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Preparation and characterization of copper- and iron-containing mesoporous silica using β-cyclodextrin as a structure-directing agent

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Copper- and iron-containing mesoporous silicas were synthesized using β-cyclodextrin as a template and characterized by XRD, SEM and N_2-BET techniques; their catalytic activity in phenol monohydroxylation and CO oxidation was demonstrated.

Mesoporous silica materials have been prepared using β-cyclodextrin as a structure-directing agent.[1–5] Cyclodextrins (CDs) are macrocyclic oligosaccharides, the molecules of which include from six to eight D-glucopyranozide units (α-, β- and γ-CDs, respectively).[6] Truncated conically shaped β-CD molecules have a hydrophobic inner surface, whereas the outer surface bearing OH groups is hydrophilic. On placing in a silicic acid sol, β-CD molecules form worm-like associates that act as template matrices for the formation of silica gel. After the removal of β-CD by vigorous washing and/or oxidative degradation, mesoporous silica materials with a worm-like pore system were obtained. The pore diameter depends on synthesis conditions and CD type and concentration in the starting solution.

The ability of CDs to form host–guest complexes with transition metals makes these compounds very attractive starting materials for preparing heterogeneous catalysts.[6,7] For example, β-CD in alkali solutions[2,8] forms copper(II) complexes that can be used for the preparation of efficient catalytic materials.

Here, we report the synthesis of Cu- and Fe-containing silicas using β-cyclodextrin as a template agent, characterization of these materials and their catalytic behavior in oxidation reactions.[†]

Table 1 Synthesis conditions[a] and textural characteristics.

Sample	$m_{\beta\text{-CD}}:(m_{\beta\text{-CD}}+m_{SiO_2})$ (wt%)	Added compounds		Surface area S_g/m^2 g^{-1}
		to β-CD solution	for β-CD removal	
MS-1	18	$(NH_2)_2CO$	H_2O	640[b]
MS-2	18	$(NH_2)_2CO$	H_2O_2	650
MS-3	11	$(NH_2)_2CO$	HNO_3	200
MS-4	11	aqueous NH_3	H_2O_2	250
MS-5[c]	—	—	—	< 1

[a] All samples after β-CD removal were dried at 120 °C for 24 h, MS-1 was then annealed at 450 °C for 6 h. [b] The average pore diameter is 2.1 nm for MS-1. [c] MS-5 was synthesized without β-CD.

Table 1 gives the texture characteristics of the test samples. The measured surface areas are consistent with published data.[1,2] In contrast, silica sample MS-5 prepared without β-CD has a very low surface area. The removal of β-CD from a solid material by water washing gives a sample MS-1 with the same specific

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[†] All reagents used were of analytical grade. A modified synthesis procedure[1,2] was applied. First, tetraethoxysilane (TEOS) was hydrolyzed in the presence of 0.1 M HCl (molar ratio TEOS:HCl = 100:1) at 25 °C for 2 h. Then, the aqueous solution of β-CD was added dropwise with vigorous stirring to the solution of hydrolyzed TEOS. To increase the solubility of β-CD, an aqueous solution of NH_3 (β-CD:NH_3 = 1:4.5 by weight) and KOH (β-CD:KOH = 5:1) or urea (β-CD:urea = 1:3) were added. An advantage of using NH_3 is the ease of its removal from solid materials by drying. Then, the gels prepared were aged for a week at 25 °C. In the case of urea, instantaneous gel formation did not occur. Therefore, after stirring for a few hours, the colloid solution was kept at 25 °C for two weeks. All samples were dried at 100–120 °C for 24 h; sample MS-1 was annealed at 450 °C for 6 h (Table 1).

β-CD was removed from the solid materials by both thermal and microwave-stimulated degradation in air. Otherwise, removal of β-CD was performed by the washing of the samples with water or aqueous solutions of urea, or 63% HNO_3 or 30% H_2O_2 followed by vigorous washing with deionized water and drying.

A similar synthetic protocol was used for preparing the Cu- and Fe-containing samples (Tables 2 and 3). $Cu(NO_3)_2\cdot 3H_2O$ and $FeCl_3\cdot 6H_2O$ were employed. The amount of β-CD used in the case of Cu- or Fe-containing samples was 11 or 14 wt%, respectively. These metal-containing samples were dried at 120 °C for 24 h. Copper samples were then annealed at 400 or 450 °C; iron samples were air-dried.

The XRD patterns of the samples were collected on an Enraf-Nonius FR-552 X-ray diffractometer and a Burevestnik DRON-4M apparatus with CuKα radiation. The data were collected and processed using the STOE software. JCPDS PDF database (PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD) was used to identify phases in the solid materials.

Thermal analysis of the aged gels was performed on a MOM Derivatograph Q-1500 D in the temperature range of 20–600 °C at a heating rate of 5 or 10 K min^{-1} in air or nitrogen flow. SEM was performed on a JEOL JSM 840A instrument with an EDX attachment. The measurements were carried out at 30 Pa. The images were obtained with scaling up from 2000$^{\times}$ to 50 000$^{\times}$. The BET surface area and pore size distribution were measured by N_2 adsorption and desorption isotherms at 77 K on a Micromeritics ASAP 2000N apparatus.

Catalytic activities of copper-containing samples were characterized in carbon monoxide oxidation. The reaction was carried out in a flow type fixed-bed reactor at 20–700 °C and 0.101 MPa, the temperature up/down modes were employed. The feed gas contained 4.0 vol% CO and 2.1 vol% O_2 (balance He). It was introduced to the reactor at a flow rate of 30–50 ml min^{-1}. The feed and product gases were analyzed by gas chromatography.

Catalytic activity of iron-containing samples was evaluated in the liquid phase oxidation of phenol by hydrogen peroxide. The reaction was carried out at 60 °C and 0.101 MPa. The mixture of 1 g of phenol, 2 ml of AcOH, 10 ml of H_2O and 10 mg of a catalyst was placed in a batch reactor and heated to 60 °C. Then, 2 ml of 40% H_2O_2 (molar ratio PhOH : H_2O_2 = 1:2) was added with vigorous stirring. Reaction products were analyzed using gas liquid chromatography.

Table 2 Synthesis conditions and characteristics of copper-containing samples.

Catalyst[a]	Added compound[b]	β-CD removal[c]	Heating rate/K min^{-1}	Annealing/°C (h)	Concentration of Cu (wt%)		$S_g/m^2\ g^{-1}$
					EDX	Calculated	
Cu-1	KOH	TD	3.6	450 (6)		0.5	434[d]
Cu-2	KOH	MW	—	450 (6)	0.8±0.3	0.5	209[d]
Cu-3	aqueous NH_3	TD	6.3	400 (2)	9.6±1.3	9.0	
Cu-4	$(NH_2)_2CO$	TD	6.3	400 (2)	8.6±0.5	9.0	183
Cu-5	$(NH_2)_2CO$	H_2O_2	—	450 (6)	5.4±0.3	4.0	

[a] Addition of copper nitrate at the stage of TEOS prehydrolysis with β-CD solution except for sample Cu-5, which was synthesized by incipient wetness impregnation of silica gel. [b] Compounds used to increase β-CD solubility. [c] Removal of β-CD from the samples by thermal decomposition (TD), microwave heating (MW, 800 W, 7 min), or treatment with an H_2O_2 solution (H_2O_2). [d] Average pore diameters are 6.6 and 10.4 nm for Cu-1 and Cu-2, respectively.

Table 3 Synthesis conditions and characteristics of iron-containing samples.

Catalyst	Iron salt deposition	Added compound[a]	Concentration of Fe (wt%)	
			EDX	Calculated
Fe-1	With β-CD	$(NH_2)_2CO$	11.3±1.6	10.0
Fe-2	Wet impregnation	$(NH_2)_2CO$	9.4±0.6	10.0
Fe-3[b]	Wet impregnation	$(NH_2)_2CO$	14±3	10.0
Fe-4	With β-CD	—	11.4±1.5	10.0

[a] Compound used to increase β-CD solubility. [b] β-CD was removed from Fe-3 by treatment with H_2O_2.

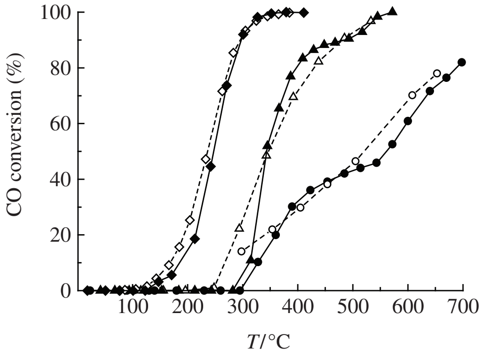

Figure 1 Light-off curves of CO conversion as a function of temperature measured with Cu-2 (circles), Cu-4 (rhombs) and Cu-5 (triangles) samples. Filled point and open point are for temperature-up and temperature-down modes, respectively.

surface area as that of the sample treated by H_2O_2 (MS-2). However, a shorter washing time is required to remove β-CD using H_2O_2. Treatment with HNO_3 to remove β-CD or the use of NH_3 to increase β-CD solubility in synthetic procedures results in a substantial decrease in the surface area (MS-3 and MS-4, respectively).

Microwave heating influences noticeably the texture of Cu silicas (Cu-1 and Cu-2). Sample Cu-2 prepared using microwave heating has a smaller surface area and a larger pore diameter in comparison with Cu-1 (Table 2). On the other hand, the microwave-assisted processing takes a much shorter time than conventional muffle-oven heating.

A comparison of nominal copper and iron concentrations and those determined by EDX shows that they are very close to each other (Tables 2 and 3). What is more important, metal atoms are distributed uniformly throughout the bulk of solids, as evidenced from relatively low standard deviations of metal concentrations. The annealing of Cu samples does not affect the homogeneous distribution of copper atoms. Thus, in the case of sample Cu-4, copper concentrations before and after annealing were 9.5±0.9 and 8.6±0.5 wt%, respectively.

Figure 1 presents the light-off curves of CO obtained with Cu-containing catalysts. Both a high concentration of CuO and its well-pronounced crystallinity in sample Cu-4 (XRD data) are responsible for a remarkably higher activity in comparison with two other samples. The poor catalytic activity of sample Cu-2 can be explained by a low copper concentration (< 1 wt%) or by a more prolonged annealing of the sample (6 h at 450 °C). These two factors are, probably, to account for the almost full inclusion of Cu atoms into the silica structure resulting in the formation of copper silicates, which are much less active than copper oxide. The catalytic activity of copper-containing silica is consistent with published data.[9,10]

Iron-containing samples Fe-1 and Fe-3 prepared by substantially different ways exhibited similar catalytic behaviors in the monohydroxylation of phenol by H_2O_2. Catalyst Fe-1 was obtained by adding $FeCl_3$ at the stage of gel formation. In the case of Fe-3, the silica gel particles were impregnated with a $FeCl_3$ solution. The catalytic activity of these iron-containing samples resulted in a 24–26% yield of pyrocatechol and a 17–18% yield of hydroquinone at a 71–72% phenol conversion after 1 h. Close values of both overall phenol conversion and selectivity to partial oxidation products clearly indicate not only similarity of the chemical nature of active centers in both catalysts and the mechanism of their action but also equal accessibility of these centres to reagent molecules.

In conclusion, the use of β-CD as a structure-directing agent in preparing Cu- and Fe-containing mesoporous silicas affords materials with a surface area of 200–600 $m^2\ g^{-1}$ and a pore diameter of 2–10 nm. The conditions of synthesis influence remarkably the texture of these materials. Moreover, copper and iron atoms are uniformly distributed in the bulk of solids. The Fe-containing materials exhibited high activity in the partial oxidation of phenol by H_2O_2, whereas the copper catalysts were active in carbon monoxide oxidation.

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References

1 J. Y. Zheng, J. B. Pang, K. Y. Qiu and Y. Wei, *J. Sol-Gel Sci. Technol.*, 2002, **24**, 81.
2 B. H. Han and M. Antonietti, *J. Mater. Chem.*, 2003, **13**, 1793.
3 S. Polarz and M. Antonietti, *Chem. Commun.*, 2002, 2593.
4 S. Polarz, B. Smarsly, L. Bronstein and M. Antonietti, *Angew. Chem. Int. Ed.*, 2001, **40**, 4417.
5 B. H. Han, S. Polarz and M. Antonietti, *Chem. Mater.*, 2001, **13**, 3915.
6 *Cyclodextrins and Their Complexes*, ed. H. Dodziuk, Wiley-VCH, Weinheim, 2006.
7 J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000.
8 E. Norkus, G. Grinciene, T. Vuorinen and R. Vaitkus, *J. Inclusion Phenom. Macrocycl. Chem.*, 2004, **48**, 147.
9 E. M. B. de Sousa, A. P. G. de Sousa, N. D. S. Mohallem and R. M. Lago, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 873.
10 M. E. Manriquez, T. Lopez and R. Gomez, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 853.

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