THE EFFECT OF THE METHOD OF COPPER INCORPORATION ON THE STRUCTURE OF Si-MCM-41 AND Al-MCM-41

Housseyn SEKKIOU*, Rachida HAMACHA*, Tewfik ALI-DAHMANE, Amine MORSLI, Abdelkader BENGUEDDACH

Laboratoire de Chimie des Matériaux, Université d’Oran BP: 31100 Oran Es-Sénia. ALGERIE.

(Reçu le 14 Novembre 2012, accepté le 12 Mars 2013)

ABSTRACT: Copper modified MCM-41 silica and AlMCM-41 materials obtained by various preparation techniques: direct synthesis, impregnation (ROT), cation exchange (IE) and template ionic exchange (TIE). Two fundamental characteristics of the materials prepared have been considered: (i) structure and texture, (ii) copper content and state. The results shows that the TIE method allow to obtain the best ordered materials with higher contain of copper.

Key words: copper, MCM-41, Al-MCM-41, impregnation, exchange.


1 Introduction:
MCM-41, a member of the newly discovered mesoporous molecular sieves M41S family, possesses a regular hexagonal array of uniform pore openings with a broad spectrum of pore diameters between 15 and 100Å [1]. 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 1000m²/g) and large pore diameter, uniform pore size, and high thermal stability [2]. All of these advantages make MCM-41 very applicable as a catalyst support. Several laboratories incorporated various elements as well as silicon in the MCM-41 such as aluminum, vanadium, niobium, etc., changing with the same way the physicochemical properties of the material [3]. Mesoporous materials containing aluminium, present a large improvement of acid characteristics; the presence of aluminium in a wide range of Si/Al ratios in the framework of mesoporous involve a significant acidity [4]. Incorporation of various metals (Ni, Al, Co, Mg, Fe and Cu) improved catalytic properties of these materials [5,6] When trivalent cations like Al³⁺, B³⁺, Ga³⁺, Fe³⁺ replace silicon in the frame of mesoporous silica, negative charges are created and can be compensated by protons, and these solids can be employed in acid reactions. When the insertion of the cations (Ti³⁺, V³⁺, Sn³⁺, Zr³⁺, Cu²⁺) are presents, the electroneutrality is maintained and the corresponding mesoporous materials are employed in specific reactions like oxidations [7]. Successful recent studies concern the incorporation of metals in the MCM-41 material, such as the incorporation of Fe [8], Ti [9,10], V [11], Cr [12], Cu [13], Zn [13]. The stability of the products by calcination depends not only on the nature of the incorporated element but also on the synthesis conditions [8]. The presence of metal in the mesoporous materials walls made possible to undertake studies on specific reactions, such as hydroxylation and alkylation of

* Corresponding authors, e-mails: housseyn11@yahoo.fr
hamacha.rachida@univ-oran.dz
phenol [15], oxidation and isomerization of hexane [16], oxidation and dehydrogenation of hydrocarbons [17] and hydrogenation of aromatic compounds [18]. MCM-41 modified by the insertion of metals (bimetallic) has also been studied and tested in the selective oxidation of styrene and benzene [19]. The incipient wetness method allowed to form efficient CuO/SBA-15 composites in benzene oxidation [20].

In this paper, we report the preparation and characterization of copper catalyst supported on MCM-41 materials synthesized using cetyltrimethylammonium bromide solution as the template and by using several methods. The materials obtained were characterized by XRD analysis, nitrogen adsorption, UV spectroscopy and atomic absorption.

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 to an aqueous solution containing 73.63g TEAOH ((C$_2$H$_5$)$_4$NOH, 35% solution, Aldrich) and 91.115g of cetyltrimethylammonium bromide (CTMABr, Biochem), with stirring for 60 min. The resulting gel was brought to a temperature of 100°C for 48h. The formed solid is filtered, washed with distilled water and dried at 80°C during 12h. Finally, the solid obtained was calcined in air at 550°C for 6 hours. 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, which contain respectively a source of aluminium (NaAlO$_3$) mixed with the TEAOH, an aqueous silica solution and an aqueous solution which contains cetyltrimethylammonium bromide. The molar ratio which corresponds to the incorporation of aluminium is Si/Al=50. The mixture obtained after homogenization of 2 h is carried to 100°C for 48h. The obtained solids was calcined in air at 550°C for 6 h.

2.2. Preparation of Cu-supported MCM-41 catalysts: Four methods were used to incorporate copper.

2.2.1 Direct synthesis: 150 g of colloidal silica were added to an aqueous solution containing 73.63g TEAOH ((C$_2$H$_5$)$_4$NOH, 35% solution, Aldrich) and 91.115g of cetyltrimethylammonium bromide (CTMABr, Biochem), with stirring during 30 min. Finely the adding of amount of Cu(NO$_3$)$_2$ (The molar ratio Si/Cu=50) with stirring during 30 min. The resulting gel was brought to a temperature of 100°C for 48h. The formed solid was filtered, washed with distilled water and dried at 80°C during 12h. Finally, the solid obtained was calcined in air at 550°C for 6 h.

2.2.2 Ionic exchange for Al-MCM-41 (IE): 2g of the calcined material is mixed, under agitation, with 250ml of an aqueous solution of Cu(NO$_3$)$_2$ (0.1M) at 50°C for 2h. After filtration and drying, the procedure is repeated three times. The solids were calcined under ambient air at 550°C during 6 h.

2.2.3 The template ionic Exchange (TIE): 3g of non-calcined material are added to 200 ml ethanolic solution of Cu(NO$_3$)$_2$ (0.1M) 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 in air at 550°C during 6 h.

2.2.4 Impregnation and treatment in the rotary evaporator (ROT): 2g of calcined material are added to 85ml of an aqueous solution of Cu(NO$_3$)$_2$ (0.024M). The treatment is carried out under stirring during 24h then we eliminate water by the rotary evaporator at 70°C. Finally the solids are calcined in air at 550°C for 6 h.

2.3. Characterization of catalyst:

Nitrogen adsorption was performed at -196°C with 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, distribution of pores was evaluated by BJH method [21]. 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 UV/Vis Perking Elmer - Lambda 14 spectrometer, and chemical analyses were carried out by atomic absorption (Varian Spectra AA 220).

3 Results

Fig1a and Fig1b shows the XRD patterns of the MCM-41 and Al-MCM-41 catalysts. It can be seen from these figures that the diffraction patterns are typical of mesoporous hexagonal MCM-41 [22,23] Table 1 summarizes, metal content and N₂ adsorption data of the various MCM-41 samples. The N₂ adsorption–desorption isotherm of calcined MCM-41 and Al-MCM-41 and the dopped materials by copper (Fig3a, Fig3b) is typical of reversible type IV as defined by IUPAC for mesoporous materials.

3.1.1 Direct method:
The low angles XRD patterns of Cu-MCM-41 and Cu-Al-MCM-41 after calcination are showed in (Fig1a, Fig1b) it can be observed the decreasing on peak intensities and the absence of d\(200\) reflection which means that the Cu/MCM-41 structure is not as well ordered as the as the parent MCM-41. For the sample Cu/Al-MCM-41 we recorded a low intensity of the peaks which indicates a less structure order. UV spectra reported in (Fig4a and 4b), for the two samples, indicates a band at 240 nm which corresponds to the presence of Cu\(^{+2}\) species [24], and a second band for Cu-MCM-41 centered at 600 nm relating to copper oxide CuO [25].

3.1.2 Template ion exchange method (TIE):
The patterns of the Cu-MCM-41 and Al-Cu-MCM-41 showed that the structure remains intact, peaks corresponding to copper oxide are visible at high angle diffraction (40°<2θ< 50°) (Fig2a, Fig2b) for the two materials. UV showed (Fig4a, Fig4b) the appearance of a wide strip from 200 to 600 nm corresponding to copper oxide CuO phase for the two materials.

3.1.3 Ionic Exchange (IE) method:
This method is only applicable for the Al-MCM-41 because of the presence of negative charge of \([\text{AlO}_4]^-\) in the frame. The X-ray powder pattern of Al-MCM-41 is presented in Fig1b, the aluminic form conserve a good structural order without copper oxide peaks presents at 40°<2θ<50° (Fig2a, Fig2b). UV spectra showed the appearance of two bands towards 210 and 263 nm relating to the presence of Cu\(^{2+}\).
3.1.4 Impregnation and treatment by the rotavapor method (Rot): Fig 1a shows reduction in the intensity of reflection (100) and the disappearance of the two reflexion peaks (110) and (200) for Cu-MCM-41 which prove that the corresponding structure is not as well ordered as the as the parent one. The structure of the aluminic form is preserved (Fig 1b). Elsewhere, the peaks of copper oxides appear for the two cases (Fig 2a, Fig 2b).

Spectroscopy UV reveal for the sample Cu-MCM-41 the appearance of two bands: the first less intense towards 265nm relating to the presence of Cu$^{2+}$ and at 270-650 nm relating to the presence of CuO. For Cu-Al-MCM-41 we observe a relative bands towards 235 nm with the presence of Cu$^{2+}$ and less intense towards 600nm which corresponds to the presence of copper oxide CuO.

Table I: Physical properties of the prepared materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore wall thickness (Å)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Lattice parameter a₀ (Å)</th>
<th>Average pore diameter (Å)</th>
<th>Cu (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MCM-41</td>
<td>1294</td>
<td>7.86</td>
<td>0.69</td>
<td>42.90</td>
<td>35.03</td>
<td>/</td>
</tr>
<tr>
<td>Cu-MCM-41 (direct)</td>
<td>870</td>
<td>10.29</td>
<td>0.56</td>
<td>46.99</td>
<td>36.7</td>
<td>0.26</td>
</tr>
<tr>
<td>Cu-MCM-41 TIE</td>
<td>1103</td>
<td>9.17</td>
<td>0.60</td>
<td>43.86</td>
<td>34.69</td>
<td>0.73</td>
</tr>
<tr>
<td>Cu-MCM-41-ROT</td>
<td>654</td>
<td>11.7</td>
<td>0.33</td>
<td>38.28</td>
<td>26.57</td>
<td>0.68</td>
</tr>
<tr>
<td>Al-MCM-41</td>
<td>1053</td>
<td>7.18</td>
<td>0.84</td>
<td>46.20</td>
<td>39.02</td>
<td>/</td>
</tr>
<tr>
<td>Cu-Al-MCM-41 (direct)</td>
<td>669</td>
<td>12.13</td>
<td>0.51</td>
<td>51.26</td>
<td>39.13</td>
<td>0.27</td>
</tr>
<tr>
<td>Cu-Al-MCM-41 IE</td>
<td>625</td>
<td>13.43</td>
<td>0.38</td>
<td>46.39</td>
<td>32.95</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu-Al-MCM-41 TIE</td>
<td>981</td>
<td>9.41</td>
<td>0.64</td>
<td>48.09</td>
<td>38.67</td>
<td>0.88</td>
</tr>
<tr>
<td>Cu-Al-MCM-41-ROT</td>
<td>825</td>
<td>9.61</td>
<td>0.62</td>
<td>48.05</td>
<td>38.44</td>
<td>0.46</td>
</tr>
</tbody>
</table>

4 Discussion:
The characterization by X-ray diffraction proves that the obtained material has a hexagonal ordered channels by the presence of the three reflections characteristics of mesoporous materials. is typical of reversible type IV as defined by IUPAC for mesoporous materials.

The X-Ray pattern of the Al-MCM-41 form presents a lower intensity for reflection (100) and the disappearance of peak (200) caused by the participation of aluminum in the construction of walls. In fact, the incorporation of aluminum leads to the distortion of mesophases before the formation of MCM-41 [26]. The Cu-MCM-41 prepared by the direct method presents a reduction of the (100) reflection intensity and the disappearance of the (200) reflection which indicates that the material is less ordered compared to as the parent silicious form and the surface area is less important compared to the Si-MCM-41 one, correlated with the results of XRD, this reduction in order can be explained by the presence of CuO (Cu = 0.26W%) which reduces surface or/and the presence of copper during the synthesis which modify the gel medium pH by precipitation of Cu(OH)₂ species. The thicker walls and the existence of Cu$^{2+}$ species confirmed by UV spectroscopy, suggest that Cu$^{2+}$ ions probably located inside the walls are inaccessible to the oxygen atmosphere during the calcination. For the aluminic form a less intense peaks are observed and less surface area showed in table I which can be explained by the presence of the two metals (Cu-Al) during synthesis. UV spectra shows the existence of only Cu$^{2+}$ species; we
think that a part of copper ions are inside the walls and the another one compensates negative charges of the tetrahedral sites (AlO$_4^-$).

The XRD patterns of the two materials (Cu-MCM-41, Cu-Al-MCM-41) obtained by TIE method indicate the conservation of the structure. These results are confirmed by the nitrogen adsorption. This results can be explained by the weak hydrolysis in ethanolic medium. Low surface area and thicker walls, compared with (MCM-41 and Al-MCM-41), are allotted to the presence of CuO occupying the pore space. The BJH distribution of Cu-MCM-41 (Fig 5) is similar to that of purely silicious form which confirms the conservation of the material structure and the peculiarity of the TIE method. 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. By comparison of the XRD patterns at high angle diffraction before and after calcinations (not shown), we deduce that the copper oxides species are formed after calcination. The nitrogen isotherms adsorption of Cu-MCM-41 and Cu-Al-MCM-41 before calcination (Fig 6) are of type IV and the surfaces area are 691 m$^2$/g and 874 m$^2$/g respectively for Cu-MCM-41 and Cu-Al-MCM-41 which indicate that there is an exchange between the template cation and the copper species. The copper content is high for the two forms processed by the TIE method (Table1).

By using IE method, the XRD pattern of Cu-Al-MCM-41 shows a conservation of the structural properties after three consecutive treatments at 50°C and the nitrogen isotherm adsorption indicates a reduction in the surface area which can explain by the increase on the wall thicknesses following the copper incorporation after the exchange. UV spectra shows the existence of only Cu$^{2+}$ cations due probably to the washing after each treatment causing the elimination of the Cu$^{2+}$ species which do not have a strong interaction with the (AlO$_4$)$^-$ sites.

The last method studied is the impregnation followed by rotary evaporation treatment (ROT). The XRD pattern of Cu-MCM-41 shows less ordered structure compared with the MCM-41. The majority of the copper is in oxide form consequently to the oxidation by air oxygen during calcinations. The nitrogen isotherm adsorption presents a stage of apparent capillary condensation and a low surface area which confirms the XRD results. Such a considerable reduction of surface area and pore volume should be allotted to two aspects: first the MCM-41 prepared in alkaline solution has a low hydrothermal stability [27], secondly, the CuO oxide occupies the space of the pore and reduces, thus, the surface and the pore volume (Table 1). On the other hand the XRD pattern of Cu-Al-MCM-41 shows a well structural conservation compared with Cu-MCM-41 result of the high hydrothermal stability [28,29], following the existence of negative charges (AlO$_4$)$^-$. During the impregnation The copper has been exchanged with the sodium which compensates (AlO$_4$)$^-$ charge, the other part being oxided during calcinations. Nitrogen isotherm adsorption is characteristic of mesoporous material with a significant surface area. The analysis by atomic absorption shows a significant copper content.
5 Conclusion

The incorporation of copper in the mesoporous materials MCM-41 and Al-MCM-41 can be done by different methods.

The template ionic exchange method gives ordered structures for the both forms Cu-MCM-41 and Cu-Al-MCM-41 which contain the highest copper content in the CuO form.

Ionic Exchange method applied to the aluminic form makes possible to obtain a mesoporous material exclusively doped by copper cation with a moderate content. The incorporation of copper modifies the textural properties.

The direct method allows the obtaining of Cu-MCM-41-50 with the characteristics of mesoporous materials. Cu$^{2+}$ species are probably located inside the walls and some of CuO oxide is probably located in the surface. As against, this method does not provide an orderly Cu-Al-MCM-41 with a SiO$_2$/Al$_2$O$_3$ = 25 and a molar ratio Si/Cu = 50.

The method of impregnation and treatment in the rotary evaporator leads to Cu-MCM-41 with a low degree of organization and a majority of copper in oxide form. However, the Al-Cu-MCM-41 is well structured with the presence of copper in the Cu$^{2+}$ form and a small quantity in oxide form.

If we compare the different methods, it seems clear that the template ionic exchange method has an undeniable interest. Moreover, by selecting the type of materials and the treatment method, we can better control the state and the content of copper in the doped materials.

References: