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Synthesis of copper mesostructured silica and functionalization by trimethyl chlorosilane (TMCS)

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Abstract Mesoporous material of MCM-41 type has been modified by the introduction of aluminum and copper, and then by grafting with trimethyl chlorosilane (TMCS). The influence of these treatments on the mesoporous materials was evaluated by the reaction of phenol degradation in the presence of H₂O₂. The characterization of the materials by several techniques (X-ray diffraction, N₂ adsorption, UV and IRTF spectroscopies, etc.) shows that the mesostructural order is retained after the different modifications and that the grafting enhances the catalytic activity in the degradation of phenol.

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1. Introduction

The contamination of water by phenol has been recognized as an issue of growing importance in recent years. Phenol is a potential human carcinogen and is of considerable health concern, even in low concentrations. For instance, Malaysian guidelines limit phenol concentration to 0.001 mg l⁻¹ in wastewater (DOE, 2002). Hence, the treatment of wastewater containing phenol is a necessity. Many technologies have been

investigated for the removal and degradation of phenolic compounds in wastewater. They included, adsorption (Rengaraj et al., 2002), biodegradation (Miland et al., 1996), UV/Fe⁺³ (Zhou et al., 2001), extraction by liquid membrane (Lin et al., 1999) and oxidation (Tahar and Savall, 1999; Awad and Abuzaid, 2000). Among these, oxidation technology has shown its potential to destroy phenol completely in wastewater. In the oxidation process, in the first step, the phenol oxidizes to hydroquinone then into benzoquinone and catechol. Subsequent oxidation of these products, after opening of the aromatic ring, leads to the formation of aliphatic carboxylic acids such as maleic acid and fumaric acid. When phenol is degraded to aliphatic carboxylic acids the wastewater will become more biodegradable (Wu and Zhou, 2001) and less toxic (Pulgarin et al., 1994). The oxidation of phenol by several oxidizing agents such as ozone, UV, and hydrogen peroxide has been extensively studied (Benitez et al., 2001; Canton et al., 2002) and a lot of studies deal with the use of clays as catalyst in the phenol oxidation (Gil and Gandia, 2000; Narayanan, 2001).

MCM-41, a member of the mesoporous molecular sieves M41S family, possesses a regular hexagonal array of uniform

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pore openings with a broad spectrum of pore diameters between 15 and 100 Å (Beck et al., 1992; Kresge et al., 1992). The control of the pore sizes of MCM-41 can be achieved by the choice of template, adding organic chemicals, or changing synthetic conditions.

Through proper control of preparation conditions, such as template, reaction temperature and time, pH value, high quality MCM-41 materials with the following properties could be obtained: high surface area (more than 1000 m²/g) and large pore volume, uniform pore size, and high thermal and chemical stability (Zhao et al., 1996). All of these advantages make MCM-41 suitable as a catalyst support for oxidation.

The large pore surface area is favorable for the loading of the active element. The mesopore size of MCM-41 makes the diffusion of reactants easier. Corma et al. (1996) prepared Ni, Mo/MCM-41 catalyst and found it has a very high activity in hydrodesulfurization and hydrodenitrogenation, which was attributed to the high surface area and large pore size that favored a high dispersion of active elements, and made large amounts of the reactive molecules easily accessible. Kuchеров (2006) studied the distribution, properties, and thermal stability of different Cu²⁺ sites supported MCM-41 modified by introducing Al, Zr, or W ions, he finds that Al-MCM-41 affords the highest thermal stability and degree of dispersion.

In this paper, we report the preparation and characterization of copper catalyst supported on Al-MCM-41 materials and grafted by the trimethyl chlorosilane (TMCS), and synthesized using cetyltrimethylammonium bromide solution as the template. The Cu/MCM-41 catalyst was characterized by XRD analysis, nitrogen adsorption and IRTF spectroscopy and the catalytic performance was evaluated in the oxidation of phenol in water solution. Results show that Cu/MCM-41 is a promising catalyst for wastewater treatment.

2. Experimental

2.1. Synthesis of MCM-41

A typical gel of synthesis for the sample MCM-41 was prepared by adding 150 g of colloidal silica (ludox 40%, Prolabo) to an aqueous solution containing 73.63 g TEAOH ((C₂H₅)₄NOH, 35% solution, Aldrich) and 91.115 g of cetyltrimethylammonium bromide (CTMABr, Biochem), under agitation for 1 h. The resulting gel was brought to a temperature of 100 °C for 48 h. The formed solid is filtered, washed with distilled water and dried at 80 °C during one night. In the end, the material obtained is calcined under air flow at 550 °C for 6 h. For the Al-MCM-41 synthesis we used the same molar composition given for the synthesis of MCM-41 with the following steps: preparing three solutions S1, S2 and S3, respectively, which contain a source of aluminium (NaAlO₃) mixed with the TEAOH (S1), an aqueous silica solution (S2) and an aqueous solution which contains CTABr (S3). The Si/Al molar ratio is equal to 50. The mixture obtained after homogenization of 2 h is carried to 100 °C for 2 days. The products are calcined at 550 °C for 6 h.

2.2. Preparation of Cu-supported MCM-41 catalysts

The used method is called TIE or Tensioactif Ionic Exchange method (Decyk et al., 2001): 3 g of as-synthesized MCM-41 is added to 200 ml of an ethanolic solution of Cu(NO₃)₂ (0.1 M)

under agitation. After 30 min exchange period at 60 °C, the products are filtered, washed by ethanol then dried at 80 °C. Finally, the samples are calcined at 550 °C during 6 h.

2.3. Preparation of (TMCS)-Cu-MCM-41 catalysts

A monolayer of trimethylsilyl (TMS) groups is covalently attached to the pore surface of MCM-41. Approximately 2 g of template-extracted MCM-41 was outgassed in a vacuum system with a residual pressure of less than 5 · 10⁻⁴ Torr at a temperature of 450 °C for a given time and then subsequently soaked in a TMCS solution in toluene with a concentration of 5 wt% (solid:liquid) at 70 °C under stirring for a desired time. The mixture was then extensively washed with toluene and acetone to rinse away any residual chemicals. Finally, the powder was dried at 50 °C.

2.4. Oxidation of phenol

The catalytic properties were evaluated in a typical oxidation system. The experimental runs were carried out in a glass, semi-batch reactor, equipped with a magnetic stirrer. The temperature of the reaction vessel was maintained constant 70 °C using a round oil-heated jacket. Amounts of catalyst were added to the substrate solution. An aqueous H₂O₂ solution (30% w/v) was added after the desired temperature was reached. We employed a constant 3:1 phenol:H₂O₂ molar ratio and the reaction medium is water. Samples were filtered in order to remove any catalyst particles. The analyzes of samples were performed by gas chromatography.

2.5. Characterization of catalyst

Nitrogen adsorption was performed at -196 °C in a TriStar 3000 V6.04 A volumetric instrument. The samples were outgassed at 80 °C prior to the adsorption measurement until a 3 × 10⁻³ Torr static vacuum was reached. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, the distribution of pores was evaluated by BJH method (Barrett et al., 1951). Powder X-ray diffraction (XRD) patterns of samples dried at 80 °C were collected at room temperature on a Bruker AXS D-8 diffractometer with Cu Kα radiation. Fourier-transform infrared (FT-IR) spectra of samples in KBr pellets were measured on a Bruker Vector 22 spectrometer. UV spectra were recorded on a UV/Vis Perkin Elmer – Lambda 14 spectrometer, and chemical analyzes were carried out by atomic absorption (Varian Spectra AA 220).

3. Results

3.1. Characterization of MCM-41

Powder low-angle X-ray diffraction (XRD) patterns of Si-MCM-41 before and after modification are depicted in Fig. 1A and B which clearly indicate characteristic peaks of mesoporous materials.

The XRD pattern of Si-MCM-41 exhibited a well ordered structure and the peaks are indexed on a hexagonal lattice which correspond to (1 0 0), (1 1 0), (2 0 0) reflections.

For the aluminium form (Fig. 1), corresponding to a ratio of Si/Al = 50, the diffractogram pattern is similar to the Al-

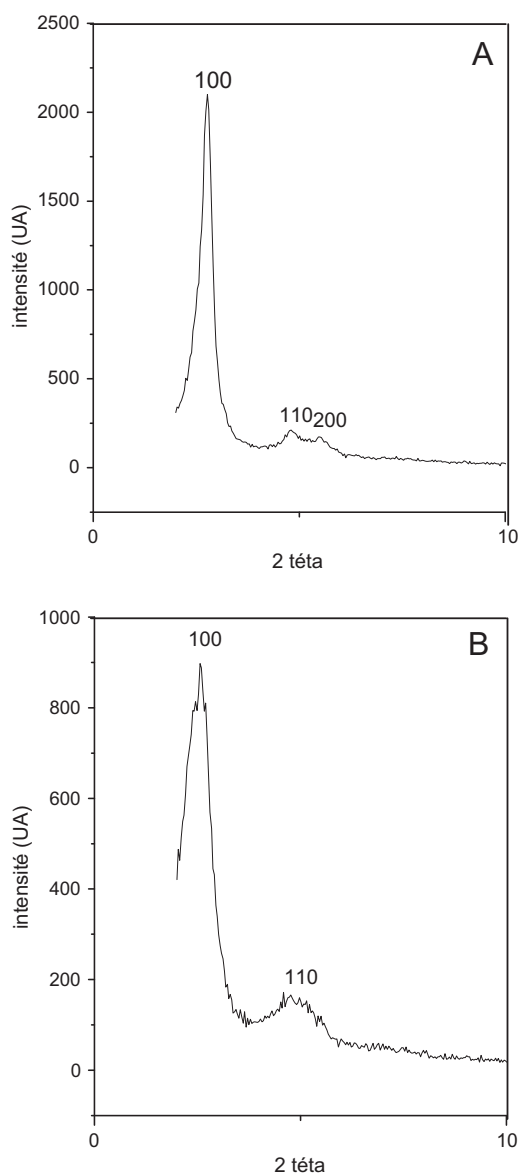


Figure 1 X-ray powder diffraction pattern of (A) Si-MCM-41 and (B) Al-MCM-41.

MCM-41 prepared by Cesteros (Cesteros and Haller, 2001). The decrease of signals intensities and the lack of d_{200} reflection relative to pure MCM-41 were caused by the participation of aluminium in the formation of the crystalline phase.

The nitrogen adsorption–desorption isotherm of the MCM-41 sample (Fig. 2) is of type IV, typical of mesoporous solids according to the Brunauer classification, the curves of adsorption and desorption are practically confused which indicates pores' uniformity with diameter < 4 nm and the specific area is high ($1294 \text{ m}^2/\text{g}$) (Table 1). The Al-MCM-41 isotherm is shown in Fig. 2, it is also of type IV with a surface area of ($1053 \text{ m}^2/\text{g}$) characteristic of mesoporous materials.

3.2. Characterization of Cu-MCM-41

The X-ray powder pattern of Cu-MCM-41 showed the existence of three peaks of reflection (1 0 0), (1 1 0), and (2 0 0),

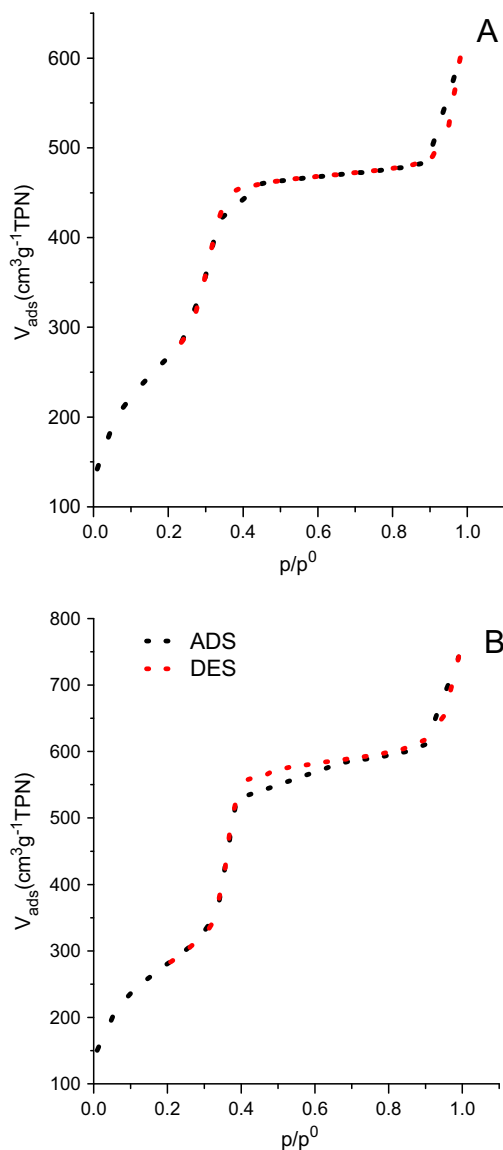


Figure 2 N_2 physisorption isotherms of (A) Si-MCM-41 and (B) Al-MCM-41.

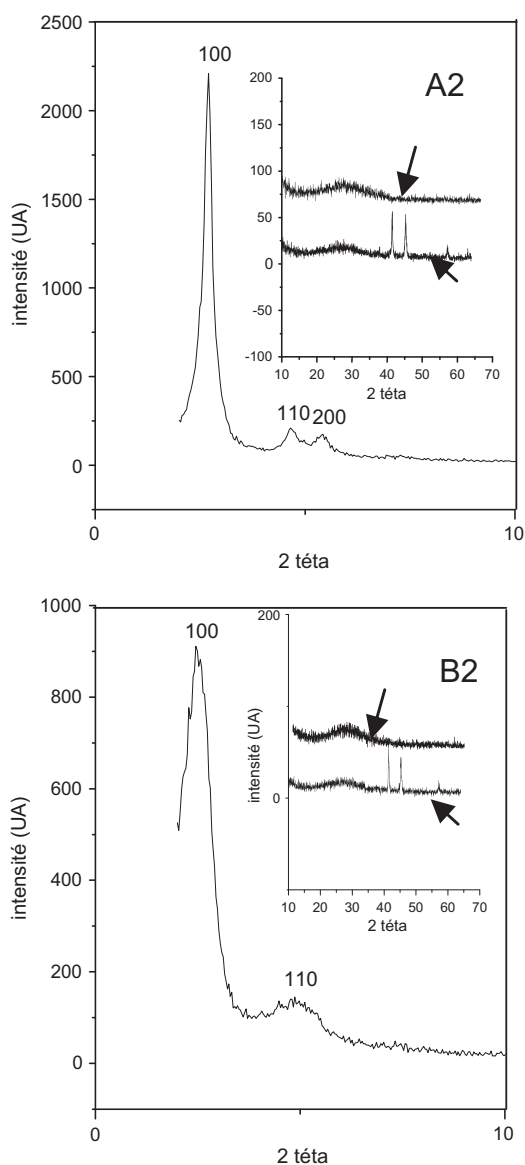
characteristic of the hexagonal phase, thus the structure remains intact (Fig. 3). Peaks corresponding to copper oxide are visible at high angle diffraction ($30^\circ < 2\theta < 40^\circ$). For Cu–Al-MCM-41 the structure remains also intact and we note also the appearance of peaks corresponding to copper oxide in the range ($30^\circ < 2\theta < 40^\circ$). By comparison of the two spectra before and after calcinations, we can deduce that the copper oxide is formed after calcination (Fig. 3). UV spectra of the calcined samples Cu-MCM-41 (TIE) and Cu–Al-MCM-41 (TIE) are reported in Fig. 5. We note the appearance of a wide band from 200 to 600 nm corresponding to copper oxide CuO phase. The nitrogen isotherm adsorption of the samples Cu-MCM-41 and Cu–Al-MCM-41 are of the type IV (Fig. 4), the S_{BET} and V_{meso} decrease and the walls become thicker (Table 1)

$$a = \frac{2}{\sqrt{3}} d_{100}, \quad D_p = 1.212522 \cdot d_{100} \left(\frac{\rho \cdot V_{\text{meso}}}{1 + \rho \cdot V_{\text{meso}}} \right)^{1/2}$$

$$w = a - D_p.$$

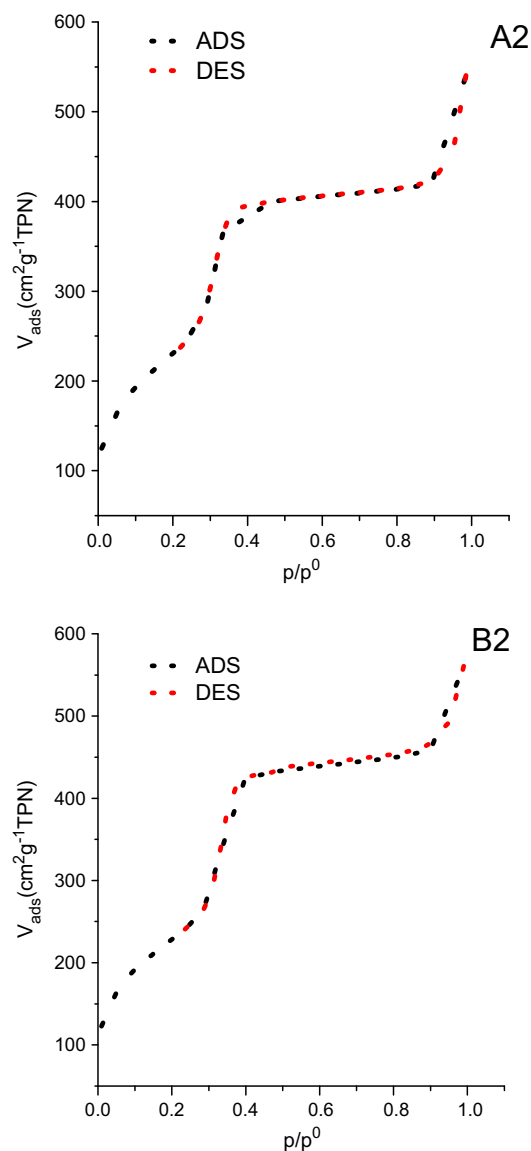
Table 1 Physical properties of copper MCM-41 materials.

Catalysts	Surface area (m ² /g)	Wall thickness (w) (Å)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (Å)	Cu (wt%)
Si-MCM-41	1294	7.86	0.69	35.03	—
Cu-MCM-41 TIE	1103	9.17	0.60	34.69	0.73
Al-MCM-41	1053	7.18	0.84	39.02	—
Cu-Al-MCM-41 TIE	981	9.41	0.64	38.67	0.88

**Figure 3** X-ray powder diffraction pattern of (A2) Cu-Si-MCM-41 and (B2) Cu-Al-MCM-41.

4. Discussion

The characterization by X-ray diffraction proves that the obtained material has hexagonally ordered channels by the presence of the three reflections characteristic of mesoporous materials. The nitrogen adsorption confirms the ordered structure of pores and the surface calculated is very high.

**Figure 4** N₂ physisorption isotherms of (A) Cu-Si-MCM-41 and (B) Cu-Al-MCM-41.

The X-ray pattern of the Al-MCM-41 form presents a lower intensity for reflection (1 0 0) and the disappearance of peak (2 1 0) because of the participation of aluminium in the construction of the walls. In fact, the incorporation of aluminium leads to a distortion of the mesophases before the formation of MCM-41 (Occelli and Biz, 2000).

The XRD patterns of the two materials (Cu-MCM-41 and Cu-Al-MCM-41) prepared by using TIE method indicate the conservation of the structure. These results are confirmed by

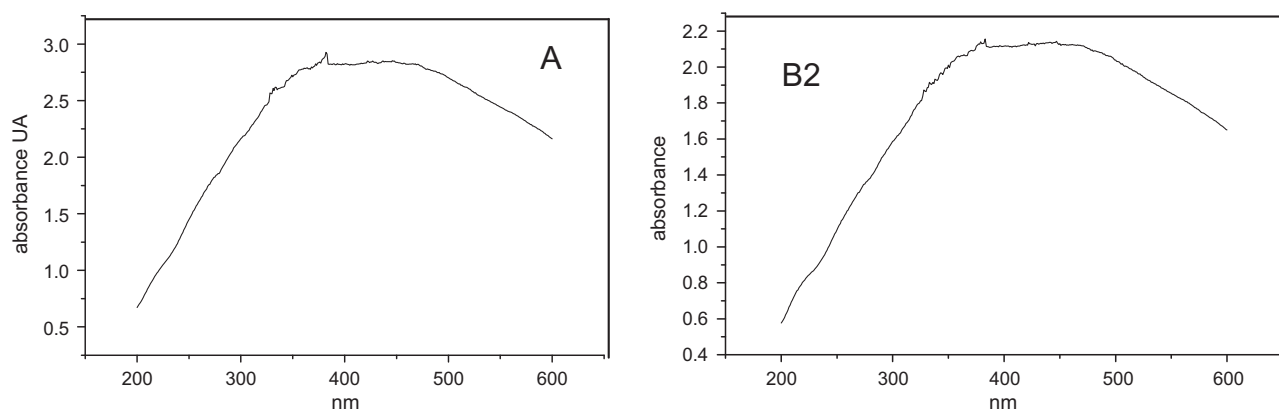


Figure 5 DR-UV-vis spectra of: (A2) calcined Cu-Si-MCM-41 and (B2) calcined Cu-Al-MCM-41.

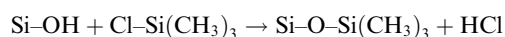
the nitrogen adsorption. This conservation of the structure is due to the weak hydrolysis in ethanolic media. Lower surface area and thicker walls after introducing the copper for the two materials (MCM-41 and Al-MCM-41), are allotted to the presence of CuO occupying the pore space of copper modified MCM-41. No difference is showed between UV spectra of Cu-MCM-41 and Cu-Al-MCM-41, indicating that the exchange is done only with the surfactant molecules. We can thus obtain Al-MCM-41 material doped only by copper oxides. By comparison of the XRD patterns at high angle diffraction before and after calcinations, we deduce that the copper oxides species are formed after calcination. The copper content is high for the two forms processed by the TIE method (Table 1).

4.1. Characterization of grafted materials

The influence of the grafting is evaluated essentially by FTIR investigation. Fig. 6 shows the FTIR spectra of sample MCM-41(C) in the range $4000\text{--}400\text{ cm}^{-1}$, we note the following bands: absorption band in the range $3200\text{--}3800\text{ cm}^{-1}$ ascribed to free SiOH groups and another in the range $1500\text{--}2000\text{ cm}^{-1}$ assigned to distortion vibrations of SiOH, and another in the range $1000\text{--}1100\text{ cm}^{-1}$ ascribed to distortion vibrations of SiO^- and AlO^- , and finally a band at 450 cm^{-1} corresponding to distortion vibrations of T-O (T = Si and Al). These results are similar with those of the literature (Corma, 1995). After the grafting with TMCS groups (Fig. 7) we found the same bands with the disappearance of the vibration and distortion band of SiOH groups of the surface ($-\text{OH}$) and

the apparition of two bands at 2964 cm^{-1} and 845 cm^{-1} assigned to the C-H vibrations.

According to the FTIR spectra of grafted Cu-Al-MCM-41, it is observed that a weak concentration of SiOH groups on the surface of these materials is due to their replacement by $\text{Si-O-Si}(\text{CH}_3)_3$ groups according to the following reaction:



After treatment by TMCS groups, the solids present a hydrophobic surface and a more hydrothermal stability (Koyano et al., 1997).

5. Catalysis

The catalytic performance of the different solids was evaluated by the reaction of phenol oxidation in water solution.

5.1. Catalysis over Cu-MCM-41 and Cu Al-MCM-41

Table 2 presents the rate conversion of phenol by using the two catalysts (Cu-MCM-41 and Cu-Al-MCM-41). The reaction realized in aqueous media leads to different conversions of phenol for the two used catalysts and a different selectivity.

The MCM-41 doped by copper prepared by the TIE method presents a low rate of phenol conversion and the formation of polymers according to literature and other products according to literature but has selectivity for hydroquinone. Catechol and benzoquinone are not observed, probably because of the weak activity of the catalyst and the formation of polymers,

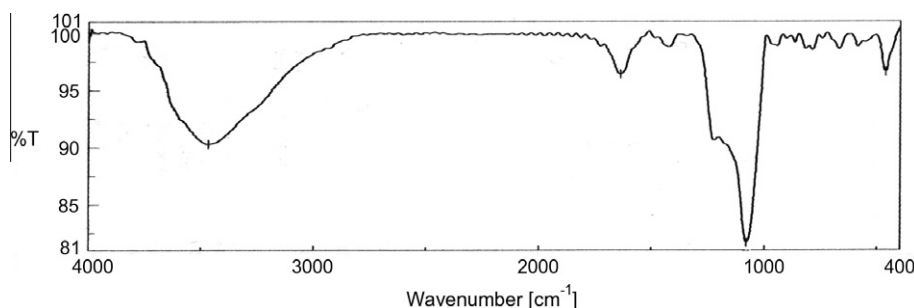


Figure 6 FTIR spectra of Cu-Al-MCM-41.

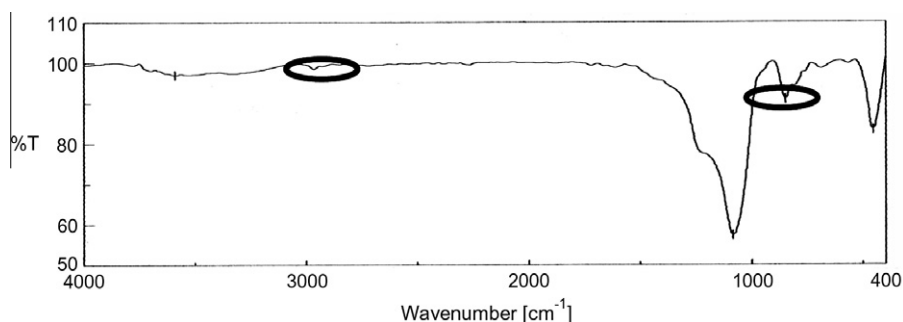


Figure 7 FTIR spectra of TMCS-Cu-Al-MCM-41.

Table 2 Activity of different catalysts in phenol degradation.

Catalysts	Rate of conversion of phenol (%)
Cu-MCM-41	27
Cu-Al-MCM-41	73

on the other hand the Al-MCM-41 prepared by the same method presents a high activity but low selectivity to hydroquinone. The formation of polymers is provoked by the fast decomposition of oxygenated water this is induced by the active species (the copper in our case). It explains the high activity to the formation of polymers (Deyk et al., 2005).

The difference in activity can be attributed to the acidity of Al-MCM-41 materials assigned to weak sites of Brönsted and strong sites of LEWIS (Corma et al., 1994). Lewis' acidity that develops these types of catalysts can play a role in the reaction (Ziolek et al., 1997).

5.2. Catalysis in the presence of TMCS-Cu-Al-MCM-41

To improve the activity of the copper mesoporous materials, we have done a second activation by grafting organic groups (TMCS).

By using Cu-Al-MCM-41 grafted by TMCS we find that the rate of conversion is very high (94%) with a negligible selectivity to phenol hydroxyls (catechol and hydroquinone). This high activity can be attributed to the modification of the materials surface, by the replacement of OH groups by hydrophobic groups that helps the adsorption of the phenol on the surface.

6. Conclusion

The tensioactive ionic exchange method gives ordered structures for both the forms, Cu-MCM-41 and Cu-Al-MCM-41. These later contains the highest copper content in the CuO form.

Mesoporous MCM-41 modified by the incorporation of active elements (Al-Cu) is a promising catalyst support for wastewater treatment. With the aid of uniform pore structure and large surface area and pore volume, it can assist the active element in removing organic pollutants such as phenol with high efficiency and speed.

Modified Cu-Al-MCM-41 materials by TMCS exhibit more hydrophobic surface property and therefore it is more applicable as a catalyst for the removal of organic compounds such as phenol, in the presence of water.

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