Direct Synthesis and Spectroscopic Evidence of Framework Co(II) ions in SBA-15 Mesoporous Molecular Sieves

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CoSBA-15 with different n_{Si}/n_{Co} ratio have been synthesized in acidic media using nonionic surfactants and characterized, for the first time, by XRD, AAS, N_2 adsorption, UV–vis DRS and ESR spectroscopy. Spectroscopic data show that all cobalt atoms in CoSBA-15 are extensively in tetrahedral coordination.

Highly ordered large pore mesoporous silica SBA-15, possess a regular 2-D array of tubular channels with considerably thicker pore walls as compared to MCM-41, has been recently synthesized using an amphiphilic triblock copolymer with hydrophobic and hydrophilic segments as the structure-directing agent in highly acidic media.[1] However, incorporation of metal ion into the framework of SBA-15 and SBA-1 is very difficult because of the strongly acidic synthesis conditions.[2,3] Several studies are dealing with incorporation of metal ions such as Al, V, and Ti into SBA-15 by only post synthetic grafting method.[4,5] During materials preparation via post synthetic methods often metal oxides are formed in the channels which may reduce the specific surface area, pore volume and pore diameter or play a negative role in catalysis.[7] Cobalt-substituted molecular sieves are of tremendous interest in catalysis since these materials contain redox active sites. Recently, Thomas et al.[6] have reported the terminal oxidation of *n*-pentane, *n*-hexane and *n*-octane by air yielding alcohols, aldehydes and the corresponding acids using a cobalt-containing molecular sieve with AEI structure. In the present communication, we report the direct synthesis of Co in SBA-15 with different n_{Si}/n_{Co} molar ratio in acidic media and characterize the above materials extensively by XRD, N_2 adsorption, AAS, UV–vis DRS, and ESR spectroscopy.

CoSBA-15 materials with various n_{Si}/n_{Co} ratios were prepared by using the following procedure: Amphiphilic triblock copolymer (4 g) were dispersed in 30 g of water and stirred for 4 h. Thereafter, 10 mL of 2 M HCl solution in 60 mL of water was added and stirred for 2 h. Then 9.0 g of tetraethyl orthosilicate (TEOS) and appropriate amount of cobalt acetate were added directly into the homogeneous solution under stirring. The resulting gel was aged at 40 °C for 24 h and finally heated to 100 °C for 24 h. The molar gel composition of the synthesis mixture was 1 TEOS : 0.07–0.2 CoO : 0.016 P123:0.46 HCl:127 H_2O. After synthesis, the solids obtained were calcined in flowing air at 540 °C to decompose the triblock copolymer.

The n_{Si}/n_{Co} molar ratios of all the samples under investigation are summarized in Table 1. It can be seen from the Table 1 that Co in the gel are incorporated into the solid is lower than the input gel composition. This could be due to the higher solubility of Co source in highly acidic medium. However, n_{Si}/n_{Co} ratio of >41 has been achieved. Figure 1 shows the powder XRD patterns of CoSBA-15 samples after calcination. The relatively well-defined patterns are similar to those of SBA-15 materials as described by Zhao et al.[1] As can be seen in Figure 1, the XRD pattern of all calcined CoSBA-15 materials displays three or four well resolved peaks which are indexed to (100), (110), (200), and (210) reflections of the hexagonal space group *p*6*mm*. The existence of (200) and (210) peaks indicates excellent textural uniformity of the material. Upon calcination of the as-synthesized materials, the XRD patterns of CoSBA-15 became better resolved and the intensity of the XRD patterns increased significantly as a result of the removal of the intercalated polymeric template. The unit cell parameter (a_0) of all calcined CoSBA-15 samples is given in Table 1. The unit cell parameter of CoSBA-15 samples is higher than its pure silica analog. It is important to note that a_0 of CoSBA-15(41) is very low compared with those of other CoSBA-15 samples. Moreover, the intensity of (100) peak decreases with decreasing n_{Si}/n_{Co} ratio. This may be due to minor structure collapse of high cobalt content SBA-15 samples upon calcination.

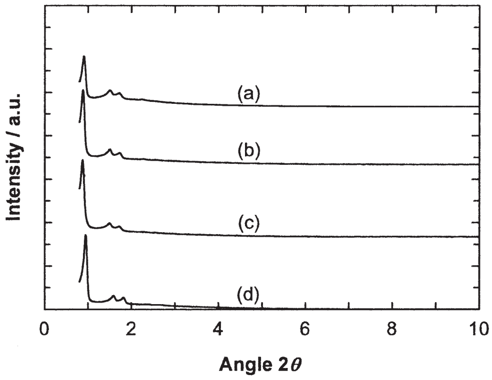

Figure 1. XRD powder patterns of calcined CoSBA-15: (a) SBA-15, (b) CoSBA-15(41), (c) CoSBA-15(60), and (d) CoSBA-15(74).

The nitrogen adsorption–desorption isotherms and textural parameters such as specific surface area, specific pore volume

Table 1. Synthesis and physicochemical properties of CoSBA-15 materials with different n_{Si}/n_{Co} ratio

Catalyst	n_{Si}/n_{Co}		a_o/	A_{BET}/	d_p,	V_p/
	Gel	AAS	nm	m^2/g	BJH/nm	cm^3/g
SBA-15	–	–	10.1	910	9.2	1.25
CoSBA-15(41)	5	41	10.8	951	8.5	1.18
CoSBA-15(60)	7	60	11.8	1020	9.7	1.31
CoSBA-15(74)	14	74	11.7	1027	9.2	1.32

and pore diameter of the CoSBA-15 prepared using different n_{Si}/n_{Co} ratios are shown in Figure 1S (see supplementary information) and Table 1, respectively. All the isotherms are found to be of type IV in nature as per the IUPAC classification and exhibited a H1 type broad hysteresis loop, which is typical of SBA-15 material.[1] As can be seen in Table 1, the specific surface area and specific pore volume systematically increases as the n_{Si}/n_{Co} ratio increases. The specific surface area amounts to 951 m^2/g for CoSBA-15(41) and increases to 1027 m^2/g for CoSBA-15(74) and the specific pore volume increases from 1.18 to 1.32 cm^3/g for the same samples. Moreover, the pore diameter of CoSBA-15(41) is small as compared with its pure silica analog. The low specific pore volume, specific surface area and pore diameter of CoSBA-15(41) sample could be attributed to either the partial collapse of the structural order or the formation of cobalt oxide species inside the mesopores during calcination.

The UV–visible DRS spectra of calcined CoSBA-15 samples are shown in Figure 2. It exhibits a strong absorption in the region 15500–20000 cm^{-1} which is characteristics of a d–d electron transition of tetrahedrally coordinated Co with d^7 configuration, and its intensity increases with increasing Co content. This absorption consists of three components with maxima at 19531, 16977, and 15600 cm^{-1} which are caused by Jahn–Teller distortions and/or by spin–orbit coupling during the spin-allowed ${}^4A_2 \rightarrow {}^4T_1$ transition of the tetrahedrally coordinated divalent cobalt species.[7] Moreover, a broad band in the UV region between 35000 and 40000 cm^{-1} centered at 37174 cm^{-1} is also observed for all samples. This has been assigned to a low-energy charge transfer between the oxygen ligands and central Co^{2+} ion in tetrahedral symmetry[8] or own absorption of the molecular sieves.[9,10] All these results revealed that the majority of the cobalt ions in the CoSBA-15 samples are tetrahedrally coordinated.

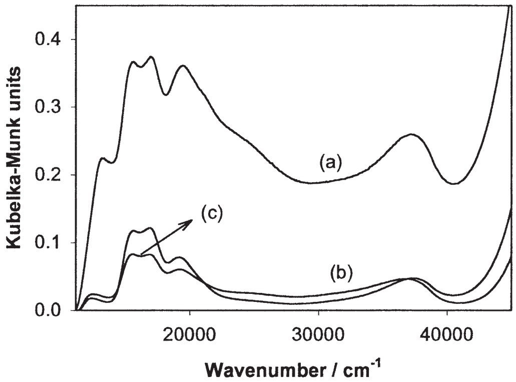

Figure 2. UV–vis DRS spectra of calcined CoSBA-15 samples: (a) CoSBA-15(41), (b) CoSBA-15(60), and (c) CoSBA-15(74).

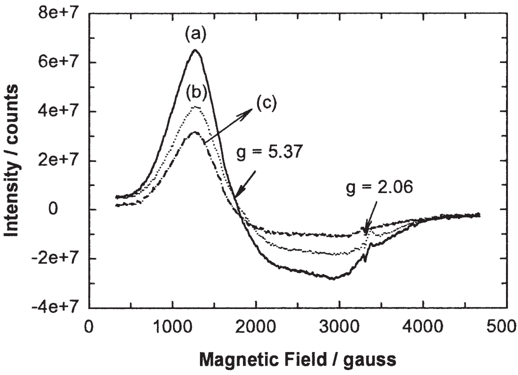

Figure 3. ESR spectra of calcined CoSBA-15 samples: (a) CoSBA15(41), (b) CoSBA-15(60) and (c) CoSBA-15(74).

The X-band EPR spectrum of the calcined CoSBA-15 samples with different n_{Si}/n_{Co} ratios in the synthesis gel were recorded at 6 K using BRUKER ESP 380E spectrometer with a continuous flow liquid helium cryostat is shown in Figure 3. The spectrum shows two major components at $g = 5.37$ and 2.06. With increasing n_{Si}/n_{Co} ratio from 40 to 75, the corresponding spectra show ESR signal increase in intensity. The ESR signal with $g = 5.37$ and $g = 2.06$ are attributed to Co^{2+} in an elongated tetrahedral environment. Similar spectra were also reported in cobalt-substituted aluminophosphate molecular sieves.[11,12]

In conclusion, we have incorporated cobalt in SBA-15 by direct synthesis method in acidic media and characterized extensively by XRD, N_2 adsorption, UV–vis DRS and ESR spectroscopic techniques. The ESR and UV–vis data show that most of the cobalt atom in divalent state and coordinated tetrahedrally in the framework of SBA-15 mesoporous molecular sieves.

References

1 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998).
2 M. Hartmann and A. Vinu, *Langmuir*, **18**, 8010 (2002).
3 A. Vinu, V. Murugesan, and M. Hartmann, *Chem. Mater.*, **15**, 1385 (2003).
4 Z. Luan, M. Hartmann, D. Zhao, W. Zhou, and L. Kevan, *Chem. Mater.*, **11**, 1621 (1999).
5 R. Murugavel and H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, **109**, 4491 (1997).
6 J. M. Thomas, R. Raja, G. Sankar, and R. G. Bell, *Nature*, **398**, 22 (1999).
7 J. Šponer, J. Čejka, J. Dědeček, and B. Wichterlová, *Microporous Mesoporous Mater.*, **37**, 117 (2000).
8 R. A. Schoonheydt, in "Diffuse Reflectance Spectroscopy," Characterisation of Catalysts, ed. by F. Delannay, Marcel Dekker, New York (1984), p 220.
9 D. Kaucký, J. Dědeček, and B. Wichterlová, *Microporous Mesoporous Mater.*, **31**, 75 (1999).
10 J. Dědeček, D. Kaucký, and B. Wichterlová, *Microporous Mesoporous Mater.*, **35–36**, 483 (2000).
11 S. Thomson, V. Luca, and R. Howe, *Phys. Chem. Chem. Phys.*, **1**, 615 (1999).
12 B. M. Weckhuysen, A. A. Verberckmoes, M. G. Uytterhoeven, F. E. Mabbs, D. Collison, E. de Boer, and R. A. Schoonheydt, *J. Phys. Chem. B*, **104**, 37 (2000).