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Article

Immobilization of Cobalt Phthalocyanine and Tetrasulfophthalocyanine onto MCM-41 and MCM-48: Effect of Immobilization Method on Catalytic Activity

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Tetra-sulfoftalocianina de cobalto (CoPcS) foi ancorada quimicamente à superfície das MCM-41 e MCM-48 modificadas com aminas. Estas sílicas mesoporosas foram preparadas por processo hidrotérmico. Misturas físicas de CoPc em MCM-41 e em MCM-48 também foram preparadas para fins de comparação. Os quatro catalisadores preparados, 10 wt.% CoPcS/NH_2-MCM-41, 10 wt.% CoPcS/NH_2-MCM-48, 10 wt.% CoPc/MCM-41 e 10 wt.% CoPc/MCM-48 foram caracterizados por difratometria de raios X (XRD), espectroscopia de reflectância difusa UV-Vis e análise de superfície específica BET. A atividade catalítica dos catalisadores imobilizados foi testada na epoxidação aeróbica de cicloexeno. CoPcS/NH_2-MCM-41 e CoPcS/NH_2-MCM-48 mostraram relativamente elevada seletividade para epóxido, mas baixa conversão de cicloexeno comparada a CoPc/MCM-41 e CoPc/MCM-48. Nenhum processo lixiviação da metaloftalocianina dos catalisadores imobilizados por ligação química foi observado no meio reacional e esses catalisadores puderam ser reutilizados quatro vezes.

Cobalt tetrasulfophthalocyanine (CoPcS) was chemically anchored to amine-modified MCM-41 and MCM-48 surface. These mesoporous silica were prepared by hydrothermal procedure. Physical mixtures of CoPc in MCM-41 and in MCM-48 were also prepared for comparison purposes. The four prepared catalysts, 10 wt.% CoPcS/NH_2-MCM-41, 10 wt.% CoPcS/NH_2-MCM-48, 10 wt.% CoPc/MCM-41 and 10 wt.% CoPc/MCM-48, were characterized by X-ray diffractometry (XRD), diffuse reflectance UV-Vis spectroscopy and BET specific surface analysis. The catalytic activity of the immobilized catalysts was tested in the aerobic epoxidation of cyclohexene. CoPcS/NH_2-MCM-41 and CoPcS/NH_2-MCM-48 showed relatively high epoxide selectivity but low conversion of cyclohexene compared to CoPc/MCM-41 and CoPc/MCM-48. No leaching of metallophthalocyanine from the catalysts immobilized by chemical bonding into the reaction medium was observed and these catalysts could be reused four times.

Keywords: MCM-48, MCM-41, cobalt tetrasulfophthalocyanine, immobilization, epoxidation of cyclohexene

Introduction

Molecular oxygen has been recently utilized as an attractive and environmentally benign oxidant for oxidation reactions because it is of easy accessibility, inexpensive and non-toxic. On the other hand, the reactivity of cobalt(II) complexes toward dioxygen has been long recognized.[1,2] For example, cobalt(II) phthalocyanines are efficient catalysts for the oxidation of ascorbic acid, cysteine, mercaptoethanol, hydrazine, hydroxylamine and sulfite.[3]

Despite the selectivity advantage of homogeneous catalysts, almost all of the industrial catalytic processes use heterogeneous catalysts because of their one major advantage, their easy separation from the reaction product. In addition, the problem of recovering and/or recycling the catalysts is addressed.[4]

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The use of structured and insoluble supports as a strategy to immobilize catalysts was reported in the late sixties. Despite the desirable catalytic properties of zeolites they become inadequate when reactants with sizes above the dimensions of the pores have to be processed. In this case, the rational approach to overcome such a limitation would be to increase their diameter to bring them into the mesoporous region.[5]

In 1992, scientists in the Mobil Oil Corporation research group discovered M41S family with exceptional large and uniform pores,[6,7] in which diameters can be varied in the range of approximately 15-100 Å. At the beginning, three members of these materials were introduced, namely MCM-41, MCM-48 and MCM-50. MCM-48 is unique among the mesoporous materials. Narrow pore size distribution and its three dimensional pore network make MCM-48 as a matrix to immobilize catalytically active species.[8-11]

Four common methods for the immobilization of homogeneous catalysts can be identified, based on the interaction between the catalyst and the solid support:[12] covalent binding, electrostatic interaction, adsorption and encapsulation.

Covalent binding is by far the most frequently used method. Immobilization via electrostatic ionic interactions is a facile method for immobilizing ionic catalysts or those catalysts that can be ionized under the immobilization conditions. While the adsorption method is simple, it tends to yield an unstable catalyst because of the weak interaction between catalyst and support. Encapsulation is the only catalyst immobilization method that does not require any interaction between catalyst and support.

In our previous report,[13] we synthesized and characterized iron tetrasulfophthalocyanine grafted onto amine-modified MCM-41 and MCM-48, which were synthesized via a non-hydrothermal procedure. It was observed that the supported catalysts worked well for the selective oxidation of styrene to benzaldehyde and FePcS/NH_2-MCM-48 showed higher activity and durability compared with FePcS/NH_2-MCM-41 and unsupported catalyst. In continuation of our previous study in this field, MCM-41 and MCM-48 were prepared by hydrothermal synthesis and it was applied amine-modified mesopores for immobilization of CoPcS. The encapsulated CoPcS was used as catalyst for oxidation of cyclohexene with O_2 to the corresponding epoxide. To investigate the effect of adsorption of catalysts on the walls of MCM-41 and MCM-48, the CoPc/MCM-41 and CoPc/MCM-48 catalysts were also prepared by physical adsorption and used for the epoxidation reaction of cyclohexene.

Experimental

Reagents and equiments

All reagents were purchased from Merck or Fluka and used as received. Infrared spectra were recorded (KBr pellets) on a Shimadzu model FTIR 4600 spectrometer. UV-Vis spectra in the range of 300-800 nm were recorded on a Shimadzu 2100 spectrophotometer, using a quartz cell. X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu K_α radiation. Textural properties of the immobilized complexes were determined from N_2 adsorption isotherms measured using a Quantachrome Nova 2200 version 7.11 instrument.

Preparation of immobilized cobalt tetrasulfophthalocyanine

First, MCM-41 and MCM-48 were synthesized using a hydrothermal approach (abbreviated as MCM-$41_{(hydro)}$ and MCM-$48_{(hydro)}$, respectively),[14] and then functionalized by 3-aminopropyltriethoxy silane.[15] The organosilane and amine group characteristic peaks (2930 and 1550 cm^{-1}, respectively) in the FTIR spectra of the grafted materials confirmed the presence of amine groups on the surface of the mesoporous silica.

Sodium salt of cobalt tetrasulfophthalocyanine was prepared according to the literature[16] and was converted to corresponding acid by ion exchange resin (CoPcS). IR (KBr, ν/cm^{-1}): 649, 745, 779, 929, 1092, 1137, 1177, 1315, 1392, 1464, 1511, 1616. CoPcS/NH_2-MCM-$41_{(hydro)}$ and CoPcS/NH_2-MCM-$48_{(hydro)}$ with 10 wt.% CoPcS content were synthesized according to the procedure described in detail in our previous publication.[13]

Preparation of immobilized cobalt phthalocyanine

Cobalt phthalocyanine (CoPc) was prepared as described elsewhere.[17] Then, cobalt phthalocyanine was grafted onto hydrothermally synthesized mesopores using the published procedure.[18] So, a solution of 0.05 g of CoPc in 20.0 mL of toluene was stirred and slowly added to a suspension of 0.45 g of HSi-MCM-41 and HSi-MCM -48 in toluene (resulting in 10 wt.% CoPc/MCM-$41_{(hydro)}$ and CoPc/MCM-$48_{(hydro),}$ respectively). It was refluxed overnight. A dark blue material was separated by filtration and treated with toluene and chloroform, respectively.

General procedure for catalytic aerobic oxidation

Oxidation of cyclohexene with dioxygen in the presence of mesopore-encapsulated metallophthalocyanines as catalyst was performed at room temperature. In a typical experiment, 0.004 mmol of catalyst, 1 mmol (0.1 mL) of cyclohexene, 1 mmol (0.091 mL) of isobutyraldehyde and 5 mL of acetonitrile were loaded into a tube. Then, air was bubbled for 2 h at room temperature. Products were analyzed in a Finnigan Trace GC Ultra gas chromatograph equipped with a flame ionization detector and a capillary RTX-1 column. Each experiment was repeated thrice and reproducible data were obtained. The activities of bare and functionalized MCM-41 and MCM-48 were also measured in the absence of CoPcS. Conversion for blank test was below 3%.

For testing the reusability of the catalysts, they were separated from the reaction mixture by centrifugation, washed with methylene chloride, dried and directly subjected to the next run. For the investigation of CoPcS leaching into the solution, the supported catalysts were filtered out and the filtered solutions were analyzed for CoPcS using a UV-Vis spectrophotometer.[19] UV-Vis spectrum of the recovered filtrate did not show any absorption peaks in the 600-700 nm region.

Results and Discussion

Preparation of the supported catalysts

Cobalt was chosen as metal center to the metallophthalocyanine complexes due to its reported oxidation properties. For example, mercaptant removal from the petroleum catalyzed by cobalt phthalocyanines, especially cobalt tetrasulfophthalocyanine (CoPcS), is one of the primary methods used for the deodoration of petroleum products (Merox process).[20]

Using MCM-41 and MCM-48 as support, the CoPcS catalyst was immobilized by a multi-step grafting method. As previously reported, strong interaction of CoPcS acidic protons with amine groups result in the retention of CoPcS on the silica surface.[13] To investigate the influence of immobilization method on the stability and catalytic properties of cobalt phthalocyanine, heterogenized catalysts were also prepared by physical adsorption. This results in weak adsorption of metallocomplex on the mesoporous surface.

X-ray diffraction patterns

As reported in the literature,[6,7,21] XRD patterns of MCM-41 and MCM-48 exhibit peaks in the low angle region, the most intense peak being the (100) and (211) reflection, respectively. Results of the XRD study of MCM-41$_{(hydro)}$ and MCM-48$_{(hydro)}$ supported cobalt tetrasulfophthalocyanine catalysts (CoPcS/NH$_2$-MCM-41$_{(hydro)}$ and CoPcS/NH$_2$-MCM-48$_{(hydro)}$) reveal that the MCM-41 and MCM-48 supports remain structurally unchanged. This indicates that the structure of mesopores is retained when the phthalocyanine complex is anchored onto the channels (Figures 1 and 2). Furthermore, XRD patterns show a decreased intensity for main peaks compared to the primary materials. A similar observation was earlier made by our group when FePcS was grafted in the channels of NH$_2$-MCM-41$_{(non-hydro)}$ and NH$_2$-MCM-48$_{(non-hydro)}$.[13]

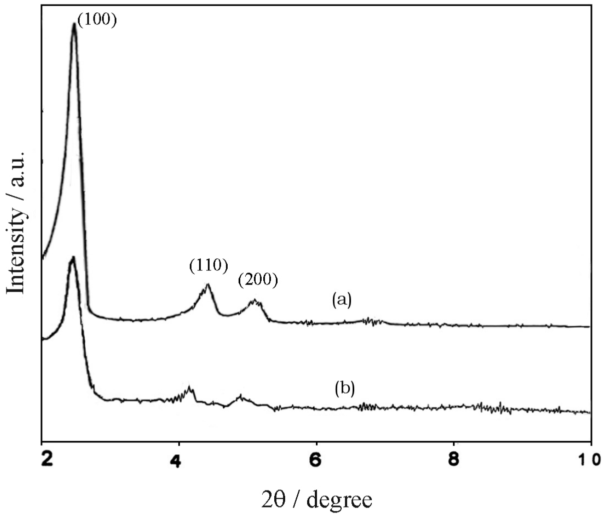

Figure 1. Low angle XRD patterns of (a) MCM-41$_{(hydrothermal)}$ and (b) CoPcS/NH$_2$-MCM-41$_{(hydrothermal)}$.

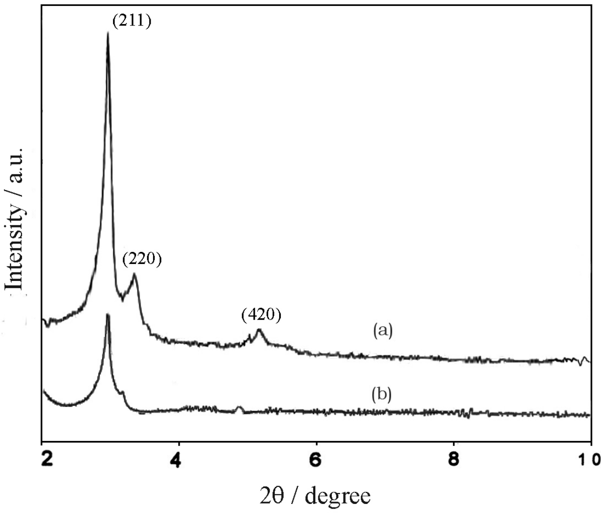

Figure 2. Low angle XRD patterns of (a) MCM-48$_{(hydrothermal)}$ and (b) CoPcS/NH$_2$-MCM-48$_{(hydrothermal)}$.

X-ray diffraction patterns of the CoPc/MCM-41$_{(hydro)}$ and CoPc/MCM-48$_{(hydro)}$ samples, prepared by physical adsorption (Figure 3), show the characteristic patterns for the hexagonal array found in MCM-41$_{(hydro)}$ and MCM-48$_{(hydro)}$, respectively (Figures 1a and 2a). But compared to bare MCM-41$_{(hydro)}$ and MCM-48$_{(hydro)}$, the peak positions shift to lower angles. It is probably due to the accommodation of the complex on mesoporous surface. In addition, the decrease in the intensity of reflections, which is well known in the immobilization of various catalysts inside mesopore channels,[22] was not observed. It might be because of two reasons: (*i*) CoPc was exclusively located at the outer surface of these mesopores; (*ii*) there is no strong interaction between cobalt phthalocyanine and surface of the mesoporous supports.

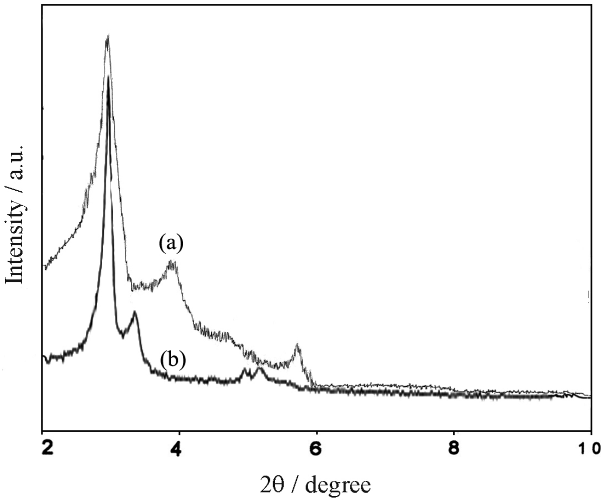

Figure 3. Low angle XRD patterns of (a) CoPc/MCM-48$_{(hydrothermal)}$ and (b) CoPc/MCM-41$_{(hydrothermal)}$.

Adsorption studies

The textural properties were determined by N_2-sorption studies carried out at 77 K (Table 1). As reported in a previous work,[13] a large decrease in BET surface area of MCM-41$_{(hydro)}$ and MCM-48$_{(hydro)}$ was observed after immobilization of CoPcS (from 1029 to 187 and 1084 to 475 m^2 g^{-1}, respectively), with a reduction in the pore volume compared with the parent mesopores, suggesting that CoPcS was present inside the channels of the support materials. It is similar to the the earlier report of Sorokin *et al.*[23] and Zanjanchi *et al.*[24] that the surface area and pore volume decreased as iron and cobalt tetrasulfophthalocyanine grafted onto amine-modified silica or MCM-41. Table 1 also presents the specific surface areas and total pore volumes of the MCM-41 and MCM-48 before and after CoPc adsorption. The specific surface area and pore volume of CoPc/MCM-41$_{(hydro)}$ and CoPc/ MCM-48$_{(hydro)}$ are very close to that of MCM-41$_{(hydro)}$ and MCM-48$_{(hydro)}$, indicating the presence of CoPc complexes at the external surface of the mesoporous support rather than inside the pore system.

Table 1. Texture parameters for the mesoporous materials before and after anchoring with CoPcS and CoPc sample

	BETspecific surface area / (m^2 g^{-1})	Total pore volume / (mL g^{-1})
CM-41$_{(hydrothermal)}$	1029	0.81
CoPcS/NH$_2$-MCM-41$_{(hydrothermal)}$	187	0.09
CoPcS/NH$_2$-MCM-41$_{(hydrothermal)}$	187	0.09
CoPc/MCM-41$_{(hydrothermal)}$	1031	0.84
MCM-48$_{(hydrothermal)}$	1084	0.65
CoPcS/ NH$_2$-MCM-48$_{(hydrothermal)}$	475	0.28
CoPc/MCM-48$_{(hydrothermal)}$	1082	0.76

Diffuse reflectance spectroscopy

Figure 4 shows diffuse reflectance UV-Vis spectra of cobalt tetrasulfophthalocyanine immobilized on NH$_2$-MCM-41$_{(hydro)}$ and NH$_2$-MCM-48$_{(hydro)}$ in the wavelength range 400-800 nm. Generally, the metallophthalocyanines exhibit characteristic bands in their optical spectra;[25] a strong absorption, termed the Q band, is detected in the visible region between 650 and 690 nm, and another between 320 and 370 nm, called the Soret band (correspond to $\pi \rightarrow \pi^*$ transitions). The electronic spectra of metallotetrasulfonated phthalocyanine (MPcS) complexes have been well studied.[26-28] These complexes exist as dimers in equilibrium with monomers, the spectra of MPcS, thus, consists of two peaks in the Q-band region.[28] The high energy absorption band near 620 nm is associated with the dimeric species and the low energy band near 670 nm is due to the monomeric species.[26,28]

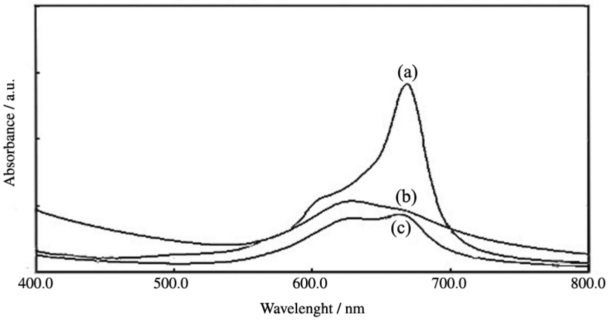

Figure 4. Diffuse reflectance spectra of (a) CoPcS, (b) CoPcS/NH$_2$-MCM-48$_{(hydrothermal)}$ and (c) CoPcS/NH$_2$-MCM-41$_{(hydrothermal)}$.

The presences of absorption a band about 670 nm and a shoulder at 630 nm in diffuse reflectance spectrum of the catalyst indicated that CoPcS did not degrade significantly inside molecular sieves. CoPc/MCM-41$_{(hydro)}$ and CoPc/MCM-48$_{(hydro)}$ materials showed two broad peaks around 610 and 660 nm (Figure 5), which is attributed to the Q-band of CoPc. Broad bands of CoPc from 500 to 800 nm suggest the presence of dimers or higher aggregates of CoPc at these mesoporous silicas.

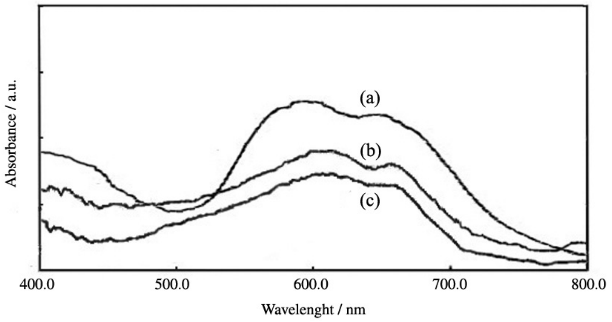

Figure 5. Diffuse reflectance spectra of (a) CoPc, (b) CoPc/MCM-48$_{\text{(hydrothermal)}}$ and (c) CoPc/MCM-41$_{\text{(hydrothermal)}}$.

Catalytic properties of the immobilized catalysts

Aerobic epoxidation of cyclohexene has been extensively studied previously.[29-31] Oxidation of cyclohexene with metalloporphyrins or metallophthalocyanines gave cyclohexene oxide as the predominant product and some allylic oxidation products, cyclohexenol and cyclohexenone, as minor products. The product distributions were different for each metal complex. Oxidation of cyclohexene with the catalysts prepared by both chemical (first set, Table 2) and physical adsorption (second set, Table 3) gave cyclohexene oxide as the main product. Several parameters influencing the catalytic properties were investigated. The results indicate that higher yields of epoxide were obtained with first set catalysts although second set showed higher conversion. With the second set of catalysts, 2-cyclohexene 1-ol and 2-cyclohexene1-one are minor products, but when first set was employed as catalyst, 2-cyclohexene1-ol just obtained.

It was observed that catalysts anchored on the surface of amine functionalized MCM-48 showed higher activity in comparison to MCM-41 supported catalysts. This is in full agreement with data published in our earlier report.[13] In addition, mesoporous supports synthesized by non-hydrothermal method gave higher conversion of cyclohexene in comparison to mesopores synthesized by the hydrothermal procedure (Table 2). It is attributed to a uniform distribution of the epoxidation products on regular arrangement of hydrothermally synthesized mesopores. This factor improves the product stacking inside the channels comparing to non-hydrothermal ones.

Table 2. Comparison of various catalytic systems (CoPcS/NH$_2$-MCM (chemical adsorption)) for cyclohexene epoxidation using isobutyraldehyde and O$_2$[a]

Catalyst		Conversion / %	Turn over number[d]	Product selectivity[b] / %		
				Epoxy cyclohexane	2-Cyclohexene-1-ol	2-Cyclohexene-1-one
CoPcS	1st run	27.4	68.5	69.5	13.2	17.3
	4th run[e]	10.7	26.8	47.8	18.9	33.3
CoPcS/NH$_2$-MCM41$_{\text{(non-hydrothermal)}}$	1st run	33.8	84.5	80.1	19.9	-
	4th run	31.8	79.5	60.1	15.8	24.1
CoPcS/NH$_2$-MCM48$_{\text{(non-hydrothermal)}}$	1st run	50.6	126.6	90.5	9.5	-
	4th run	46.4	116.1	55.5	16.1	28.4
CoPcS/NH$_2$-MCM41$_{\text{(hydrothermal)}}$	1st run	21.9	54.8	88.5	11.5	-
	4th run	18.7	46.8	58.8	9.5	31.7
CoPcS/NH$_2$-MCM48$_{\text{(hydrothermal)}}$	1st run	34.3	85.7	81.0	19.0	–
	4th run	30.3	75.7	51.8	13.3	34.9

[a]Reaction conditions: cyclohexene (1 mmol), catalyst (0.004 mmol), isobutyraldehyde (1 mmol) in CH$_3$CN (5 mL), O$_2$ = 1 atm, 2 h. [b]By gas chromatography determination based on external standards and using authentic samples for comparison. [c]Based on cyclohexene. [d]Molar ratio of converted substrate to catalyst. [e]No considerable catalyst activity was observed after second run.

Table 3. Comparison of various catalytic systems (CoPc/MCM (physical adsorption)) for cyclohexene epoxidation using isobutyraldehyde and O$_2$[a]

Catalyst		Conversion[c] / %	Turn over number[d]	Product selectivity[b] / %[b]		
				Epoxy cyclohexane	2-Cyclohexene-1-ol	2-Cyclohexene-1-one
CoPc	1st run	50.3	125.6	85.4	2.5	12.1
	recycled	35.3	88.2	84.2	5.0	10.8
CoPc/MCM41$_{\text{(hydrothermal)}}$	1st run	73.6	183.9	81.0	2.8	16.3
	4th run	21.2	53.1	82.2	6.9	11.0
CoPc/MCM48$_{\text{(hydrothermal)}}$	1st run	81.5	203.6	80.1	4.2	15.7
	4th run	33.4	83.5	83.7	5.9	10.4

[a]Reaction conditions: cyclohexene (1 mmol), catalyst (0.004 mmol), isobutyraldehyde (1 mmol) in CH$_3$CN (5 mL), O$_2$ = 1 atm, 2 h. [b]By gas chromatography determination based on external standards and using authentic samples for comparison. [c]Based on cyclohexene. [d]Molar ratio of converted substrate to catalyst.

Interestingly, when CoPcS/NH_2-MCM-41$_{(hydro)}$ and CoPcS/NH_2-MCM-48$_{(hydro)}$ were employed, the selectivity improved only slightly beyond that for CoPc/MCM-41$_{(hydro)}$ and CoPc/MCM-48$_{(hydro)}$, though conversion significantly decreased. This activity loss suggests that externally bound metallophthalocyanine species experience no diffusional limitations that would affect adversely the performance of centers buried within the mesopore system. In addition, the enhanced activity of CoPc compared to the activity of the CoPcS complex may be attributed to the more hydrophobic character of it that favors adsorption of alkenes and results in the increase of the number of active sites.

Furthermore, the influence of the phthalocyanine immobilization method on the stability of the catalyst was investigated by reusing the catalysts. The supported catalysts prepared in chemical method are almost stable, and so, it was possible to reuse them for four times (Table 2), but the epoxide selectivity decreased. When the second set of catalysts was used, after second run, a considerable decrease in the catalytic activity was observed (Table 3). Comparing the result in the second run with that in the first run, the conversion decreased about 71.15% for MCM-41 and 59.02% for MCM-48, though the epoxide selectivity almost kept constant. It is well known, that O_2 and iBu-aldehyde give a peroxocarboxylic acid, which is the real oxidizing agent. In the presence of CoPc, it might decompose to give radicals which might attack either the CoPc complex or the amine linker. So, the degradation of CoPc on the outer surface might be a problem. Additionally, there are μ-oxo species known from transition metal porphyrines and phthalocyanines, which are much more active than their non-bridged counterparts.[23] Acetonitrile shifts the dimer/monomer equilibrium towards a monomeric CoPcS complex maybe due to axial coordination on the cobalt center of CoPcS. So, the monomerization would also occur preferentially on the outer surface of the materials and could explain the strong activity decrease. These results showed that chemical adsorption of catalysts inside mesopores channels is a better method for phthalocyanine immobilization due to the formation of stronger bonds of the catalyst with amine functionalized support.

Conclusions

The immobilization of cobalt tetrasulfophthalocyanine (CoPcS) complex on the inner surface of the pores of NH_2-MCM-41 or NH_2-MCM-48 occurs by means of chemical bonding with the amine groups. Different characterization techniques such as diffuse reflectance UV-Vis spectroscopy, X-ray powder diffraction and BET specific surface area measurements, revealed that CoPcS is distributed in the channels of molecular sieves. These samples were compared with the samples prepared by physical mixing, CoPc/MCM-41$_{(hydro)}$ and CoPc/MCM-48$_{(hydro)}$, in cyclohexene oxidation. The chemically immobilized catalyst has relatively high epoxide selectivity, they can be run for four times. On the other hand, CoPc/MCM-41$_{(hydro)}$ and CoPc/MCM-48$_{(hydro)}$, which were prepared by physical adsorption, are more active than CoPcS/NH_2-MCM-41$_{(hydro)}$ and CoPcS/NH_2-MCM-48$_{(hydro)}$.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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Supplementary Information

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Immobilization of Cobalt Phthalocyanine and Tetrasulfophthalocyanine onto MCM-41 and MCM-48: Effect of Immobilization Method on Catalytic Activity

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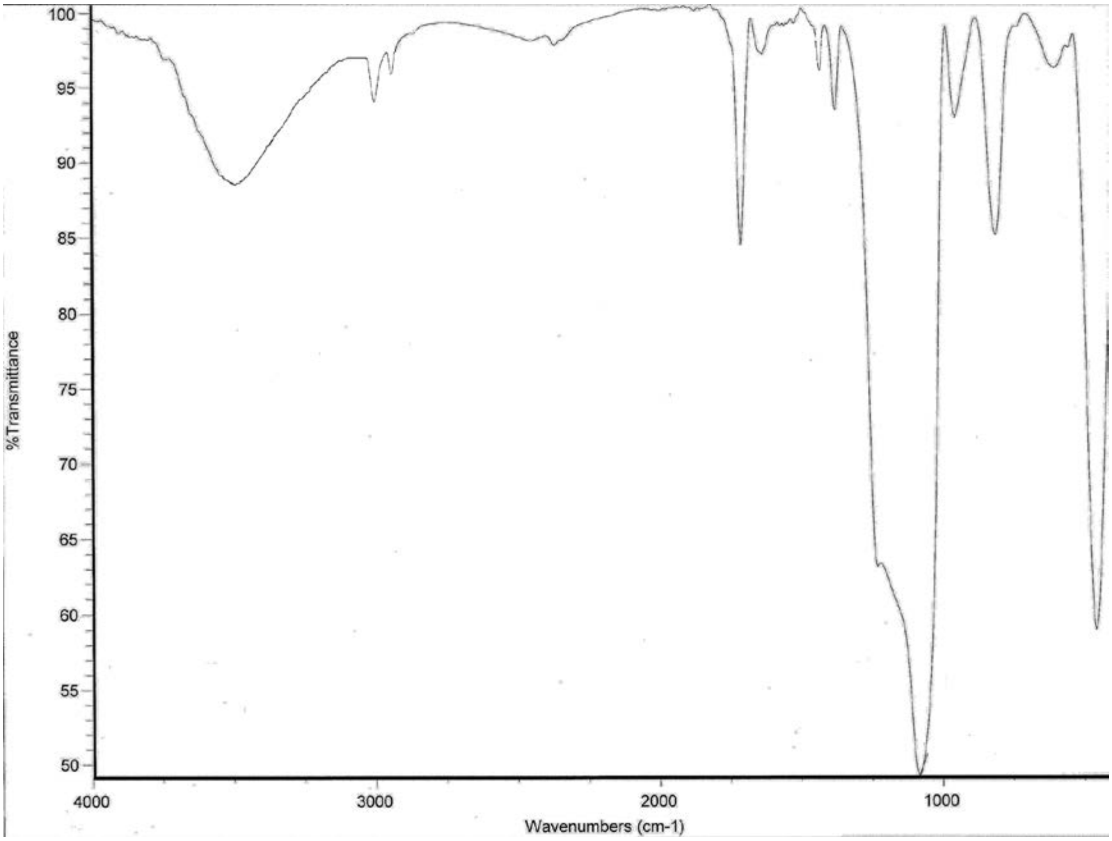

Figure S1. FTIR spectrum of NH_2-MCM-41.

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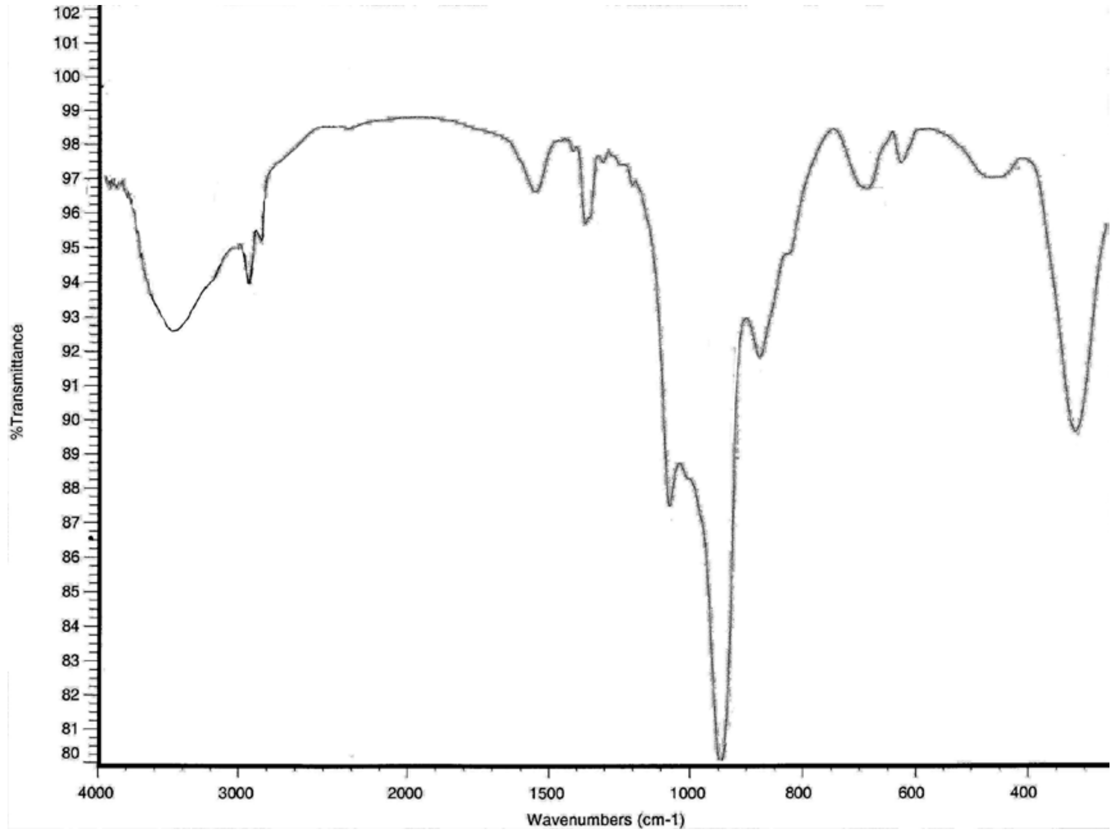

Figure S2. FTIR spectrum of NH_2-MCM-48.

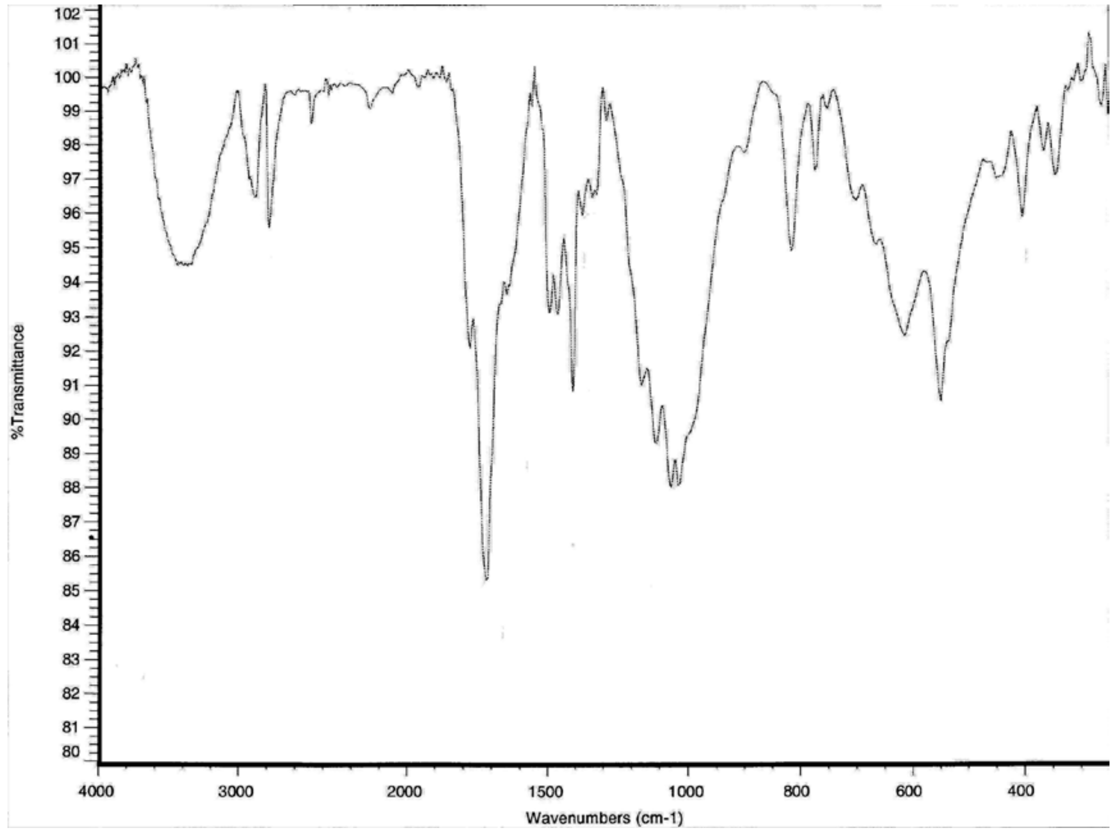

Figure S3. FT-IR spectrum of CoPcS.

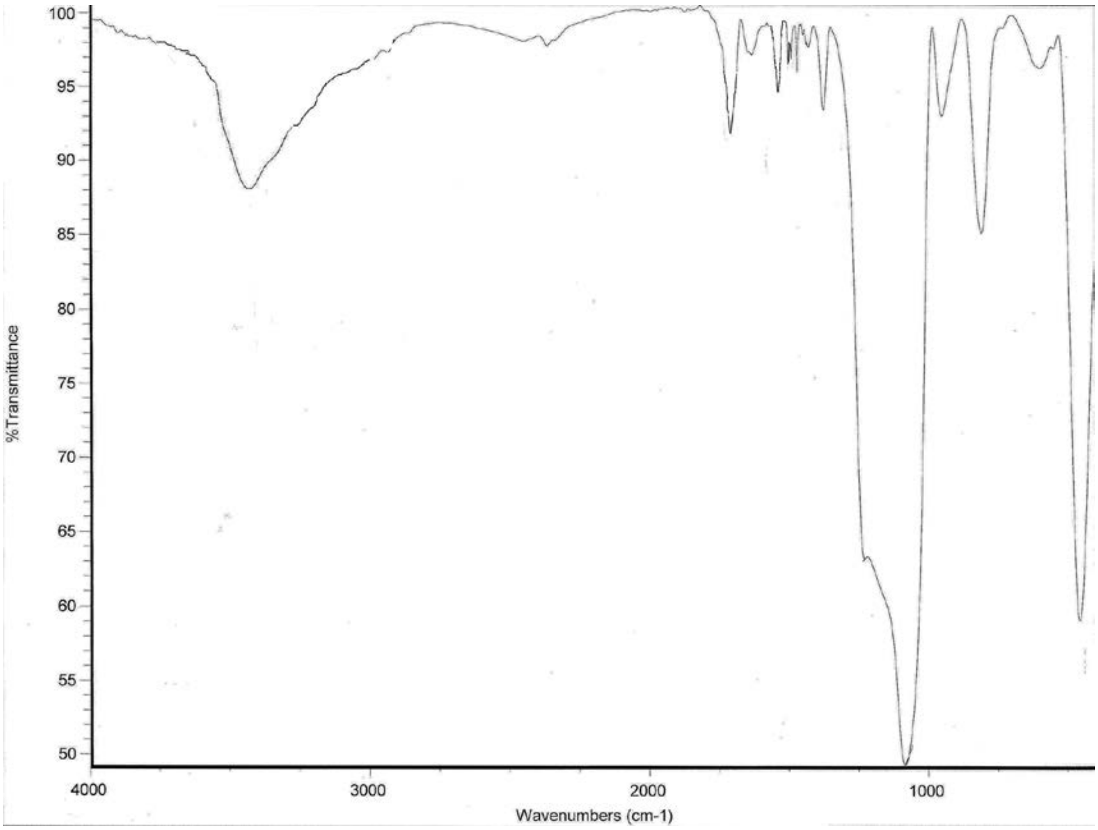

Figure S4. FTIR spectrum of CoPc/MCM-41.

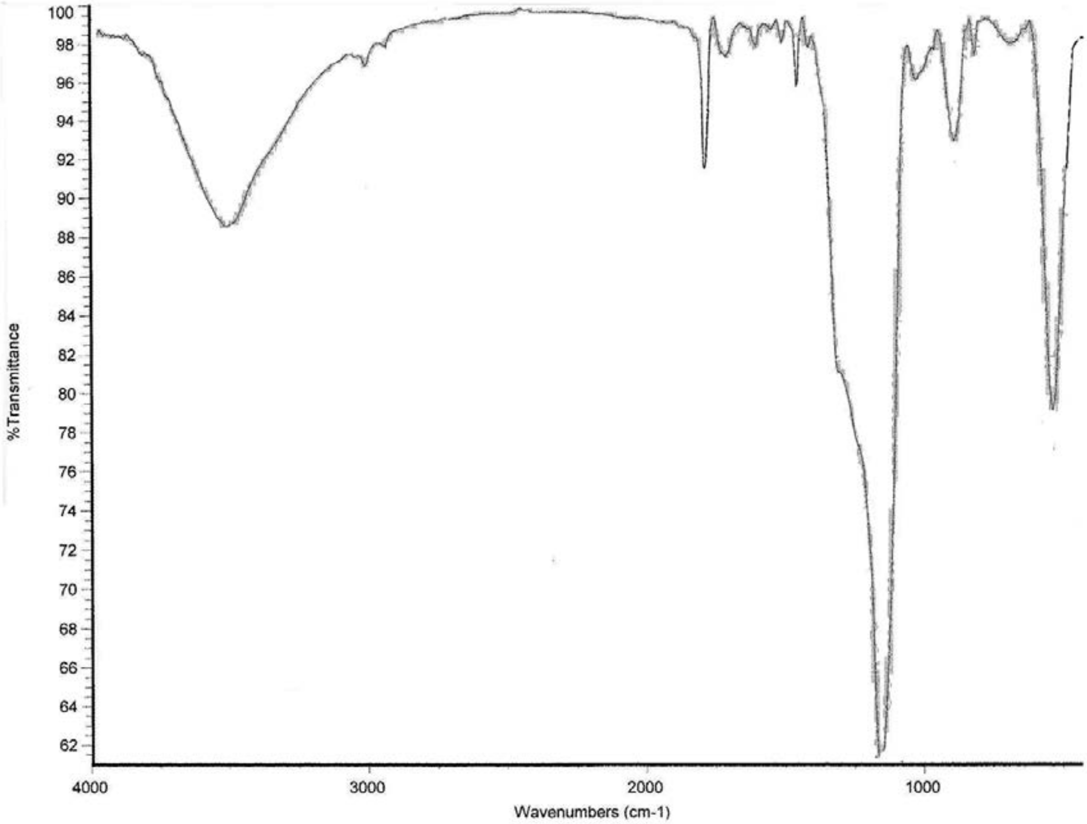

Figure S5. FTIR spectrum of CoPcS/NH_2-MCM-48.

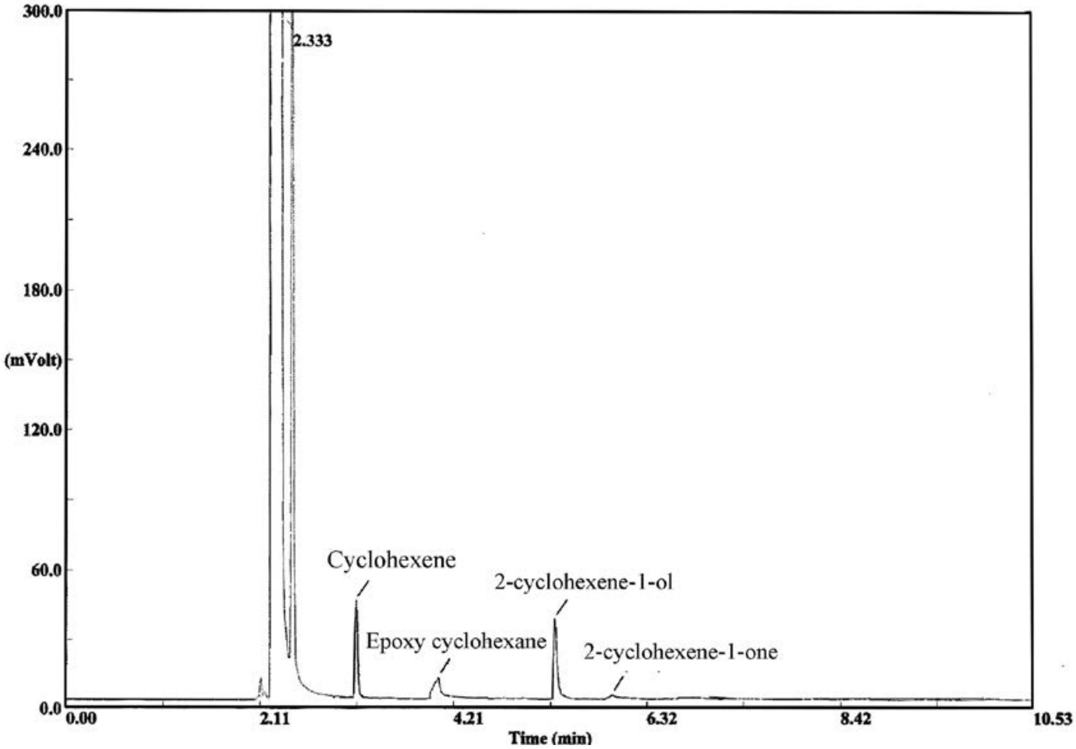

Figure S6. Gas chromatogram of cyclohexene epoxidation, based on external standards and using authentic samples.