of higher linear hydrocarbons are considerably increased.

Mesoporous silica SBA-15 was obtained by a procedure described elsewhere.[9] A triblock polymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_{av}$ = 5800, BASF) was used as the structure-directing agent, and anhydrous sodium metasilicate ($Na_2SiO_3$, Aldrich) was used as the silica source for the SBA-15 material. Silylation of SBA-15 was carried out with hexamethyldisilazane (HMDS, Aldrich, 99%). The procedure for silylation of SBA-15 was as follows:[10,11] a sample of SBA-15 was evacuated at 150 °C for 2 h to remove any residual surface water. The SBA-15 sample (1 g) was placed in a hexane solution of HMDS. Three different levels of silylation were achieved using 1.03, 5.16 and 10.33 mmol of HMDS dissolved in hexane. Each mixture was stirred under reflux at 80 °C for 24 h, and then the samples were filtered, washed three times with hexane, and dried under vacuum ($1.0 \times 10^{-2}$ torr) at room temperature for 8 h. Cobalt supported on SBA-15 catalysts (6 wt% in cobalt content) were prepared with (cyclooctadiene)(cyclooctenyl)cobalt ($Co(C_8H_{12})(C_8H_{13})$) using gas-phase incorporation. The silylated SBA-15 sample was placed in a rotary mixer, and mixed with the cobalt compound supplied from an external flask for 96 h. Complete incorporation was confirmed by analysis of the $^1H$ NMR spectra for discontinuous evolution of cyclooctene. The cobalt impregnated sample was calcined in air at 550 °C for 12 h. The calcined sample was reduced under hydrogen at 450 °C for 4 h to obtain active metallic cobalt for the FT synthesis. The reduction of cobalt oxides in the sample was evaluated by temperature programmed reduction (Micromeritics). The $H_2$ consumption of the sample was calculated using the reduction of CuO as the standard.

The FT synthesis was carried out in a fixed-bed stainless steel reactor (5 mm I. D. and 168 mm length) at 100 psi and 265 °C. A gas hourly space velocity of 2100 $h^{-1}$ at STP and a $H_2$–CO molar ratio of 2 were used. The gas flow rates for reactant gases (CO, $H_2$) and internal standard (Ar) were controlled by mass flow controllers (MKS). Iron carbonyl impurities in the CO reactant stream were removed by using a $PbO_2$–$Al_2O_3$ trap. The test for the FT synthesis was carried out for 12 h after stabilization of the catalyst activity was reached in 4 h. Reactant gases and hydrocarbon products below $C_5$ were analyzed by gas chromatography (Shimadzu) with a TCD detector and a capillary column (CarboPlot, 0.53 mm I. D. and 30 m length). Hydrocarbon products higher than $C_5$ were analyzed with an online GC-MS (Hewlett-Packard) and a capillary column (DB-5, 0.25 mm I. D. and 1 m length).

All the samples exhibit XRD patterns which are typical of the 2-D hexagonal structure of the original SBA-15, as shown in Fig. 1. It is noteworthy that the mesopore structure is strongly retained

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† Electronic supplementary information (ESI) available: Fig. S1. See http://www.rsc.org/suppdata/cc/b4/b417536k/

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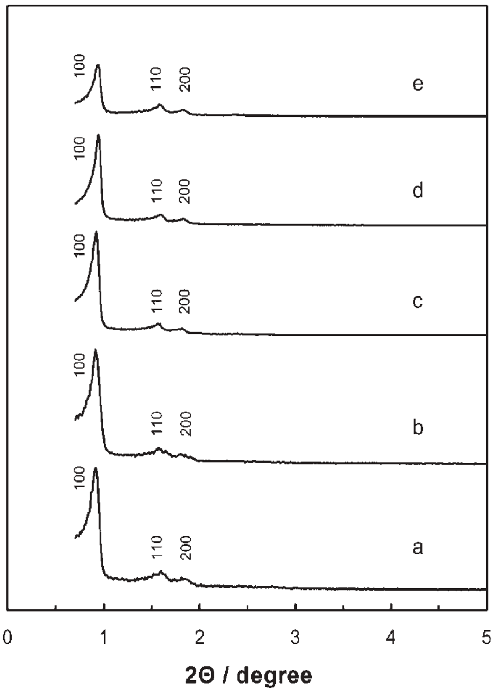

**Fig. 1** XRD patterns for the cobalt–SBA-15 catalysts: (a) SBA-15, (b) 6CoSBA, (c) 6CoSBA-H1, (d) 6CoSBA-H2 and (e) 6CoSBA-H3.

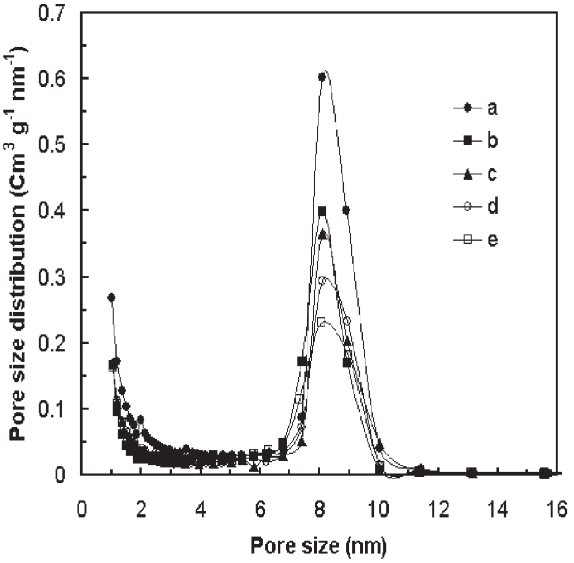

**Fig. 2** Pore size distributions calculated from nitrogen adsorption data at 77 K for the cobalt–SBA-15 catalysts: (a) SBA-15, (b) 6CoSBA, (c) 6CoSBA-H1, (d) 6CoSBA-H2 and (e) 6CoSBA-H3.

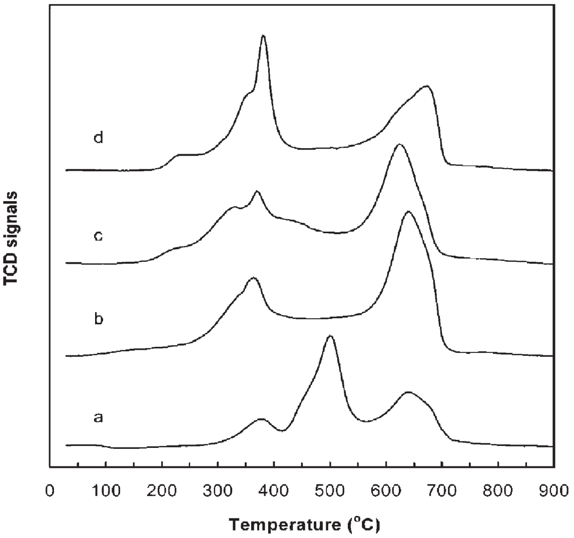

**Fig. 3** TPR profiles for the cobalt–SBA-15 catalysts: (a) 6CoSBA, (b) 6CoSBA-H1, (c) 6CoSBA-H2 and (d) 6CoSBA-H3.

after silylation with HMDS and cobalt impregnation. Pore structural parameters calculated from nitrogen adsorption and desorption isotherms for the cobalt SBA-15 catalysts are listed in Table 1. The shape of the nitrogen adsorption isotherms for the cobalt SBA-15 catalysts was similar to that of the original SBA-15 (see Fig. S1 of the ESI†). After the silylation, the BET surface area and pore volume of the SBA-15 are slightly decreased. However, after cobalt impregnation, the BET surface area and pore volume for the cobalt SBA-15 catalysts are significantly further decreased. These results indicate that cobalt impregnation impacts both BET surface area and pore volume more than silylation does. Table 1 and Fig. 2 indicate that after the silylation and cobalt impregnation of the catalyst, the pore structure is nearly unchanged. This is in good agreement with the XRD patterns for the cobalt SBA-15 catalysts.

The mean $Co_3O_4$ crystallite sizes deduced from the XRD data using the Scherrer equation and the reduction percentage of the cobalt oxides at temperatures less than 450 °C are presented in Table 1. The crystallite size shows a clear dependence on the amount of the silylating agent, with larger particles being formed at higher HMDS loading. The peak in the 420–570 °C range in the TPR profiles, corresponding to the reduction of cobalt oxides strongly interacting with the SBA-15, disappears with the introduction of the HMDS as shown in Fig. 3. Furthermore, the

**Table 1** Physical and chemical properties of the cobalt–SBA-15 catalysts

| Catalyst | HMDS[a]/mmol $g^{-1}$ | $S_{BET}$[b]/$m^2$ $g^{-1}$ | $V_p$ [c]/g $cc^{-1}$ | $D_p$[d]/nm | $Co_3O_4$ diameter[e]/nm | Reduction[f](%) |
|---|---|---|---|---|---|---|
| SBA-15 | — | 724 | 1.24 | 8.09 | — | — |
| 6CoSBA | — | 463 | 0.90 | 8.09 | 10.4 | 15 |
| 6CoSBA-H1 | 1.03 | 453 | 0.87 | 8.09 | 11.2 | 45 |
| 6CoSBA-H2 | 5.16 | 432 | 0.78 | 8.09 | 12.1 | 48 |
| 6CoSBA-H3 | 10.33 | 421 | 0.76 | 8.07 | 14.7 | 49 |

[a] Amount of HMDS doped in 1 g of SBA-15. [b] Surface area calculated with BET method from $N_2$ adsorption. [c] Total pore volume calculated at $p/p_0 = 0.993$. [d] Pore diameter calculated using BJH method. [e] $Co_3O_4$ crystallite diameter calculated from the widths of XRD peaks using the Sherrer equation ($2\theta = 36.68°$). [f] Reduction degree of cobalt oxides during TPR at 30–450 °C.

**Table 2** CO conversion, hydrocarbon selectivity and chain growth probability of the cobalt–SBA-15 catalysts

| | | Product selectivity/C mol% | | | | |
|---|---|---|---|---|---|---|
| Catalyst | CO conversion (%) | $C_1$ | $C_2$–$C_4$ | $C_5$–$C_{10}$ | $C_{10+}$ | $\alpha$[a] |
| 6CoSBA | 5.2 | 12.5 | 48.8 | 34.3 | 4.4 | 0.83 |
| 6CoSBA-H1 | 10.7 | 4.1 | 25.9 | 57.8 | 12.2 | 0.86 |
| 6CoSBA-H2 | 10.4 | 3.9 | 24.3 | 58.7 | 13.1 | 0.87 |
| 6CoSBA-H3 | 9.6 | 4.0 | 14.4 | 64.6 | 17.0 | 0.90 |

[a] Chain growth probability obtained from Anderson–Schulz–Flory equation.

reducibility of cobalt oxides to metallic cobalt increases with silylation, and the degree of the reducibility depends on the HMDS loading. It is reasonable that the silylation can hinder the strong interaction between the cobalt oxide species and the surface of SBA-15, which is probably due to the hydrophobic surface nature. Therefore, it can stimulate the cobalt–SBA-15 catalyst to contain highly reducible cobalt oxides even though the mean diameter of the $Co_3O_4$ particles increases.

The FT synthesis results are summarized in Table 2. In principle, the CO conversion is proportional to the dispersion of reduced metallic cobalt. The low CO conversion of the unsilylated cobalt–SBA-15 catalyst can be related to the low reducibility of the cobalt oxides. The formation of methane and light hydrocarbons ($C_2$–$C_4$) is greatly decreased with the silylation of SBA-15, and the selectivity for higher hydrocarbons ($C_{5+}$) and chain growth probability are significantly enhanced with the addition of HMDS. Furthermore, Table 2 shows that the CO conversion and the distribution of hydrocarbon products are influenced by the loading of HMDS.

Silica materials such as SBA-15 have surface functional groups such as silanol (Si–OH) that can interact with cobalt oxides.[12] These cobalt oxides are not easily reduced at lower temperatures. Silylation acts as a grafting method which modifies the surface silanol groups, yielding a highly hydrophobic silica-like surface.[10,11] In the present work, we observed that when HMDS is added, the reducibility of the cobalt oxides increased remarkably and the crystallite size of $Co_3O_4$ also increased. Many studies have shown that the addition of costly metals such as Ru and Re promote the reduction of cobalt oxides supported on silica.[13,14] It seems that the silylation method presented in this study is more cost effective for the enhancement of reducibility of cobalt oxides than expensive doping with metals such as ruthenium and rhenium.

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## Notes and references

1 B. Ernst, S. Libs, P. Chaumette and A. Kiennemann, *Appl. Catal., A*, 1999, **186**, 145.
2 G. Jacobs, T. K. Das, Y. Zhang, J. Li, G. Racoillet and B. H. Davis, *Appl. Catal., A*, 2002, **233**, 263.
3 J. Panpranot, J. G. Goodwin, Jr. and A. Sayari, *Catal. Today*, 2002, **77**, 269.
4 Y. Ohtsuka, Y. Takahashi, M. Noguchi, T. Arai, S. Takasaki, N. Tsubouchi and Y. Wang, *Catal. Today*, 2004, **89**, 419.
5 Y. Wang, M. Noguchi, Y. Takahashi and Y. Ohtsuka, *Catal. Today*, 2001, **68**, 3.
6 A. Y. Khodakov, A. Griboval-Condtant, R. Bechara and F. Villain, *J. Phys. Chem. B*, 2001, **105**, 9805.
7 A. Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson and P. Chaumette, *J. Catal.*, 1997, **168**, 16.
8 J. Panpranot, J. G. Goodwin, Jr. and A. Sayari, *J. Catal.*, 2002, **211**, 530.
9 J. M. Kim and G. D. Stucky, *Chem. Commun.*, 2000, 1159.
10 R. R. Sever, R. Alcala, J. A. Dumestic and T. W. Root, *Microporous Mesoporous Mater.*, 2003, **66**, 53.
11 H. Yang, G. Zhang, X. Hong and Y. Zhu, *Microporous Mesoporous Mater.*, 2004, **68**, 119.
12 J. El Haskouri, S. Cabrera, C. J. Gomez-Garcia, C. Guillem, J. Latorre, A. Beltran, D. Beltran, M. D. Marcos and P. Amoros, *Chem. Mater.*, 2004, **16**, 2805.
13 H. Schultz, *Appl. Catal., A*, 1999, **186**, 3.
14 A. Martinez, C. Lopez, F. Marquez and I. Diaz, *J. Catal.*, 2003, **220**, 486.