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Study on the Adsorption of a Cobalt(III) Complex on Micelle Templated Silica Prepared by Ion-exchange Method

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Abstract

The amount of cobalt (III) ions introduced into the mesopores has been controlled by the concentration of the cobalt complex in the exchange solution and the existing percentage of silanolate on the surface. The obtained FTIR results show that a part of surfactants retain in the channel during the ion exchange in absolute and dry ethanol. The colour change during this process indicates that cobalt undergoes substitution reactions within its coordination sphere. UV-visible characterization, consistent with previous study of EXAFS spectroscopy confirms this evolution providing a full description of the complex. Several steps were identified for direct ion exchanged reaction that is include electrostatic adsorption of complex into the channel, formation of ion pair with macro-counter ion MTS, and grafting step with substitution reaction of macro-ligand MTS by formation of Co-O-Si bridge.

Keywords: *Modified-MTS, FTIR, UV.vis, Ionexchange, Cobalt complex, mesoporous compound.*

Introduction

Studies on the adsorption of transition metal ions (TMIs) from solutions on oxides surface is a subject of great interest in various fields of chemistry (Stumm, 1992; Che *et al.*, 1989; Bonneviot *et al.*, 1988; Che *et al.*, 1997). They include separation and environmental science, catalysis, pharmaceutics, and of course surface science. Mesoporous templated silica (MTS) is a new form of oxide originally synthesized in their siliceous forms using a surfactant templating pathway (Kresge *et al*., 1992; Beck *et al*., 1992; beck *et al*., 1993). In the as-made form, the surfactants (quaternary ammonium cation) counterbalance the silanolato ($\equiv$Si-O$^-$) surface groups. It is therefore necessary to remove the template to obtain novel materials, which exhibit high surface area with regular pore shape and size that tuned in the nanoscale range (20-100 Å) allowing high diffusivity of large molecules (Kresge *et al*., 1992). Recently, it was shown that direct cation exchange of the surfactant using transition metal ions bypassed the calcinatoin step and, constituted an innovation in the modification of surface (Badiei *et al*., 1998). In this method trans-$[Co(en)_2Cl_2]^+$ directly ion-exchanged in as-made MTS by displacement of cationic surfactant. X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) investigations exhibited that the adsorbed complex adopt the cis configuration and the both chloride ligandes were substituted during the displacement of the templating surfactants by hydroxy group and silanolato group (Beland *et al*., 1998; Beland *et al*., 1999).

In the present work, we report UV-vis diffuse reflectance spectra of the cobalt (III) complex trap on the channel of as-made MTS before and after grafting on the surface. In addition, the nature of the cobalt complex into the MTS channel in various temperatures are studied using FTIR spectra. This study completes the previous investigations of Co-MTS prepared according to the direct synthesis route (Beland *et al*., 1998; Beland *et al*., 1999; Badiei *et al*., 1998; Echchahed *et al*., 1998).

Experimental

Sample preparation

The MTS was synthesis from a gel whose composition was 100 SiO_2: 31.24 CTMABr: 8.64 Na_2O: 4.38 $(TMA)_2O$: 6330 H_2O (TMA^+ = tetramethylammonium and CTMABr = cetyltrimethylammonium bromide) (Badiei *et al*., 1998). A clear solution was obtained after 10 min of stirring a mixture containing fumed silica (Cab-O-Sil Degussa), sodium silicate, and TMA-silicate in water. The CTMABr was added by vigorous stirring for 1 hour. The obtained gel was conserved for

24h at 100°C in a Teflone lined static autoclave. The solid was washed and dried in air. The solid composition was based on weight loss at 540°C for 10h and acid titration of silanolato group (Badiei, 1998; Echchahed, 2001): SiO^-/SiO_2 = 0.201. Green trans-$[Co(en)_2Cl_2]Cl$ and yellow $[Co(en)_3]Cl_3$ were prepared according to the literature (Bailar *et al*., 1946; Bromhead *et al*., 1960). Before post-synthesis cobalt modification based on direct template cation exchange by the cobalt complexes, the solid was washed with 30 ml ethanol (95%) and allowed to dry in air. Typically, 0.5 g of as made MTS was treated with 50 ml ethanol (95%) solution of green 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 10ml ethanol and allowed to dry in air. In this experiment, when absolute or dry ethanol was used, the solid was purple. In addition, with increase of both percentage of water (about 15%) and concentration of complex solution, a purple solid was obtained.

Characterization techniques

The XRD was obtained from a Siemens D500 diffractometer employing nickel filtrated Cu Kα (λ= 1.5418 Å) where the X-ray tube was operated at 40 kV and 30 mA and spectra were scanned at 0.02° step size. The diffuse UV-vis spectra were recorded on a Perkin Elmer Lambda 5 spectrometer equipped with a Harrick reflectance attachment and reported using the Kubelka-Munk function, F(R). Nitrogen adsorption-desorption isotherms were carried out at 77K using an Omnisorb 100. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). The specific surface area of MTS was determined from the linear part of BET plot (p/p_0 = 0.05-0.03). The FTIR spectra were recorded on a Bomem spectrometer in a transmission mode using samples pressed into self-supported pellets.

Result

The low angle XRD powder patterns of ion-exchanged samples are showed in figure 1. All solids were typical of a hexagonal mesophase with the *P6m* symmetry characteristic of MCM-41 (Kresge *et al*., 1992; Beck, 1992). No lattice contraction was observed under exchange condition. According to the BET model, the pore size distribution of calcinated solid is still typical a MCM-41 and centered at 30±1 Å.

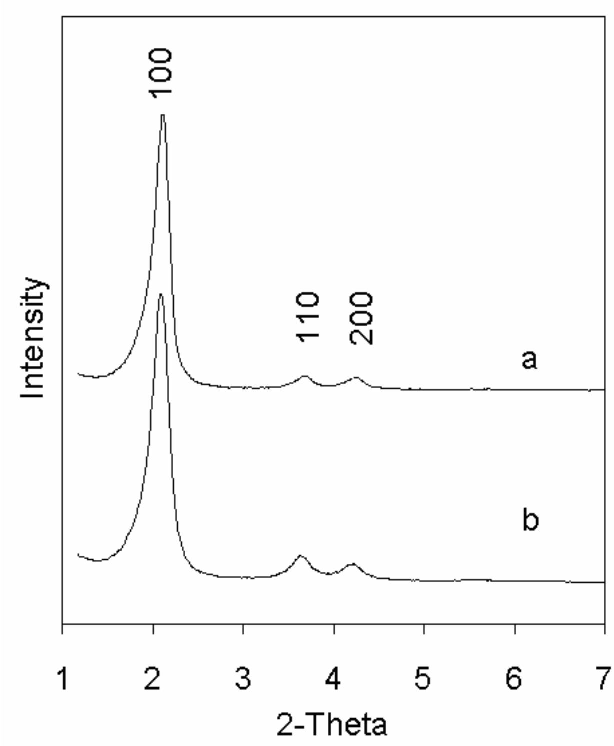

Figure 1. X-ray powder diffraction patterns of ion exchanged-MTS with trans-$[Co(en)_2Cl_2]^+$ a) the purple solid and b) the pink solid.

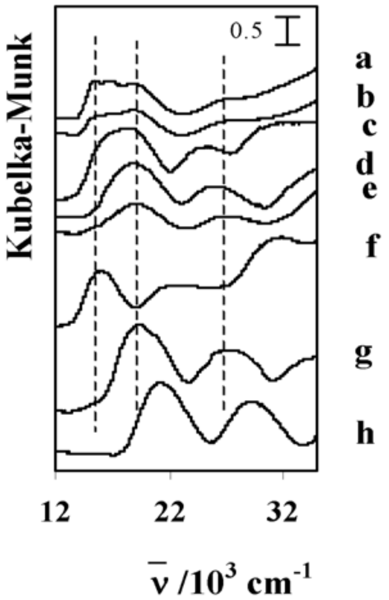

Figure 2. UV-vis diffuse reflectance spectra of, a) Co complex ion exchanged MTS in dry ethanol; b) Co complex ion exchanged MTS in absolute ethanol; c) cis-[Co(en)$_2$Cl$_2$]Cl; d) cis-[Co(en)$_2$Cl(H$_2$O)] SO$_4$; e) Co complex ion exchanged MTS; f) trans-[Co(en)$_2$Cl$_2$]Cl; g) [Co(en)$_2$CO$_3$]SO$_4$; h) [Co(en)$_3$]Cl$_3$.

The UV-vis reflectance spectra of the cobalt(III) complexes and the Co- MTS compounds are exhibited in figure2. For octahedral low spin cobalt(III), two lower energy bands are d-d Laporte forbidden to electronic transition assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ (~20000cm^{-1}) and $^1A_{1g} \rightarrow {}^1T_{2g}$ (~25000cm^{-1}). The high-energy band is generally insensitive to a decrease in symmetry. By contrast, the first band split into well resolved bands at approximately 16000 and 23000 cm^{-1} for trans-[Co(en)$_2$Cl$_2$]Cl complex with D_{2h} symmetry (see figure2f) (Basolo *et al*., 1955). However, a C_2 symmetry products a smaller splitting resulting in a mere broadening of the band for cis-[Co(en)$_2$Cl$_2$]Cl complex] (Basolo *et al*., 1955; Basolo *et al*., 1950). Absence of a distinct peak near 23000 cm^{-1} and existing of two strong bands at about 19000 and 17000 cm^{-1} in the exchanged Co-MTS (in ethanol 95%) clearly indicate that the grafted complexes are mostly adopted the cis configuration as be previously proved by EXAFS and XANES results (Beland *et al*., 1999). However, observing a shoulder at about

15000 cm^{-1} can be result of existence a fraction of those complexes retain the trans configuration. The spectra of ion exchanged Co-MTS in dry ethanol (without water) and absolute ethanol show increase of shoulder intensity (figure 2a and 2b). On the other hand, the spectra indicated that a large part of the complex change to cis form and the MTS acts as a macro-counter ion via its surface silanolato groups of the inner walls (In our previous study, it was shown the coordination of $[Co(en)_3]^{3+}$ complex was retained within the MTS channel by pure electrostatic force (Bonneviot *et al.*, 1998; Che *et al.*, 1997). The closest spectra match are obtained with the cis-$[Co(en)_2Cl(H_2O)]SO_4$ and $[Co(en)_2CO_3]SO_4$ salts (figure 2f and 2g), suggesting that the pink adsorbed on MTS is a cis form with one $\equiv SiO^-$ and the other either OH^- or H_2O ligands. As we discussed previously the complex was grafted by the formation of one Co-O-Si≡ bridge that we can say the MTS act as a monodentate macroligand. To proceed further with the comparison, the crystal field strength 10Dq and the Racha parameters, B and C (smaller for lower ionic character of ligands: nepheleuxetic effect) was calculated base on two transition energies (ν_1 and ν_2) in O_h symmetry. For the first and the second transition energy are given by $[^1A_{1g} \rightarrow {}^1T_{1g}] = 10Dq - C + 86B^2/(10Dq)$ and $[^1A_{1g} \rightarrow {}^1T_{2g}] = 10Dq + 16\,B - C + 2B^2/(10Dq)$ and for one of the energy spin forbidden transition observable in our range, $[^1A_{1g} \rightarrow {}^3T_{2g}] = 10Dq + 8\,B - 3C + 14B^2/(10Dq)$ (Lever, 1986; Lever, 1968). They are obtained from maximum of both absorption bands assuming an O_h symmetry and C = 5B as in the $[Co(en)_3]^{3+}$ complex (Lever, 1986; Lever, 1968). For cis-[Co(en)$_2$XX’] complexes where X and X’ are two of following ligands, Cl^-, H_2O, OH^-, $\equiv SiO^-$, en. The ligands can be ranked from characteristics of the complexes in spectrochemical series providing in parenthesis 10Dq and B in cm^{-1} as a following:

Cl^-, Cl^- (20310, 478) < Cl^-, H_2O (20400, 504) < OH^-, $\equiv SiO^-$ (20470, 613) < CO_3^{2-} (21510, 610) < en (23200, 579)

The FTIR spectra of Co-MTS compounds are shown in figure3. For these spectra the Co-MTS compounds were pressed (125 kg/cm^2) into a 16 mm self-supporting disk containing 2-5 mg Co-MTS/cm^2 and put in vacuum for 2 h. The spectra in figure3 show the NH_2 stretching vibration bands of ethylendiamine molecules in the range of 1560-1600 and 3100-3300 cm^{-1} (Nakamoto, 1978). The treatment by $[Co(en)_3]Cl_3$ leads to higher template removal as the stretching vibrational mode of the CH_3 and CH_2 groups decrease. The other peaks around 1630-1650 and 3300-3700 cm^{-1} attributed to deformation vibration of H_2O and stretching vibration of silanol groups (Chen, 1995; Klonkowski, 1999).

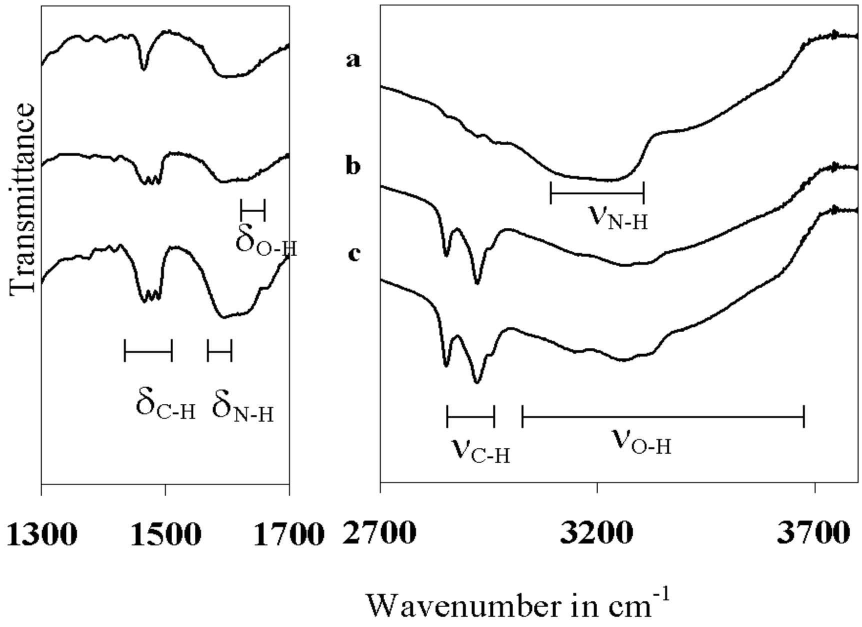

Figure 3. FTIR spectra of as-made MTS treated by a) trans-$[Co(en)_2Cl_2]Cl$ in ethanol (95%); b) trans-$[Co(en)_2Cl_2]Cl$ in dry ethanol; c) $[Co(en)_3]Cl_3$ in DMSO and ethanol. ν and δ stand stretching and bending vibrational modes of the the –CH_2-, -CH_3, and –OH groups and H_2O molecules

Figure 4 shows the FTIR spectra between 2500-4000 and 1400-2000 cm^{-1} of ion exchange MTS using trans-$[Co(en)_2Cl_2]Cl$ complex at various temperatures. At room temperature the spectrum exhibits a broad band with two NH_2 starching band and a less distinct absorbance band for CH_2 stretching (figure 4a). Under evacuation at 100°C, the CH_2 stretching bands with the same adsorption are appeared, which is due to removal of the adsorbed water. At the same time the band about 1600cm^{-1} becomes narrower. At 150°C, the NH_2 stretching vibration of ethylendiamine decreases and the color of sample change. The intensity of ethylendiamine adsorbance bands (ν and δ stretching and bending vibrational modes of the $-CH_2-$) of adsorbed complex-MTS decreases with increase of temperature, as these adsorptions disappears at 375°C, indicating removal of the organic ligands. Also, the maximum of broadband at 3200-3700 cm^{-1} shifts towards higher frequency to about 3600 cm^{-1}. At higher temperatures the absorption at 3740 cm^{-1}, which was also observed previously for MCM-41 sample heated under vacuum condition, is attributed to the isolated silanol groups (Chen, 1995; Klonkowski, 1999; Morrow, 1991).

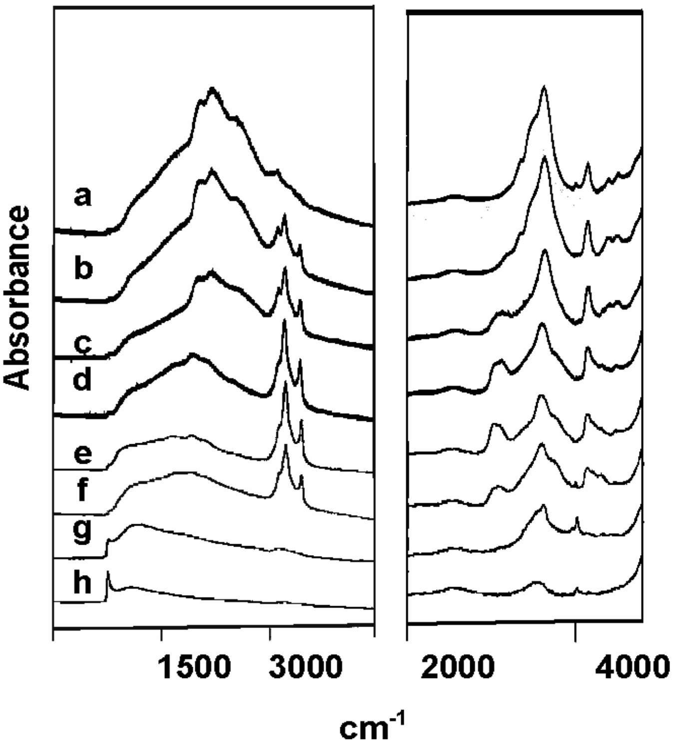

Figure 4. FTIR spectra of as-made MTS treated by trans-[$Co(en)_2Cl_2$]Cl complex in ethanol (95%)a) at different temperatures a) 25°C, b) 100°C, c) 150°C, d) 200°C, e) 250°C, f) 300°C, g) 400°C, h) 500°C.

Discussion

The mechanism of the direct ion exchange of cobalt(III) complex was previously proposed (Badiei *et al.*, 1998; Echchahed *et al.*, 1998; Beland *et al.*, 1999). Due to the UV-vis results,it was confirmed that the grafted complex lead to cis form. In addition, there is the evidence for a small fraction of grafted complexes in trans form. The trans to cis isomerization of complex occur at the charge surface of solid involve electrostatic interaction in diffuse layer. It was shown for the first time that the cis form could be fixed at surface as an ion pair. When the purple solid washed with an NH_4Cl ethanol solution the solid changed to pink color and the filtered solution was content of a cobalt complex. This is consistent with specific sorption that attributes to ion pairing of macro-counterion MTS with adsorbed complexes. The FTIR results show that a part of surfactants retain in the channel during the ion exchange in absolute and dry ethanol. In addition, due to the reactivity of the Co-Cl bonds toward hydrolysis one might wonder about the possibility that substitution of Cl^- with $\equiv Si\text{-}O^-$. Moreover, when the grafted complex on MTS was heated, there is a probability of the second substitution reaction, where substitution of OH^- with SiO^- occurred and then the complex is decomposed at about 350°C.

The exchange yield of cobalt complex is about 25-30% of silanolate of surface. As with using as-made MTS with 18.5%, 15%, and 13% SiO^- /SiO_2 the yield of cobalt complex on MTS were 5.3%, 4.3%, 3.3%, respectively. It is show when H_2O ligand substitutes by Cl^- ligand. Due to the acidity of $Co\text{-}OH_2$ some of the silanolate of surface is notarized, because the percentage of cobalt yield decreases. On the other hand, in the previous study (Echchahed *et al.*, 1998) it was shown that subsequent washing with NH_4NO_3 ethanol solution remove the existing chloride ions on the outer-sphere of grafted complex. Accordingly, the exchange process and the adsorbed complex can be showed (figure5) and written as a sequence of pure electrostatic deposition (reaction 1) and then transformation trans complex to cis (reaction 2), followed by a grafting sequence (reaction 3), a second substitution (reaction 4), acid base reaction (reaction 5) and eventually by substitution of the counter anion (reaction 6):

$$\{\equiv SiO^-,CTMA^+\} + \text{trans-}[Co(en)_2Cl_2]^+ \rightleftarrows \{\equiv SiO^-,\text{trans-}[Co(en)_2Cl_2]^+\} + CTMA^+ \quad (1)$$

$$\{\equiv SiO^-,trans\text{-}[Co(en)_2Cl_2]^+\} \rightleftharpoons \{\equiv SiO^-,cis\text{-}[Co(en)_2Cl_2]^+\} \qquad (2)$$

$$\{\equiv SiO^-,cis\text{-}[Co(en)_2Cl_2]^+\} \rightleftharpoons \{cis\text{-}[Co(en)_2(\equiv SiO)Cl]^+, Cl^-\} \qquad (3)$$

$$\{cis\text{-}[Co(en)_2(\equiv SiO)Cl]^+, Cl^-\} + H_2O \rightleftharpoons \{[Co(en)_2(\equiv SiO)(H_2O)]^{2+}, 2\,Cl^-\} \qquad (4)$$

$$\{[Co(en)_2(\equiv SiO)(H_2O)]^{2+}, 2Cl^-\} + \{\equiv SiO^-,CTMA^+\} \rightleftharpoons$$
$$\{[Co(en)_2(\equiv SiO)(HO)]^+,Cl^-\} + \{\equiv SiOH\} + CTMA^+ + Cl^- \qquad (5)$$

$$\{[Co(en)_2(\equiv SiO)(HO)]^+,Cl^-\} + NH_4NO_3 \rightleftharpoons$$
$$\{[Co(en)_2(\equiv SiO)(HO)]^+,NO_3^-\} + NH_4Cl \qquad (6)$$

Conclusion

Here, it was shown that the amount of cobalt (III) ions introduced into the mesopores has been controlled by the concentration of the cobalt complex in the exchange solution and percentage of silanolate of surface (Badiei *et al.*, 1998). The color change during this process indicates that cobalt undergoes substitution reactions within its coordination sphere. UV-visible characterization, consistent with previous study of EXAFS spectroscopy confirms this evolution providing a full description of the complex. Several steps were identified for direct ion exchanged reaction that is include electrostatic

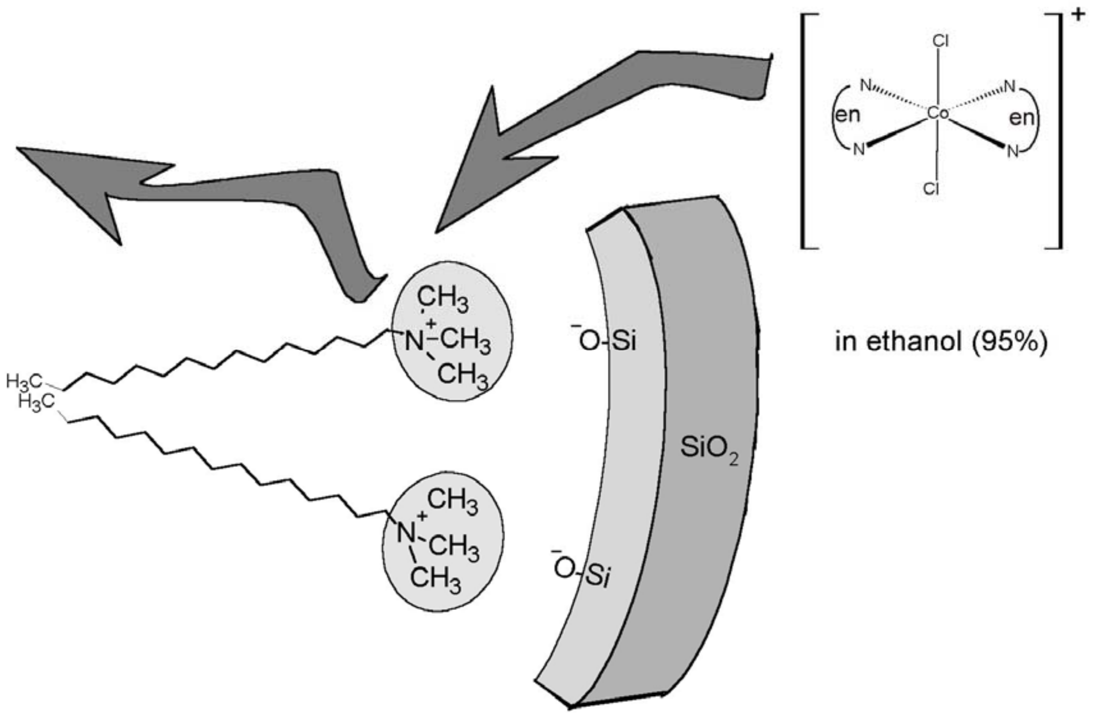

Figure 5. Schematic representation of the surface modification of mesoporous silica by direct template ion exchange using cobalt complex.

adsorption of complex into the channel, formation of ion pair with macro-counter ion MTS, and grafting step with substitution reaction of macro-ligand MTS by formation of Co-O-Si bridge.

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