

## Synthesis and catalytic properties of cobalt- and molybdenum-containing mesoporous MCM-41 molecular sieves

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MS received 19 September 1996

**Abstract.** Mesoporous MCM-41 type silicas containing molybdenum and cobalt have been prepared with pore sizes in the range 30–38 Å and 54–59 Å. Catalytic properties of these materials have been examined with respect to the oxidation of cyclooctene and aniline.

**Keywords.** Mesoporous silica; MCM-41; Co–SiO<sub>2</sub>; Mo–SiO<sub>2</sub>; molecular sieves.

Mesoporous silica of MCM-41 type was reported sometime ago by Beck *et al* (1992). Since then several derivatives of MCM-41 containing Ti, V, Mn and Fe have been prepared and tested for their catalytic activity (Reddy *et al* 1994; Schmidt *et al* 1994; Tanev *et al* 1994; Yuan *et al* 1995; Zhao and Goldfarb 1995). Many of these mesoporous materials show redox catalytic properties. Thus, chromium-containing MCM-41 type silicates with redox properties have just been reported (Ulagappan and Rao 1966). In this communication, we report the synthesis of MCM-41 type silicas containing Mo and Co and their catalytic properties.

In order to synthesize Mo-containing mesoporous silica, a gel of composition SiO<sub>2</sub>:0.15Na<sub>2</sub>O:0.25TDTAB:0.02MoO<sub>3</sub>:60H<sub>2</sub>O was prepared from tetraethylorthosilicate (TEOS), NaOH, tetradecyltrimethylammonium bromide (TDTAB), sodium molybdate and distilled water. In a typical synthesis, NaOH (12.49 mmol) solution containing TEOS (44.7 mmol) was added to the TDTAB (10.4 mmol) solution under stirring. The sodium molybdate (2.08 mmol) solution was added to the above mixture and the whole mixture stirred for 30–45 min. The gel so obtained was taken in an air-tight polypropylene bottle and heated at 363 K for a period of 24 h in a hot-air oven. The solid obtained was filtered, washed several times with distilled water and dried at 373 K for 6 h.

Cobalt-substituted mesoporous silica was prepared by starting with a gel having the composition SiO<sub>2</sub>:0.25TDTAB:0.02CoO:60H<sub>2</sub>O. The source of Co was cobalt acetate. In a typical synthesis, NaOH (11.6 mmol) solution containing TEOS (23 mmol) was added to the TDTAB (6.27 mmol) solution under stirring. The cobalt acetate (4.63 mmol) solution was added to the above mixture and the mixture stirred for 30–45 min. The gel obtained was taken in an air-tight polypropylene bottle and heated at 363 K for a period of 24 h in a hot air oven. The product was then filtered, washed several times with distilled water and dried at 373 K for 6 h. By the procedures

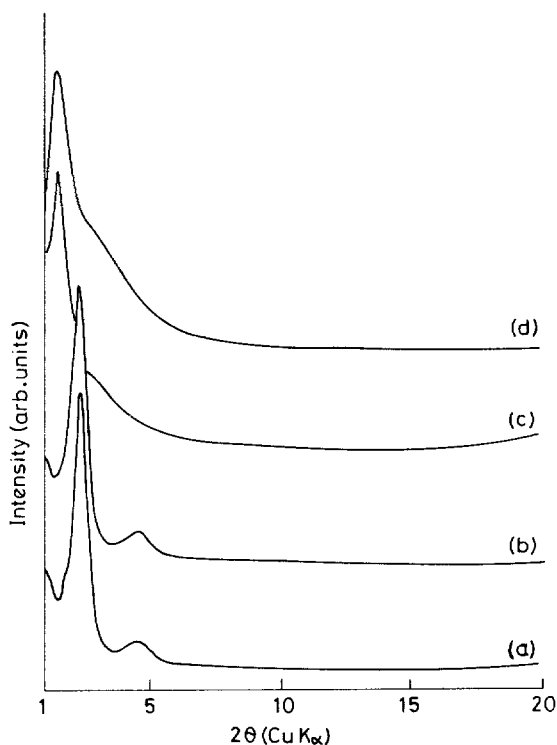
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described above, we could obtain hexagonal mesoporous silicas containing Mo or Co with  $d_{100}$  values of around 30–38 Å.

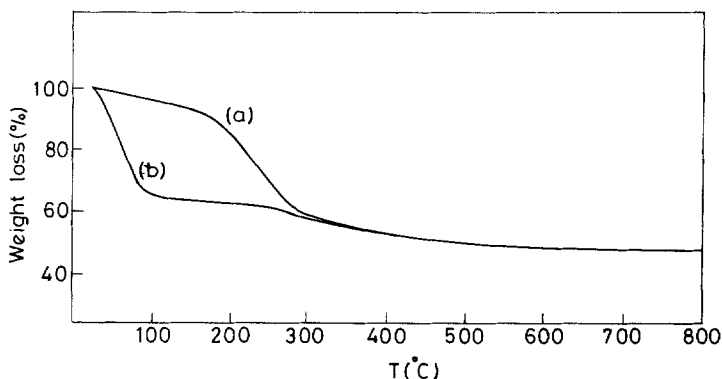
We also prepared Mo and Co containing mesoporous silica phases with larger pore sizes. We accomplished this by adding tetradecane (0.25 mol) as the solubilizing agent along with the surfactant (TDTAB) during the preparation of the gel. The actual quantities of tetradecane added in the case of Mo- and Co-containing silicas of the compositions described earlier were 5.79 mmol and 1.15 mmol respectively.

Powder X-ray diffraction (XRD) patterns were recorded using a Rich-Seifert instrument (Model XRD 3000 TT). Transmission electron microscopy (TEM) was carried out using a JEOL JEM3010 instrument operated at 300 kV. Thermogravimetric analysis was carried out with a Polymer instrument (Model STA 1500). EDAX (Leica model s 440i) analysis was done on these samples to estimate the composition of Mo and Co. Infrared spectra were recorded using a Perkin-Elmer (Model 580) spectrometer. Diffuse reflectance spectra were recorded with a Unicam (Model SP8-100) spectrometer. Surface areas were measured by the BET method employing Micromeritics rapid surface area analyser, 2200.

In figure 1, we give the XRD patterns of the Mo-containing mesoporous silicas prepared by us. The diffraction profile of the as-synthesized (AS) sample (figure 1a) gives a  $d_{100}$  value of 37.12 Å. Thermogravimetry indicates complete loss of the TDTAB



**Figure 1.** XRD profile of (a) as synthesized Mo containing mesoporous silica with a  $d_{100}$  of 37.12 Å, (b) ethanol extracted product from (a) with a  $d_{100}$  of 37.54 Å, (c) as synthesized Mo-containing mesoporous silica with a  $d_{100}$  of 56.59 Å and (d) ethanol extracted product from (c) with  $d_{100}$  of 56.58 Å.

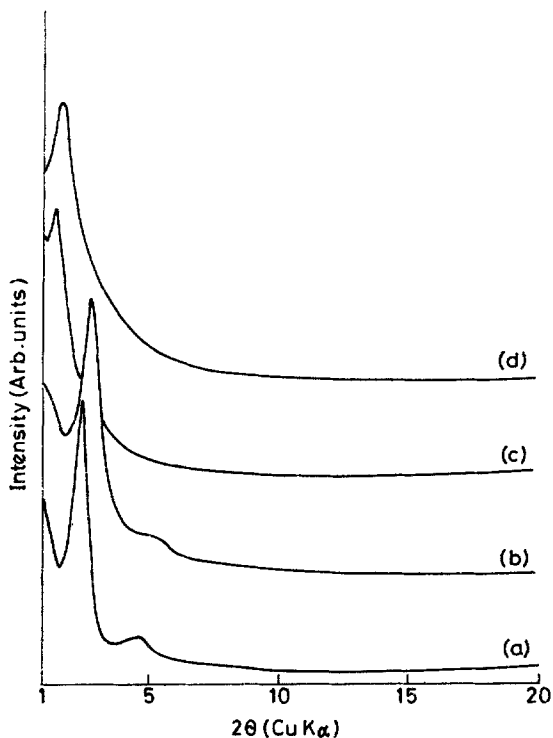


**Figure 2.** Thermogravimetric curves of (a) Mo-containing mesoporous silica with a  $d_{100}$  of 37.12 Å and (b) the ethanol extracted product from (a).

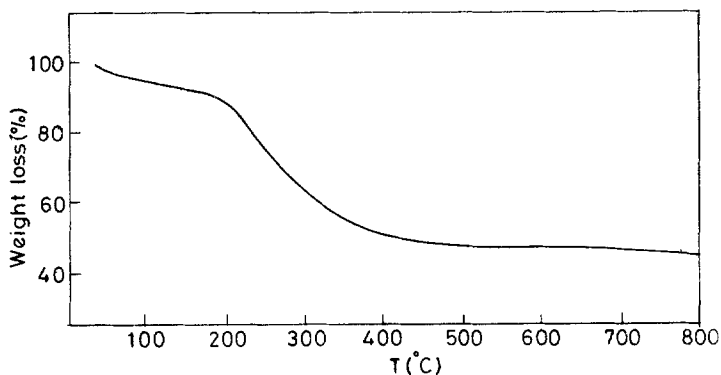
template around 673 K (figure 2). Calcination of the as-synthesized at 673 K however destroys the structure, as revealed by X-ray diffraction. We therefore removed the template by ethanol extraction. The complete removal of the template was confirmed by the absence of C–H stretching vibrations in the infrared spectrum of the product after the extraction and also from the absence of weightloss over the temperature range where the template is normally removed (figure 2). In figure 1b, we have shown the XRD pattern of the ethanol-extracted (EE) product with a  $d_{100}$  value of 37.54 Å indicating the retention of the mesoporous structure. By adding tetradecane as the solubilizing agent along with surfactant, we could get Mo-containing silica with an enhanced  $d_{100}$  value of 56.59 Å, as can be seen from figure 1c. The XRD pattern of the corresponding EE product in figure 1d shows a  $d_{100}$  value of 56.58 Å. Thermogravimetry reveals that 0.2 mol of TDTAB is incorporated in the Mo–SiO<sub>2</sub> samples prepared. The presence of Mo in the samples was established by EDAX analysis, which gave the Mo content to be 2.0(mol)%, but we cannot be entirely certain that Mo substitutes Si. The oxidation state of Mo is 6+ and the extra positive charge in the framework is probably compensated by the bromide ions. While the XRD profiles clearly demonstrate the mesoporous nature of the Mo-silicas prepared by us, we have also employed transmission electron microscopy to establish the hexagonal nature of these phases.

XRD profiles of Co-containing mesoporous silicas are given in figure 3. The as-synthesized (AS) sample gives a  $d_{100}$  value of 34.33 Å as shown in figure 3a. Thermogravimetry of this sample shows weight loss due to the removal of the template around 723 K (figure 4). When the as-synthesized sample was calcined at 873 K, we found that the mesostructure remained intact unlike in the case of mesoporous Mo-silica. The complete removal of the template was confirmed by the absence of the C–H stretching vibrations in the infrared spectrum. In figure 3b we give the XRD profile of the calcined (873 K) Co-silica material with a  $d_{100}$  value of 29.47 Å.

Addition of tetradecane to the Co-containing silica gel increases the pore size of the mesoporous phase as can be seen from the XRD profile (figure 3c) showing a  $d_{100}$  of 59.64 Å. The XRD profile of the product calcined at 873 K in air gives a  $d_{100}$  value of 53.82 Å. The template content of the mesoporous Co-silica as determined by thermogravimetry is 0.2 mol. EDAX analysis gives the cobalt content as 3.0(mol)%. The hexagonal mesoporous nature of the Co-containing silicas was also confirmed by

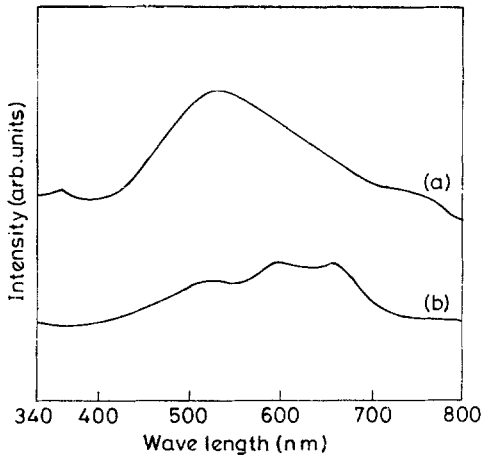


**Figure 3.** XRD profiles of (a) as-synthesized Co-containing mesoporous silica with a  $d_{100}$  of 34.33 Å, (b) sample (a) after calcination showing a  $d_{100}$  of 29.47 Å, (c) as-synthesized Co-containing mesoporous silica with a  $d_{100}$  of 59.64 Å and (d) sample (c) after calcination showing a  $d_{100}$  of 53.82 Å.



**Figure 4.** Thermogravimetric curve of Co-containing mesoporous silica with a  $d_{100}$  of 34.33 Å.

TEM. Diffuse reflectance spectra (figure 5) of as-synthesized Co-silica samples (light pink in colour) show a broad band around 550 nm, but on calcination at 873 K the product turns blue in colour and shows peaks around 520, 585 and 650 nm confirming



**Figure 5.** Diffuse reflectance spectra of (a) as-synthesized Co-containing mesoporous silica and (b) the calcined sample.

**Table 1.** Properties of Mo- and Co-containing mesoporous silicas.

Compound <sup>a</sup>	$d_{100}$ (Å)	$a_0$ (Å)	Surface area (mg <sup>2</sup> g <sup>-1</sup> )
Mo-SiO <sub>2</sub> (AS)	37.12	42.86	—
Mo-SiO <sub>2</sub> (EE)	37.54	43.35	453
Mo-SiO <sub>2</sub> (AS)	56.59	65.34	—
Mo-SiO <sub>2</sub> (EE)	56.58	65.33	1068
Co-SiO <sub>2</sub> (AS)	34.33	39.64	—
Co-SiO <sub>2</sub> (C)	29.47	34.04	552
Co-SiO <sub>2</sub> (AS)	59.64	68.87	—
Co-SiO <sub>2</sub> (C)	53.82	62.15	801

<sup>a</sup>AS represents as-synthesized material, EE represents ethanol extracted product and C represents calcined sample.

the presence of Co(II) at tetrahedral sites. We note that the tetrahedral Co(II) ions can readily substitute Si sites in SiO<sub>2</sub>, thus explaining the thermal stability of the mesoporous Co-silicas, in contrast to that of Mo-silica.

In table 1, we have listed the  $d_{100}$  values of the various mesoporous silicas prepared by us along with their unit-cell parameter  $a_0$ , using the formula  $a_0 = 2d_{100}/\sqrt{3}$ . We have also listed the values of the surface area obtained by the BET method for the template-free samples in the same table. As we can see, the surface area is generally large, varying between 453 and 1068 m<sup>2</sup>g<sup>-1</sup>, clearly establishing the mesoporous nature of the sample.

We have carried out preliminary experiments on the oxidation of cyclooctene and aniline using the various mesoporous Mo- and Co-silica materials prepared by us. The reactions were carried out at 343 K for 24 h in the presence of H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>O<sub>2</sub>: reactant

molar ratio was 1:3). In the case of Co-silica, 2.0% of cyclooctene oxide and 4.0% of the other oxidation products were obtained independent of the pore-size. With Co-silica, aniline gets oxidized to azobenzene, nitrobenzene and other products (1% each), again independent of the pore size. In the case of Mo-silica ( $d_{100} \approx 37 \text{ \AA}$ ), we found greater oxidation of cyclooctene. We obtained 8% cyclooctene oxide and 15% of the other oxidized products. With the larger pore size ( $d_{100} \approx 56 \text{ \AA}$ ), 2% cyclooctene oxide and 7% of other products were obtained. With Mo-silica ( $d_{100} \approx 37 \text{ \AA}$ ) the product distribution in the oxidation of aniline was 1% azobenzene and 7% nitrobenzene along with 8% of other products. With the  $d_{100} \approx 56 \text{ \AA}$  sample, 1% azobenzene, 2% nitrobenzene and 7% of other products were obtained. It is possible to incorporate Mo(VI) and Co(II) in mesoporous silica of the MCM-41 type. The pore size is 30–38 Å when we use tetradecyltrimethylammonium bromide as the surfactant. The pore size can be expanded to 54–59 Å by using tetradecane as the solubilizing agent. The surface areas of the Mo- and Co-containing mesoporous silicas prepared by us are in the range 453–1068 m<sup>2</sup>g<sup>-1</sup>. Mesoporous Mo-SiO<sub>2</sub> and Co-SiO<sub>2</sub> exhibit oxidizing catalytic properties.

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