

## Modification of Mesoporous Silica by Direct Template Ion Exchange Using Cobalt Complexes

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Mesoporous molecular sieves (MMS) are new forms of oxides originally synthesized in their siliceous forms using a surfactant templating pathway.<sup>1,2</sup> They are either hexagonal or cubic mesophases characterized by a regular array of uniform mesopores structured as channels whose diameter is determined by the hydrophobic chain length of the surfactant. The former and the latter were designated, by their discoverers as Mobil Corporation Materials, MCM-41 and MCM-48, respectively. Their large surface area (ca. 1000 m<sup>2</sup>/g) and regular pore shape and size provide very valuable properties for the development of new absorbers and catalysts. In the latter type of applications, their modification by incorporation of transition metal ions (TMIs) in their structure seems very promising.<sup>3–7</sup> For instance, it has been shown that titanium confers them a unique activity for selective oxidation of large organic substrates.<sup>8</sup> The TMI-modified MMS are usually prepared via the so-called direct synthesis route based on the addition of the TMI to the sol-gel containing silicon precursors (most often sodium silicate, alkoxides, etc.) and templating amphiphilic molecules. During hydrothermal treatment, the TMI is supposed to be incorporated in the SiO<sub>4</sub> network of the pore walls leading to tetrahedral TMI sites. However, very few TMIs such as Ti<sup>4+</sup>,<sup>8</sup> V<sup>5+</sup>,<sup>9</sup> and Fe<sup>3+</sup><sup>10,11</sup> are stable in these sites. To circumvent this difficulty, the TMI can be grafted to surface silanol groups of an already formed MMS from which the template has been removed. This leads to highly exposed TMIs sites according to the interfacial coordination chemistry concepts.<sup>12</sup> The grafting of Ti to the walls of a MMS hexagonal mesophase indeed leads to the most active Ti-MMS ever reported.<sup>13</sup> Vanadium has also been incorporated in such a postsynthesis sequence on the more fragile cubic MCM-48 mesophase.<sup>14</sup> Nevertheless, highly reactive complexes such as alkoxides or cyclopentadienyl chlorides compounds are necessary to create M–O–Si linkages

owing to the poor acidity and ion exchange properties of the silanol groups.<sup>15,16</sup> However, one may directly proceed with the as-synthesized form still containing the template. In both MCM types, the latter are quaternary ammonium cations that counterbalance silanolate groups ( $\equiv\text{Si}-\text{O}^-$ ) of the inner surface. They can be removed using HCl,<sup>3,5</sup> NaCl,<sup>10</sup> NH<sub>4</sub>NO<sub>3</sub>,<sup>5</sup> and NH<sub>4</sub>-Cl<sup>11</sup> solutions. This is likely related to their cation exchangeable properties (vide infra reaction 1). In that connection, a cation metal complex should also displace the template and remain electrostatically attached to the MMS inner surface. This is tested here using inert *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> and [Co(en)<sub>3</sub>]<sup>3+</sup> complexes and the siliceous MCM-41 stabilized by cetyltrimethylammonium (CTMA<sup>+</sup>).

The MCM-41 was synthesized according to Reddy and Song<sup>17</sup> using a gel composition (in mol) of 100 SiO<sub>2</sub>, 8.64 Na<sub>2</sub>O, 4.38 (TMA)<sub>2</sub>O, 31.24 CTMABr, and 6330 H<sub>2</sub>O (TMA<sup>+</sup> = tetramethylammonium and CTMABr = cetyltrimethylammonium bromide). A clear gel was obtained after 10 min of stirring a mixture containing fumed silica (Cab-O-Sil Degussa), sodium silicate, and TMA-silicate in water. The addition of CTMABr was followed by vigorous stirring for 60 min. The so-obtained dense foam was maintained for 24 h at 100 °C in a Teflon-lined static autoclave. A white solid was filtered off and dried in air. The green *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and yellow [Co(en)<sub>3</sub>]-Cl<sub>3</sub> were prepared according to the literature.<sup>18,19</sup> The 0.5 g of dried MCM-41 (100 °C) was treated with 50 mL of the *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ethanol (95%) solution of the complex at 47 °C for 20 min. The green solution turned to purple, and a pink solid was filtered off. The solid was washed with 10 mL ethanol and allowed to dry in air. Na, Co, and Si analyses were performed using atomic absorption of the solution obtained from HF digestion. In the as-synthesized and exchanged forms of the MCM-41, Na was hardly detectable (0.003 ± 0.002 Na/Si mole ratio), the other data are reported in Table 1. For [Co(en)<sub>3</sub>]<sup>3+</sup>, the solubility in ethanol was too low and dimethyl sulfoxide was found to be a better solvent (DMSO, 99.0% from Aldrich). In the same conditions adopted above, the MCM-41 turns to yellow in contact to the [Co(en)<sub>3</sub>]<sup>3+</sup> solution, i.e., the same color than the complex. The adsorbed complex did not leach out during washing with DMSO or EtOH solutions (the latter was used to remove the DMSO molecules). However, 65 ± 5% was displaced after 30 min of contact time at 47 °C with a DMSO solution containing 0.1 M of NH<sub>4</sub>Cl. Comparatively, the pink adsorbed complex obtained from the treatment

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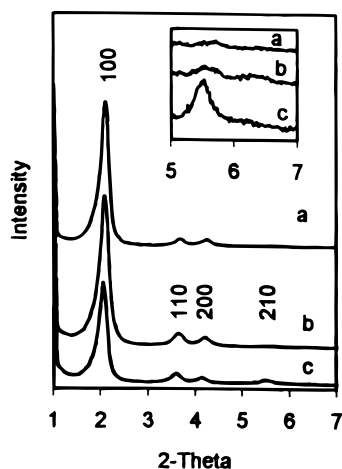
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**Table 1.** Analytical Characteristics of the MCM-41 Treated with Either Cobalt Complex or  $\text{NH}_4\text{Cl}$  Solutions

complex or $\text{NH}_4$ (concn $\times 10^{-3}$ M)	template removed (mol % per Si) <sup>e</sup>	incorporated Co (mol % per Si) <sup>f</sup>	template removal yield (%) <sup>g</sup>	cobalt exchange yield (%) <sup>h</sup>
1.96 <sup>a</sup>	6.4	1.8	38	77
4.0 <sup>a</sup>	9.3	2.9	71	60
5.0 <sup>a</sup>	11.0	4.0	94	68
5.0 <sup>a,b</sup>	13.9	4.4	98	37 (7) <sup>i</sup>
4.2 <sup>c</sup>	14.1	3.8	88	75
50 <sup>d</sup>	14.3	0.0	99	—

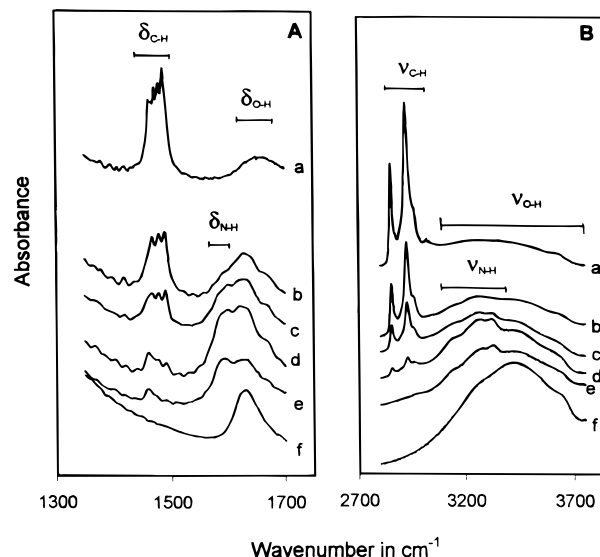
<sup>a</sup>  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$  complex in ethanol. <sup>b</sup> MCM-41 treated twice with a  $5 \times 10^{-3}$  M  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$  solution. <sup>c</sup>  $[\text{Co}(\text{en})_3]^{3+}$  complex in DMSO. <sup>d</sup> MCM-41 treated twice with an  $\text{NH}_4\text{Cl}$  ethanol solution (see text). <sup>e</sup> From colorimetry (see ref 20, relative accuracy ca. 2%); figures consistent with literature data for total template content (see refs 1, 29, 30). <sup>f</sup> From atomic absorption (absolute error ca. 0.2%). <sup>g</sup> From the FT-IR spectra (see text, relative accuracy 4%). <sup>h</sup> Co exchanged over total Co calculated from columns 1 and 3 of the table. <sup>i</sup> Yield for both the first and the second exchange treatment, the latter in parentheses (relative accuracy 3%).

**Figure 1.** X-ray powder diffraction patterns of MCM-41 modified with (a)  $[\text{Co}(\text{en})_3]^{3+}$ , (b)  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ , and (c) unmodified (as-synthesized); insert, detail of the  $\theta$  range  $5\text{--}7^\circ$ .

using the  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$  were much more difficult to displace (only  $10 \pm 1\%$ ) in the same conditions.

The BET surface area were measured from nitrogen adsorption-desorption isotherms performed using an Omnisorb 100. The surface areas are 1050, 990, and  $760 \pm 20$   $\text{m}^2/\text{g}$  for calcined material ( $500^\circ\text{C}$  for 3 h) when the template was previously removed either by calcination or using 50 mL of 0.1 M  $\text{NH}_4\text{NO}_3$  in ethanol or as described above with cobalt solutions, respectively. According to the Barrer-Joyner-Halenda model, the pore size distribution is still typical of a MCM-41 and centered at 31.5 and 29.0  $\text{\AA}$ , with a fwhm of ca. 1.6 and 2  $\text{\AA}$  respectively. In addition, the presence of high order reflections after template removal is consistent with the preservation of the channel structure (Figure 1). By contrast, the same experiments performed in water rather than 95% ethanol or DMSO 99.0% leads to a drastic broadening of all the XRD lines attesting of profound structure damages in agreement with literature data.<sup>20</sup>

Transmission FT-IR measurements were performed on samples pressed into pellets (70 mg self-supported wafers containing 1% sample in KBr) using a Bomem spectrometer (Figure 2).

**Figure 2.** FT-IR spectra of MCM-41 (a) as-synthesized and treated with  $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]^+$  complex, (b)  $1.96 \times 10^{-3}$  M, (c)  $4 \times 10^{-3}$  M, (d)  $5 \times 10^{-3}$  M, (e)  $5 \times 10^{-3}$  M (treated twice), and (f) treated with a  $\text{NH}_4\text{NO}_3$  solution followed by calcination;  $\nu$  and  $\delta$  stand for stretching and bending vibrational modes, respectively, of the  $-\text{CH}_2-$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$ , and  $-\text{OH}$  groups and  $\text{H}_2\text{O}$  molecule.

The bands attributed to the stretching vibrational mode of the  $\text{CH}_3$  and  $\text{CH}_2$  groups (range  $2800\text{--}3000$   $\text{cm}^{-1}$ )<sup>21</sup> were calibrated using the strong bending vibrational mode of the  $\text{SiO}_4$  units of the MCM-41 at  $450$   $\text{cm}^{-1}$  for quantitative analysis. Alternatively, the amount of extracted template was measured in the filtrated solution using a colorimetry method for quaternary amines.<sup>22</sup> Repeated treatments or replacement of monovalent by trivalent complex leads to higher template removal (Table 1). Concomitantly, the bands assigned to both  $\text{CH}_3$  and  $\text{CH}_2$  stretching and bending modes decrease in intensity while those of the  $\text{NH}_2$  groups pertaining to ethylenediamine molecules appear in the ranges  $1560\text{--}1600$  and  $3100\text{--}3300$   $\text{cm}^{-1}$ .<sup>23</sup> Both IR spectra and chemical analysis show that the displacement of the template can almost reach completion. A band at ca.  $1640$   $\text{cm}^{-1}$ , though slightly broader and shifted toward lower energies in the as-synthesized form than in the hydrated material after calcination, is likely due the  $\delta_{\text{OH}}$  vibrational mode of  $\text{H}_2\text{O}$  localized at the template-silanolato interface. Their presence precludes any attempt for strict nonaqueous post treatments of a MCM-41.

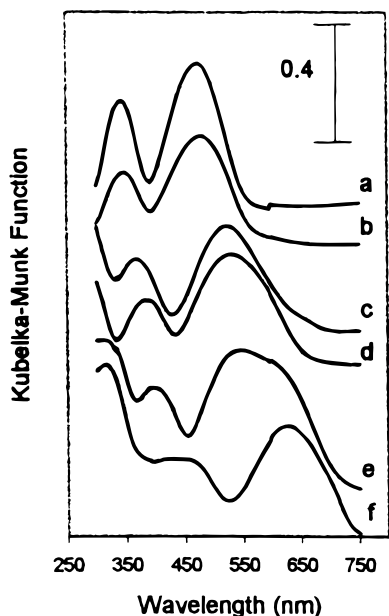
The UV-visible reflectance spectra was recorded on a Perkin-Elmer Lambda 5 spectrometer equipped with an Harrick reflectance attachment and reported using the Kubelka-Munk function  $[F(R_\infty)]^{11,12,24}$  (Figure 3). The diffuse reflectance spectra of both  $[\text{Co}(\text{en})_3]^{3+}$  modified materials and  $[\text{Co}(\text{en})_3]^{3+}$  complex in ethanol are basically identical with two strong bands assigned both to  $^1\text{A}_1 \rightarrow ^1\text{T}_1$  and  $^1\text{A}_1 \rightarrow ^1\text{T}_2$  spin-allowed d-d electron transitions (Figure 3a).<sup>24</sup> In comparison, the solid  $[\text{Co}(\text{en})_3]\text{Cl}_3$  salt exhibits slightly broader bands somewhat shifted toward higher wavelengths (Figure 3b). These shifts are smaller

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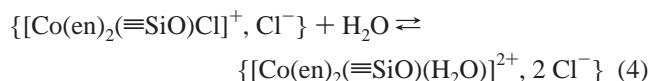
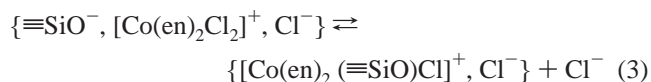
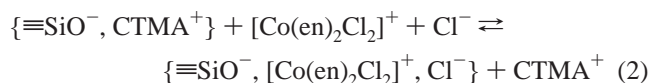
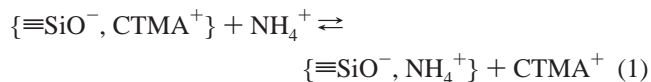
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**Figure 3.** UV-visible diffuse reflectance spectra (wavelengths at peak maximum) of (a)  $[\text{Co}(\text{en})_3]^{3+}$  modified MCM-41 (335 and 466 nm), (b)  $[\text{Co}(\text{en})_3]\text{Cl}_3$  salt diluted at 25 wt % in MgO (338 and 469 nm, respectively), (c) *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  modified MCM-41 (360 and 516 nm), (d) *cis*- $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{SO}_4$  salt (377 and 522 nm), (e) *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  salt (390, 530, and 650 nm), and (f) *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  salt (414, 454, and 621 nm), diluted at 35% in MgO for the latter three.

than those expected for the substitution of an ethylenediamine ligand. The  $[\text{Co}(\text{en})_3]^{3+}$  complex which keeps its coordination unchanged, is more likely retained within the MCM-41 by pure electrostatic forces. In this case, the MMS acts as a macro counterion via its surface silanolato groups of the inner walls.<sup>12</sup> This is consistent with its easy displacement using a  $\text{NH}_4^+$  DMSO solution. By contrast, the color changes and the spectral modifications when the *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is used, indicate a drastic modification of the Co coordination. The spectra of the pink modified MCM-41 (Figure 3c) indeed do not resemble that of the starting complex (Figure 3f) nor that of *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (Figure 1e).<sup>25</sup> The band shift to lower wavelengths indicates that isomerization cannot explain the data. The closest spectral match is indeed obtained with the *cis*- $[\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]\text{SO}_4$  salt<sup>26</sup> (Figure 3d), suggesting that the pink adsorbed complex is a *cis*- $[\text{Co}(\text{en})_2\text{Cl}(\text{X})]$  where X is either  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\equiv\text{SiO}^-$ . The resistance of this adsorbed complex to subsequent displacement using an  $\text{NH}_4^+$  solution strongly supports the formation of a  $\text{Co}-\text{O}-\text{Si}\equiv$  bridge. In this case, the MCM-41 acts as a monodentate macroligand (reaction 3). Common knowledge of the hydrolysis of such a complex suggests that the second Cl ligand may also have been substituted for  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or potentially for a second  $\equiv\text{SiO}^-$ .<sup>27</sup> In both hypotheses, the grafted complex necessitates outersphere exchangeable  $\text{Cl}^-$  anions for electrical balance (reactions 3 and 4). A treatment using an  $\text{NH}_4\text{NO}_3$  solution indeed displaces  $\text{Cl}^-$  for  $\text{NO}_3^-$  characterized by a single IR band at  $1384\text{ cm}^{-1}$

consistent with its role of outersphere counterion.<sup>28</sup> The exchange and grafting mechanisms using  $\text{NH}_4^+$  (reaction 1) or a cobalt complex (reactions 2 and 3) are reversible and can be written tentatively according to the surface ion pair formalism adopted earlier,<sup>12</sup>



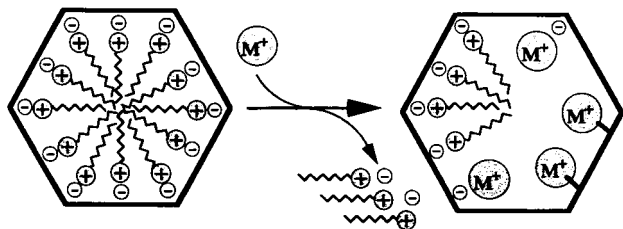
where reaction 4 could also occur more likely with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  than with  $\equiv\text{SiO}^-$  according to surface silanol density.<sup>29</sup>

The grafting of the *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  with *trans* to *cis* isomerization was also observed on the amorphous silica surface. However, basic media were necessary ( $\text{pH} > 8$ ) to activate the silanol groups, and water was the solvent<sup>30</sup> that probably led to surface damage by formation of silicates.<sup>12</sup> In the present case, the cobalt DMSO or EtOH solutions are rather slightly acidic (typically  $\text{pH} = 5.0-5.4$ ) due to the presence of residual HCl (see synthesis recipes). After exchange, the solutions are neutral or slightly basic ( $\text{pH} = 7.0-7.7$ ), indicating that some silanol groups have been protonated. However, this should account for fewer than 1 or 2 protons for 10 exchanged cobalts. Therefore, a Co/surfactant displacement ratio of 1 is expected on the basis of electrical neutrality (reaction 2). Surprisingly, this ratio was  $0.31 \pm 0.04$  according to the chemical analysis (Table 1, ratio between column 2 and 3). The rationale for this low value lies in the fact that not all the surfactant molecules counterbalance surface electrical charges. Since proton (or hydroxyl) ions are discarded with respect to the weak pH evolution, the bromide ions present in the gel are more likely retained in the MCM-41 structure in the as-synthesized form. The titration using ionic chromatography indeed reveals that both exchange processes using either  $\text{NH}_4^+$  or the cobalt complexes release all the  $\text{Br}^-$  anions of the as synthesized form providing a  $\text{Br}/\text{Si}$  ratio of  $\text{ca. } 9.0 \pm 0.1\%$ . Accordingly, the  $\text{Br}/\text{surfactant}$  ratio is  $0.64 \pm 0.03$  leading to a  $\equiv\text{SiO}^-/\text{surfactant}$  ratio of  $0.36 \pm 0.03$ . As expected, the latter figures lead to an electrical yield (Co exchanged over silanolato groups) close to one ( $0.9 \pm 0.2$ ).

Taking into account a template loading of  $\text{ca. } 14.3 \pm 0.3\%$  (Table 1),<sup>1,31,32</sup> the electrical balance within the MCM-41 leads to a  $\equiv\text{SiO}^-/\text{Si}$  ratio of  $5.3 \pm 0.4\%$ . Since the specific surface area is  $760\text{ m}^2/\text{g}$ , the silanolato surface density is  $0.55 \pm 0.05/\text{nm}^2$ . This is much lower than the OH density of  $\text{ca. } 3.0/\text{nm}^2$ ,

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**Figure 4.** Template-TMI ( $\text{CTMA}^+ - \text{M}^{n+}$ ) ion exchange scheme (water molecules and silanol are withdrawn); negative charges stand for silanolato surface groups and bromide anions, while positive charges account for hydrophilic heads of  $\text{CTMA}^+$  surfactants.

but close to the number of isolated silanol groups ( $0.7/\text{nm}^2$ ) reacting with trimethylchlorosilane.<sup>32</sup> Surprisingly, the presence of a large concentration of the surfactant counterion,  $\text{Br}^-$ , in MCM-41 synthesized in basic media has not been previously noticed. This point is under current investigation in our

laboratory to clarify whether this is a general feature or a specificity of the synthesis route used in the present work.

In conclusion, the removal of the templating surfactant (Figure 4) from MCM-41 materials occurs via an ion exchange process that liberates highly reactive silanolato groups and allows to introduce transition metal ions at their inner surface. This technique provides a novel postsynthesis metal modification route that preserves the channel structure and, save one calcination step. In addition, the electrical balance provides for the first time a measure of the exchangeable silanolato group density and reveals for the first time the presence of a significant amount of template counterion in the as-synthesized form of MCM-41 mesoporous silicas.

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