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Immobilization of Cobaloxime on MCM-41

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Abstract

This work reports, immobilization the Cobaloxime [Co $(DH)_2Cl$;DH,dimethylglyoximato)] onto the MCM-41.The surface of MCM-41 was initially functionalized with 3-aminopropyltrimethoxysilane and 3-pyridine. For the electrostatic immobilization this was reacted with Cobaloxime and immobilization was achieved by an electrostatic interaction between the Co Cobaloxime and the N of the pyridine and NH_2 amine. Additional information was obtained by powder X-ray diffraction (XRD), BET, ICP and DR-UV-Vis, FT-IR spectroscopy.

***Keywords**: Cobalt, Cobaloxime, MCM-41, Immobilization.*

Introduction

Cobaloximes, the trivial name for complexes containing the bis(dimethylglyoximato) cobalt unit($Co(DH)_2$), were studied as model systems in the elucidation of the mechanism of action of vitamin B_{12} coenzyme [1]. Organocobaloximes have recently been used for the synthesis of organic compounds [2-5]. The Co-C bond of organocobaloximes is weak, and its cleavage is achieved by light or heat exposure [6-14]. Many attempts have been reported concerning immobilization of the homogeneous catalysis onto solid supports, combining their high activity and selectivity with the advantages of the heterogeneous catalysis [15-18]. MCM-41 materials are very attractive supports, due to their very high surface areas and a regular array of large pore channels. In addition, the high concentration of silanol groups allows the development of different strategies to covalently attach metal complexes. Many published work report the anchoring of salen complexes on the MCM-41 surface. Different coupling agents have been used, such as organosilanes bearing specific functional groups, e. g. chloride, carboxylic

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acid, thiol, amine, isocyanate, which are available for binding to the complex ligand or to the central itself [19-27]. For this study, the Cobaloxime was immobilized onto the MCM-41 by simplified method. The electrostatic immobilization of Cobaloxime on modified MCM-41 achieved by an electrostatic interaction between the Co Cobaloxime and the N surfaces of modified MCM-41.

Experimental

Materials

Hexadecyltrimethylammonium bromides (CTMABr), tertaethylorthosilicate (TEOS), Ethylamine ($C_2H_5NH_2$), 3-aminopropyltrimethoxysilan, 3-pyridineca boxyaldhyde were purchased from Aldrich. Cobalt Chlorid hexahydrate ($CoCl_2.6H_2O$), dimethylgolyoxime (DH_2), HCl, diethyl ether, dichloromethane, ethanol, toluene were obtained from Merck.

Preparation of MCM-41

The MCM-41 was synthesized according to the following procedure previously reported by Aghmasjadei [28].Generally, ethylamine ($C_2H_5NH_2$, 2.7g) was added to pure water (42ml) and this mixture was stirred for 10 min. n-hexadecyltrimethylammonium bromide (CTMABr,1.58g) was added dropwise and the mixture was stirred for 30 min. Then 2.24 ml tertaethylorthosilicate (TEOS, 2.085g) was added and the mixture was stirred. Then dilute HCl was added dropwise in this final mixture to obtained PH=8.5.After stirring for 2h the white precipitate was filtered and washed with 100ml of warm deionized water. After drying at 318k for 12h, the sample was heated to 823K (rate: 2 $kmin^{-1}$) in air and kept at this temperature for 5h to remove the template.

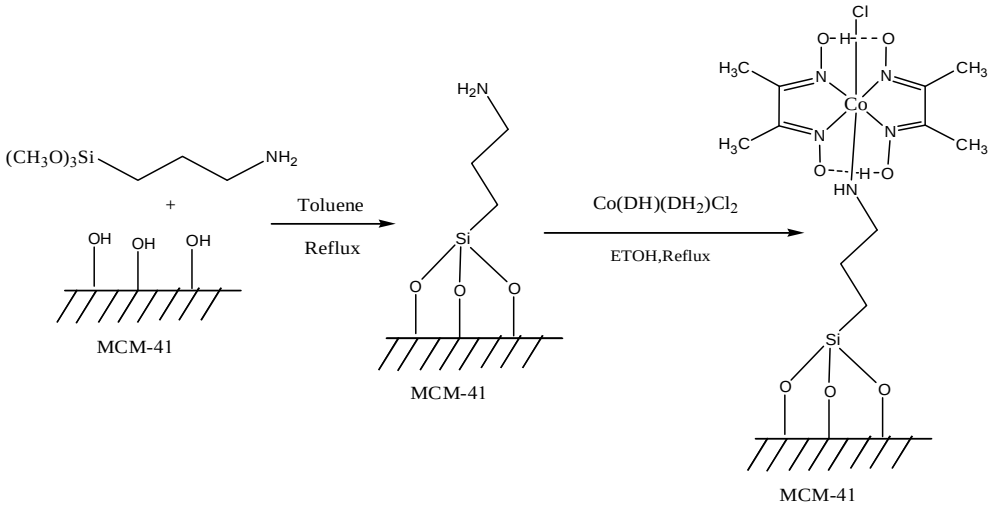
Preparation of 3-aminopropylsilyl-functionalised MCM-41

After dehydration of MCM-41 (200°C, under vacuum for 2h), 0.5 g MCM-41 and 2.1ml 3-aminopopyltrimethoxysilan were added in 30ml dry toluene, and the suspension stirred at reflux temperature under nitrogen atmosphere for 24h. The solid was filtered and stirred with dichloromethane/diethyl ether for 24h.Then filtering the solid; MCM-41 modified was dried at 80°C for 24h.

Modifying of 3-aminopropylsilyl-functionalised MCM-41 by 3-pyridinecaboxyaldhyde

Surface of 3-Aminopropylsilyl-functionalised MCM-41 was modified by 3-pyridinecaboxyaldhyde. After dehydration of 3-aminopropylsilyl-functionalised MCM-41 (200°C, under vacuum for 2 h), 0.2 g 3-aminopropylsilyl-functionalised MCM-41 was add in 100ml dry toluene and then 0.12g 3-pyridinecaboxyaldhyde add to this mixture, the suspension stirred at reflux temperature under nitrogen atmosphere for 24 h. The solid was filtered and stirred with dichloromethane/

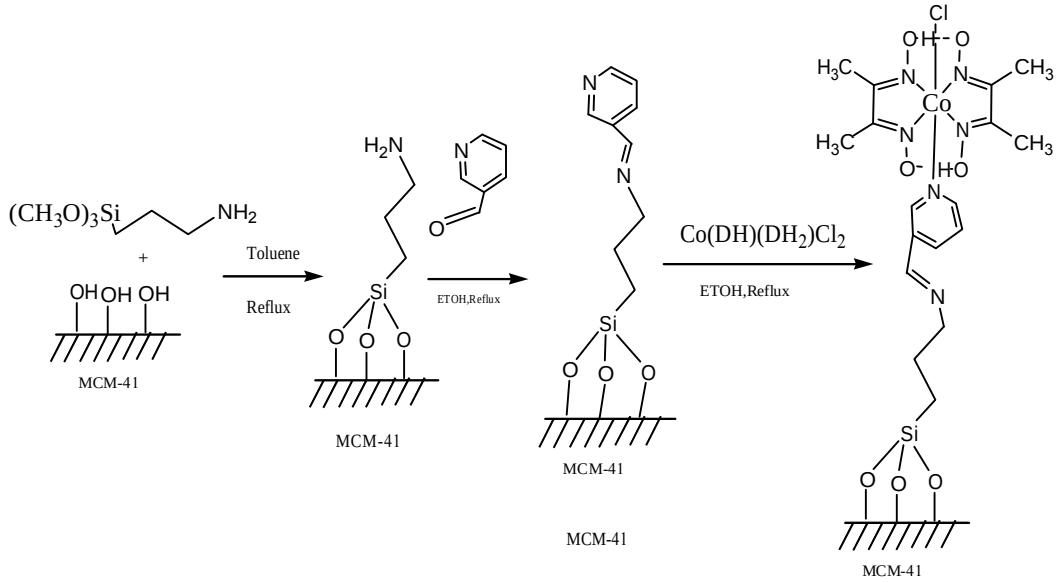
diethyl ether for 24 h. Then filtering the solid; MCM-41 modified was dried at 80°C for 24 h.



Scheme1.

Immobilizing of Cobaloxime onto 3-aminopropylsilyl-functionalised MCM-41

The Cobaloxime immobilized on the MCM-41 surface by using 3-aminopropylsilyl as axial lignd of Cobaloxime (see Scheme1). For this purpose, to a solution of dimethylgolyoxime (0.002 mmol, 0.67g) in ethanol (30ml); was added $CoCl_2.6H_2O$ (0.001mmol, 0.274g). The mixture was stirred for 10min at 60oC and then 0.2g 3-aminopropylsilyl-functionalised MCM-41 was added in mixture, and stirred for 24h at r.t. and brown solid filtered, washed with ethanol. The solid was added to diethyl ether (50 ml); the mixture was stirred for 24 h at r.t. and the solid filtered, washed with diethyl ether, and dried in vacuum to give the heterogeneous Cobaloxime.



Scheme 2.

Immobilizing of Cobaloxime onto MCM-41 modified by Pyridine

The Cobaloxime immobilized on the MCM-41 surface by using 3-pyridine as axial lignd of Cobaloxime (see Scheme 2). For this purpose, to a solution of dimethylgolyoxime (0.001mmol, 0.3499g) in ethanol (12.5ml); was added $CoCl_2.6H_2O$ (0.0005mmol, 0.1369g). The mixture was stirred for 10min at 60°C and then 0.1g 3-aminopropylsilyl-functionalised MCM-41 was added in mixture, and stirred for 24h at r.t. and brown solid filtered, washed with ethanol. The solid was added to diethyl ether (50ml); the mixture was stirred for 24 h at r.t. and the solid filtered, washed with diethyl ether, and dried in vacuum to give the heterogeneous Cobaloxime.

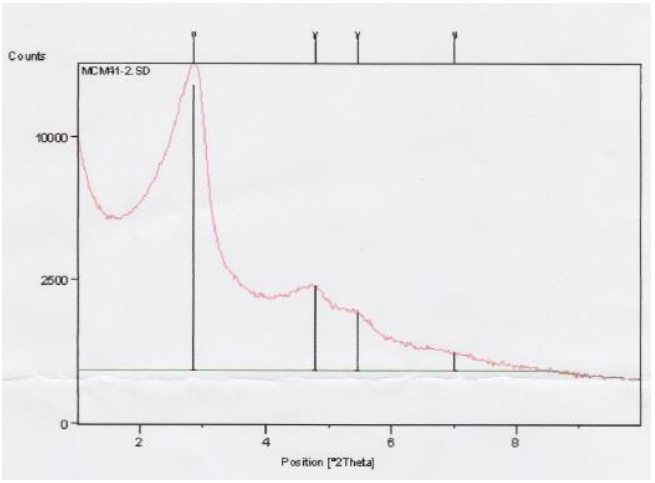


Figure 1. XRD of MCM-41.

Results and discussion

Characterization of MCM-41

MCM-41 synthesized was characterized by x-ray diffraction using a Philips Analytical powder diffractometer on finely powdered sample using Cu Ka radiation and 40kV and 30mA. Fig.1 shows the low angle range of XRD patterns for the MCM-41. The x-ray diffraction of calcined MCM-41 exhibits a peak pattern typical of the mesoporous silica with hexagonal symmetry: four well resolved peaks, a stronger one at 2θ=2.85, assigned to the (100) reflection, and three weaker peaks at higher angles, which can be assigned to the (110), (200) and (210) reflections. The d value found for the (100) reflection was 30.95Ao leading to a lattice parameter, a_o (repeating distance a_o between two pore centers may be calculated by $a_o = (2\ d100/\sqrt{3})$.), of 35.74Ao. By BET specific surface area of MCM-41 obtained 933 m^2g^{-1}; and the specific pore volume obtained 0.332 mlg^{-1}[27, 29].

Adsorption of nitrogen was carried out at 77k using a ASAP2010 apparatus for analyzing surface areas and pore-size distribution of the synthesized MCM-41. Specific surface area was calculated following the BET procedure. Pore-size distribution was obtained by using BJH

pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherms. The adsorption and desorption isotherms of nitrogen show the typical type IV isotherm according to the IUPAC nomenclature for MCM-41 (Figure 2). At the adsorption branch, the adsorbed amount increased gradually with an increase in relative pressure by multilayer adsorption. A sudden uptake of the adsorption amount was observed over a narrow range of relative pressure (P/P_o) between 0.3 and 0.4 caused by capillary condensation of nitrogen in the mesopores. The desorption branch of the isotherm coincides with the adsorption branch.

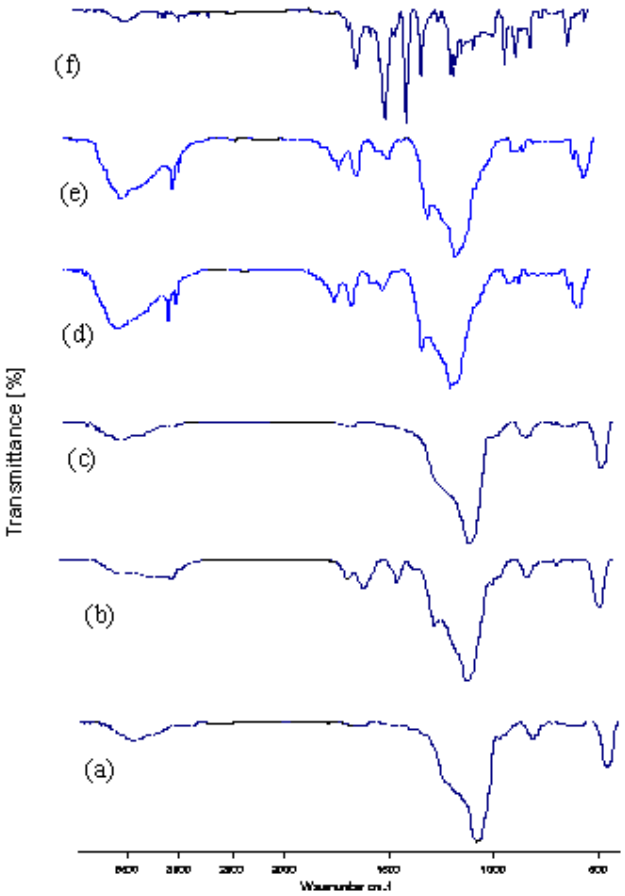


Figure 2. N_2 adsorption, desorption isotherm of MCM-41.Inset shows the BJH pore size distribution of MCM-41.

The FTIR spectra were recorded on a solid samples diluted with anhydrous KBr were recorded at room temperature in transmission mode, in the range 4000 to 450 cm^{-1}.

Figure 3a shows the FTIR spectroscopy of the as-synthesized MCM-41.Bands at ranges of 3300-3770 cm^{-1} are due to the surface hydroxyl groups and to lattice vibration, in the range 1300-750 cm^{-1}. Band at about 1233, 1080, 794 and 468 cm^{-1} are assignable to the asymmetric and symmetric stretching (ν_{as}(Si-O-Si) and ν_s(Si-O-Si)) of support framework, the band present at about 981 cm^{-1} is attributable to ν(Si-O) vibrations [29-33].

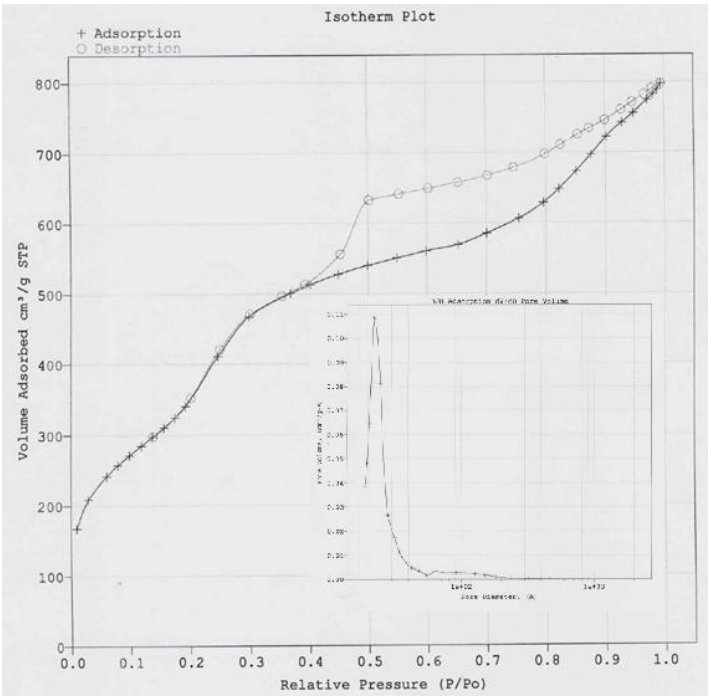


Figure 3. FTIR of (a)MCM-41,(b)MCM-41-modified with 3-aminopropyltrimethoxysilan ,(c)MCM-41 with pyridine , (d) MCM-41-3-aminopropylsilyl-Cobaloxime,(e) MCM-41- pyridine-Cobaloxime, (f) Cobaloxime.

Characterization of Cobaloxime immobilized onto the modified MCM-41

The spectrum of the all modified MCM-41(Figure 3b, 3c) as well as the spectra of the modified MCM-41 (Figure 3a) is dominated by strong band characteristic of the support matrix, indicating the supper framework remained unchanged. Figure 3d and 3e shows the modified MCM-41 with 3-aminopropyltrimethoxysilan and pyridine cabaldhyde. The spectra of MCM-41 modified with the 3-aminopropyltrimethoxysilane (Figure 3b) shows new weak bands arise at 2960 and 2850 cm-1 probably due to the aliphatic ($-CH_2$) stretching of the propyl chain of the silylating agent, which suggest that the modification of MCM-41 was achieved. After condensation 3-pyridinecarbaldhyde with 3-amnopropyltrimethoxysilyl group anchoring onto MCM-41(Fig. 3c), exhibit a new band at about 1640 cm^{-1}, assignable to the C=N imine vibration [34].

The FTIR spectra of Cobaloxime shows (Figure 3f) , bands at about 1565, 509, 423 cm^{-1} are assignable to the stretching ν(C=N), ν(Co-N, dimethylgolyoxime) and ν(Co-N, pyridine as axial ligand) respectively. FTIR spectrums of MCM-41-modified-Cobaloxime are coincident with that recorded for Cobaloxime (Figure 3d, 3e, 3f). The FTIR the MCM-41s modified with Cobaloxime show bands that correspond to the Cobaloxime and MCM-41-modified. Peaks due to the MCM-41-modified dominate the spectra. These include the O-H vibration in the range 3700-3300 cm^{-1}. Some of the bands characteristic of

Cobaloxime could however, be distinguished. Major MCM-41-modified framework bands appeared around 2930, 1083, 970 and 796 cm^{-1}. Vibration bands due to C=N, Co-N (dimethylgolyoxime), Co-N (NH_2, 3-aminopropylsilane) occur around 1570, 506, 420 cm-1 respectively, broadly similar to those of the neat Cobaloxime. However, the cobaloxime immobilized onto two modified MCM-41 exhibited similar absorption FTIR band of pure cobaloxime. It indicates that the cobaloxime was successfully immobilized onto the all modified MCM-41.

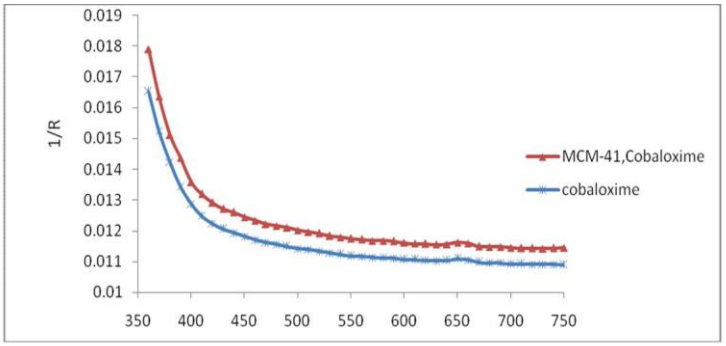


Figure 4. DR UV-VIS spectra (plotted as the inverse of the reflectance, R) of cobaloxime and cobaloxime immobilized onto MCM-41 modified with 3-aminopropylsilyl.

The diffuse reflectance UV-VIS spectra in the 400-700 nm ranges were recorded with a Color-Eye 7000 spectrometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference. The diffuse reflectance spectra (400-700 nm) of Cobaloxime immobilized onto MCM-41 modified with 3-aminopropylsilyl showed in Figure 4. The Cobaloxime shows a characteristic absorption bands at 670 nm corresponding to metal-ligand charge transfer Cobaloxime. DR UV-VIS Cobaloxime immobilized onto MCM-41 modified with pyridine shows absorbance bands at 670 and 430 (Figure 5) corresponding to metal-ligand charge transfer Cobaloxime.

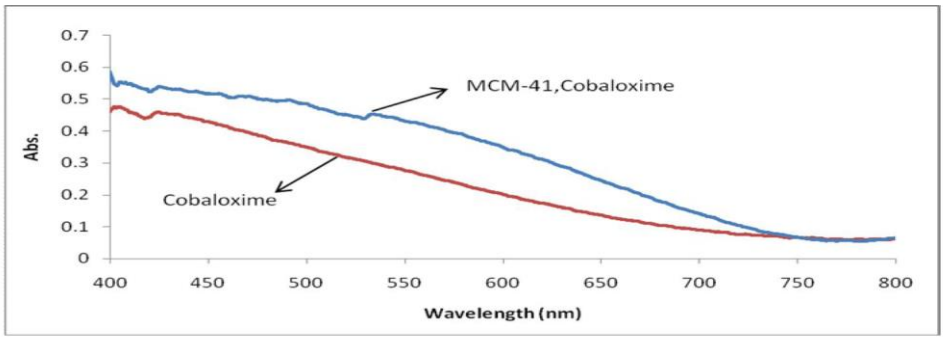


Figure 5. DR UV-VIS spectra of cobaloxime and cobaloxime immobilized onto MCM-41 modified with pyridine.

The bulk cobalt contents of two samples (Cobaloxime immobilized with MCM-41 modified with 3-aminopropylsilyl and pyridine) determined by ICP analysis. When similar concentrations of Cobaloxime were treated with similar concentration of MCM-41 modified with 3-aminopropylsilyl and pyridine, the uptake of cobalt through MCM-41 modified with pyridine (5.3%) higher than MCM-41 modified with 3-aminopropylsilyl (3.2%). The uptake Cobaloxime increases, with increase of an electrostatic interaction between the Co Cobaloxime and N of pyridine (scheme2) and N of aminopropyl (scheme1) surfaces of modified MCM-41.This interaction increase with increase electron donating N of pyridine and N of NH_2 surfaces of modified MCM-41.

Conclusion

The Cobaloxime immobilized on the modified MCM-41 by simplified method. Surfaces of MCM-41 modified with 3-aminopopyltrimethoxysilan and 3-pyridinecaboxyaldhyde, can be act as axial ligand for sixteen sites of co Cobaloxime and formation electrostatic interaction between the N surfaces modified of MCM-41 and co Cobaloxime.

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