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Selective hydroxylation of phenol employing Cu–MCM-41 catalysts

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Abstract

We studied the oxidation reaction of phenol in aqueous and acetonitrile media under mild conditions, employing Cu-modified MCM-41 mesoporous catalysts. The stability of the catalysts under reaction conditions was confirmed by XRD, UV–VIS and FTIR techniques. Results obtained indicate that the selective oxidation of phenol with H_2O_2 by a radical substitution mechanism produces three main reaction products: catechol, hydroqinone and benzoquinone. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Selective hydroxylation; Phenol; Cu–MCM-41 catalysts

1. Introduction

The strong demand in the chemical industry for phenolic compounds have led the development of improved catalyst-based technologies for partial oxidation reactions. Traditional methods employ manganese and chromium salts in the presence of oxygen or air, with the corresponding environmental drawbacks [1–4]. Transition metal complexes are well known oxidizing agents for organic compounds in homogeneous processes [5–7], however, the main limitation of the application of these complexes to environmentally friendly oxidation reactions or to the synthesis of fine chemicals are the difficult recovery of the complexes and their short life-times. Immobilization of transition metal complexes in different types of matrices and supports such as charcoal, polymers, zeolites and layered structures (pillared clays and hydrotalcites) either by direct intercalation, ion exchange or encapsulation (ship-in-the-bottle) has been recently reported [8–10].

On the other hand, because of their regular, hexagonal mesoporous structure and potential application in catalytic reactions, MCM-41 molecular sieves have attracted a considerable scientific attention in recent years. The catalytic properties of these materials can be significantly improved if specific transition metal cations or metal complexes are introduced into the structure [11,12,13,14]. In this work, we report the synthesis, characterization and catalytic behavior of copper complexes encapsulated in MCM-41 molecular sieves for the partial oxidation of phenol.

2. Experimental

2.1. Catalyst preparation and characterization

Cu^{2+} acetate and nitrate salts in alcoholic solution were employed as catalysts for the hydroxylation of phenol using H_2O_2 as oxidant. The performance of these catalysts was compared to Cu-impregnated MCM-41 catalysts.

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Table 1
Catalytic behavior and textural properties of Cu–MCM-41 in acetonitrile medium[a]

Catalyst	Cu (%w)	Products			Conversion/site[b]
		HQ	BQ	CT	
Cu acetate	–	32.50	12.21	55.29	
9Cu/MCM	0.089	33.27	0.00	66.73	8.32
14Cu/MCM	0.14	48.1	7.62	44.28	6.77
30Cu/MCM	0.29	83.17	16.83	0.00	7.13
1CuN/MCM	0.10	1.23	0.05	98.7	4.25
16CuN/MCM	0.16	0.63	0.00	99.37	3.56

[a] Cu/MCM: copper acetate in MCM-41; CuN/MCM: copper nitrate in MCM-41; HQ: hydroquinone; PBQ: *para*-benzoquinone; CT: catechol (product distribution is given on a tar-free basis) $Ph/H_2O_2 = 3.5$, $T = 70\,^{\circ}C$, catalyst $= 55$ mg.

[b] Moles of phenol converted per mole of copper.

Siliceous MCM-41 was prepared by mixing 14 g of hexadecyltrimethylammonium chloride, 10 g of tetrabuthylammonium silicate and 3 g of fumed silica [15]. This preparation was kept inside a Teflon bottle at 368 K for 48 h, thoroughly washed, filtered and calcined at 813 K for 7 h under flowing nitrogen. The MCM-41 had a pore diameter of approximately 38 Å (XRD) and a BET surface area of approximately 1130 m^2/g.

The Cu–MCM-41 catalysts were prepared by adding with stirring 200 ml of the alcoholic solutions of copper acetate and copper nitrate to 1.5 g of MCM-41. The copper compounds were added according to the compositions shown in Table 1. The preparations were kept in ethyl alcohol for 8 h at 308 K. The materials were washed with alcohol and filtered under vacuum (10^{-3} Torr) until the filtrate became free from copper ions and further dried at 393 K.

The structural properties of the solid catalyst were determined by XRD (Siemens D500 Powder Diffractometer), FTIR-DR (Nicolet Magna 750) and UV–VIS (Varian Cary IG) spectroscopy. Textural properties were determined by TPD, TPR and BET analyses.

2.2. *Phenol hydroxylation and analytical procedure*

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 and an immersion cooler. The temperature of the reaction vessel was maintained constant using a round oil-heated jacket. Catalyst of 20–70 mg were added to the substrate solution. An aqueous H_2O_2 solution (30% w/v) was added after the desired temperature was reached. We employed a constant 3:1 phenol:H_2O_2 molar ratio in two reaction media: water and acetonitrile. Samples were obtained periodically and filtered in order to remove any catalyst particles. The analyses of samples were performed by gas chromatography (Hewlett Packard 5890, with a 32 m × 0.25 mm capillary column of cross-linked methyl silicone gum) and liquid chromatography (Varian 5000, equipped with 250 mm × 4.4 mm of hypersil ODS 5 μm column), employing FID and UV detectors respectively. The identity of the products was further confirmed by GC–MS (Hewlett Packard 6890 Series).

3. Results and discussion

3.1. *Characterization*

The percent of copper in the catalysts, determined by atomic absorption, was between 0.1 and 0.3% w/w (Table 1). Characterization by X-ray diffraction did not reveal any major structural changes in the structure of MCM-41, which could have been caused by the incorporation of the copper complexes (Fig. 1). TPR analysis showed that the copper species are all practically in a divalent state and there is no evidence of monovalent copper.

The infrared spectrum of copper acetate in solution exhibited three absorption bands at 2960, 1630 and 1420 cm^{-1} (Fig. 2). The first band at 2960 cm^{-1} corresponds to symmetric and asymmetric vibrations of

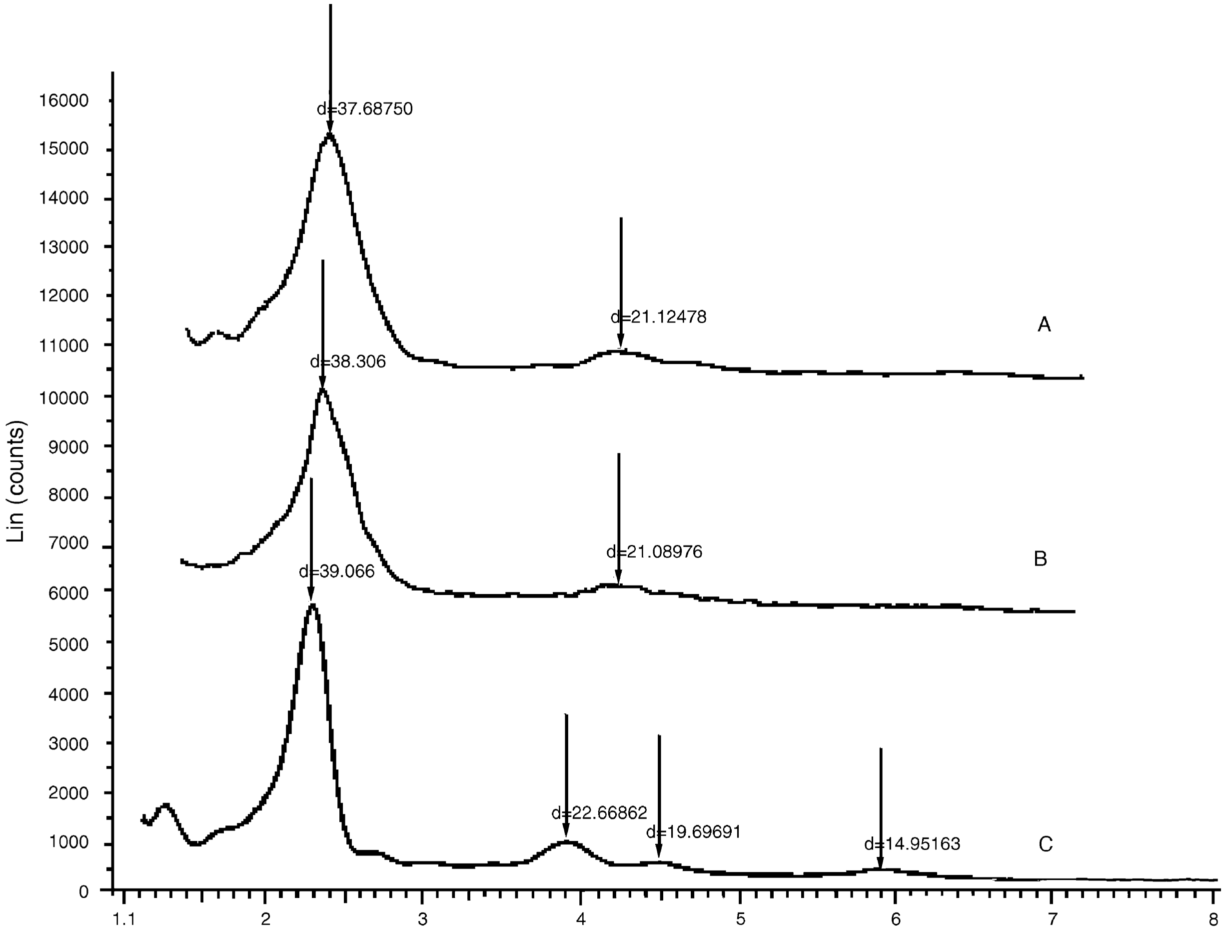


Fig. 1. X-ray diffraction patterns of: (A) 14Cu/MCM-41; (B) 1CuN/MCM-41; (C) parent siliceous MCM-41.

the CH_3 group, whereas second and third bands correspond to the carboxylic group. Copper acetate is partially dissociated in solution, the band at 1630 cm^{-1} belongs to the carboxylic group bonded to the metal atom whereas the band at 1420 cm^{-1} belongs to the dissociated ion. Fig. 2 also shows the spectra of copper acetate encapsulated inside MCM-41, before and after the hydroxylation reaction. The broad band at approximately 3500 cm^{-1} is common in MCM-41 samples and it has been associated to silanol groups. The absorption bands at 2960 and 1630 cm^{-1} provide evidence that the structure of the encapsulated copper species remains intact when they are incorporated into the structure of MCM-41. The same conclusion can be drawn from the UV–VIS diffuse reflectance spectra of copper acetate in MCM-41, which exhibit absorption peaks at 665 and 374 nm. Considering the absorption peaks of the original copper acetate at 652 and 373 nm, they show that the integrity of the structure of encapsulated copper acetate is preserved. In a similar way, the IR and UV–VIS spectra of copper nitrate show that the integrity of the copper salt is maintained when encapsulated in MCM-41.

3.2. Catalytic activity

From the experimental results, we found that except for MCM-41 with no copper, all catalytic systems in Table 1 are able to oxidize phenol at 70 °C and atmospheric pressure. Under the reaction conditions, it was

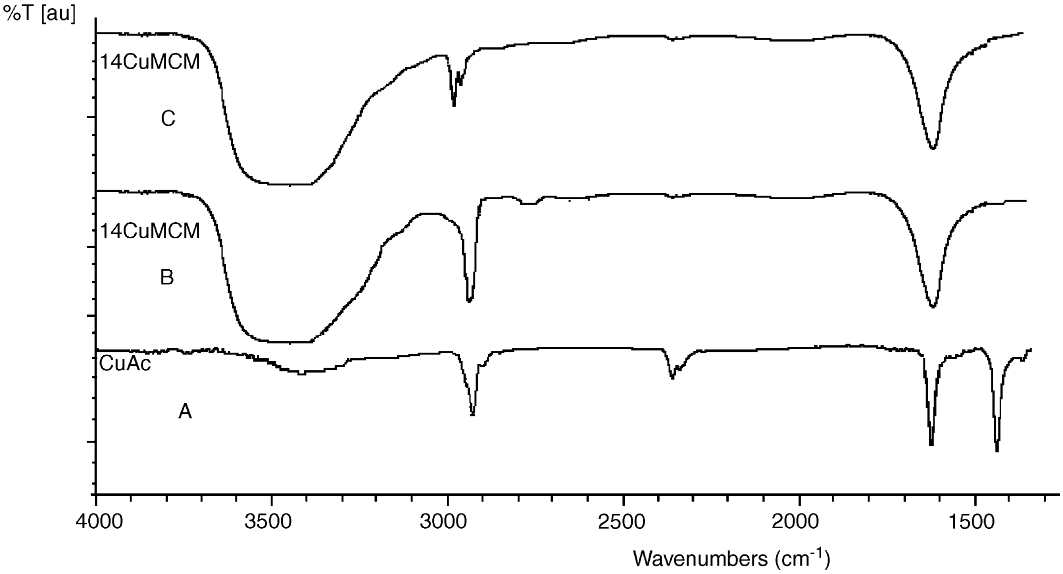


Fig. 2. FTIR spectra of: (A) copper acetate in solution; (B) 14Cu/MCM-41 before the reaction; (C) 14Cu/MCM-41 after the hydroxylation reaction.

observed that in absence of Cu–MCM-41 or H_2O_2 the hydroxylation reaction does not take place.

Fig. 3 shows the low activity of Cu^{2+} in solution (homogeneous process), compared to the activity of Cu–MCM-41 catalysts. The highest activity was obtained with copper acetate–MCM-41 catalysts, being 9Cu/MCM the most active, however, 1CuN/MCM and 16CuN/MCM, the copper nitrate–MCM-41 catalysts, yielded higher selectivity to catechol (Table 1).

There are three main reaction products: catechol, hydroquinone and benzoquinone; the concentration of tar products was less than 1%. Results also showed that the influence of the residence time on phenol conversion and product distribution is negligible.

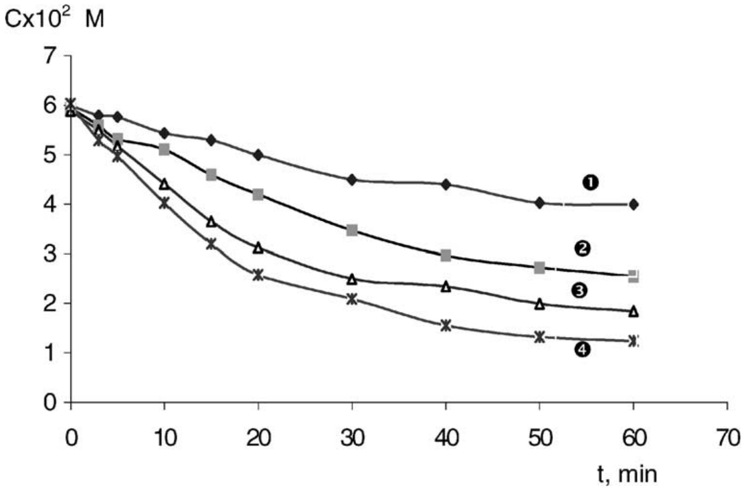
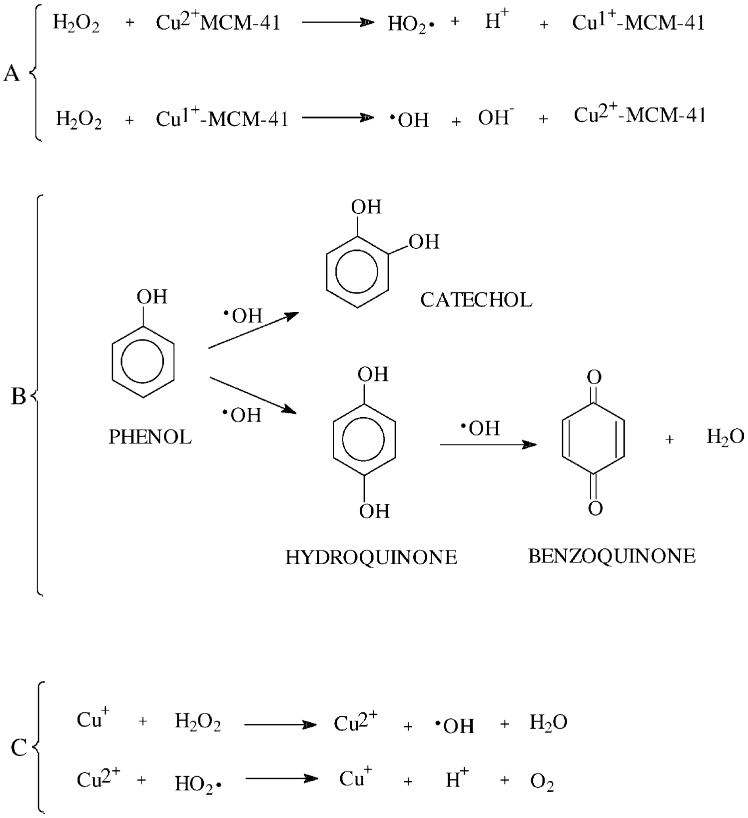


Fig. 3. Phenol concentration vs. time at pH = 7 and 363 K: (1) copper acetate in solution; (2) 1CuN/MCM; (3) 30Cu/MCM; (4) 9Cu/MCM.



Scheme 1. Reaction path for the hydroxylation of phenol.

The reaction mechanism for the oxidation of aromatic compounds employing transition metals has been previously studied [16]. The reaction path proposed for the present study involves a first stage, where the interaction of Cu–MCM-41 catalysts with hydrogen peroxide yields $HO^{\bullet}$ and $HO_2^{\bullet}$ species, via a redox mechanism (Scheme 1A). Hydroquinone and catechol are subsequently obtained in parallel processes, involving the attack of $HO^{\bullet}$ radicals to the aromatic ring (Scheme 1 B). Benzoquinone can be formed by the consecutive oxidation of hydroquinone. Oxygen and water are formed in side reactions by the decomposition of the hydroperoxi radical and hydrogen peroxide, respectively (Scheme 1 C).

For maximum utilization of hydrogen peroxide in the conversion of phenol into catechol and hydroquinone, the phenol/hydrogen peroxide ratio must be kept as high as possible, whereas the catechol/hydroquinone ratio decreases at high concentrations of hydrogen peroxide.

Fig. 4 shows the kinetic study of the 9Cu/MCM catalytic system. The rate of production of catechol is approximately two times more than that of hydroquinone and there is almost no production of benzoquinone. Increasing the copper salt content decreases the catechol/hydroquinone ratio and increases the production of benzoquinone. The relative difference of hydroquinone and benzoquinone amounts is due to the redox reaction in equilibrium of both products.

The amount of copper in the copper nitrate–MCM-41 catalysts had little influence on the product distribution.

A distinct feature of the copper nitrate–MCM-41 catalysts is their very high selectivity towards catechol, in contrast with the catechol–hydroquinone mixture obtained with copper acetate–MCM-41

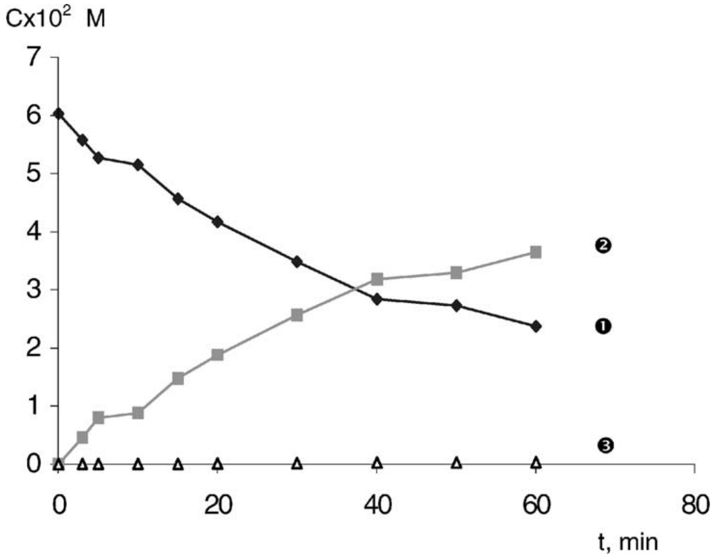


Fig. 4. Kinetic Study of 1Cu/MCM at pH = 7 and 363 K. Concentration vs. time for: (1) phenol; (2) catechol; (3) benzoquinone. Insert: oxygen production rate.

catalysts and other current commercial processes such as Rhone–Poulenc, Brichima and Enichem industrial processes [16]. Tars in commercial processes account for more than 10% of the products.

We are carrying out some investigations in order to explain these differences in selectivity. At the time, we think they can be explained by considering that thermodynamically, substitutions at both, orto and para positions are possible, whereas kinetically, substitutions at orto positions are favored. Steric factors can play an important role. Acetate groups impose relatively larger steric constraints on orto positions than nitrate groups. The steric constraints become more relevant when the copper species are fixed within the MCM-41 channels and considering the reaction might have a transition stage, involving a copper complex with the OH of phenol and the OH radical of the peroxide.

In conclusion, the results obtained in this study have shown that Cu^{2+} salts encapsulated inside mesoporous MCM-41 supports can be used as selective oxidizers of phenol. Relevant features of the copper-based catalytic systems employed in this study are: very high selectivity to catechol of copper nitrate–MCM-41 catalysts; very low production of tars; and absence of leaching of copper from the solid phase during the course of the reaction.

The absence of leaching of copper was assessed by atomic absorption spectroscopy of the effluent. This will become a significant advantage in separation and purification processes.

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