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Copper/MCM-41 as catalyst for photochemically enhanced oxidation of phenol by hydrogen peroxide

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Abstract

Heterogeneous copper catalyst was developed using the mesoporous molecular sieve MCM-41 as the catalyst support. Copper was impregnated onto the support. Catalysts with different copper loadings were obtained. The performance of the developed catalysts was evaluated in photochemically enhanced oxidation of phenol using hydrogen peroxide as the oxidant. The catalyst was found to significantly increase the oxidation rate and enhance the removal level of phenol with UV light present. The effects of copper loading on the catalyst, photo (UV), H_2O_2 concentration, and catalyst dosage on the photo-oxidation of phenol were studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper/MCM-41; Photo-oxidation; Hydrogen peroxide

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1. Introduction

Photochemical degradation process is gaining an increasing important place in water purification and wastewater remediation [1]. This process is based on oxidative reactions initiated by hydroxyl radicals ($^\bullet$OH), which are often generated by the photolysis of hydrogen peroxide. Hydroxyl radicals are highly reactive and nonselective oxidants being able to decompose many organic compounds. Since hydrogen peroxide does not absorb significantly beyond 300 nm and absorbs weakly in the range 200–300 nm, the UV/H_2O_2 process is not suitable for the treatment of polluted water with a high UV absorbance and/or a high background total organic carbon concentration [2].

Adding iron(II) as a catalyst, coupled with H_2O_2, can also generate hydroxyl radicals. This is referred to as Fenton's reagent. With the presence of UV light, the Fenton's reaction can be significantly improved in the oxidation of organics [3]. However, the Fenton reagent is good only in the pH range 2–5. Its performance declines quickly as pH goes up. Because the pH value of most wastewater is in the range 6–8, it is necessary to study the feasibility of other metal catalysts being able to generate hydroxyl radicals with H_2O_2 near neutral pH.

It has been reported that Cu^+ in aqueous solution might behave as "Fenton-like" catalyst [4]. Hydroxyl radicals can be generated using Cu^+/H_2O_2 and this is not pH sensitive

$$Cu_{aq}{}^{+} + H_2O_2 \rightarrow Cu_{aq}{}^{2+} + OH^- + {}^\bullet OH$$

Furthermore, in order to recover the catalyst after reaction and not to generate secondary pollutants (metal ions), it is better that the metal catalyst is

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immobilized onto some porous solid support. Mesoporous MCM-41 is one of the good choices as the support. It has a high surface area and a hexagonal arrangement of uniform mesopores. The pore size may be engineered in the range from 1.5 to 10 nm approximately [5], which is large enough to accommodate the big organic pollutants to be oxidized.

In this paper, the objective is to prepare heterogeneous copper catalyst supported on MCM-41 and evaluate its photocatalytic activity in the oxidation of phenol using hydrogen peroxide as the oxidant and at the presence of UV light.

2. Experimental

In this study, dodecyltrimethylammonium bromide ($C_{12}H_{25}(CH_3)_3NBr$) was used as the template to obtain MCM-41 of 3 nm in pore diameter [6]. Copper was coated onto MCM-41 by impregnation and then reduced by hydrogen. The photocatalytic activity of the developed Cu/MCM-41 catalyst with H_2O_2/UV system was evaluated in the photochemically enhanced oxidation reaction of phenol. The procedure in preparing the Cu/MCM-41 photocatalyst is described below.

A certain amount (22 g) of dodecyltrimethylammonium bromide was mixed with 273 ml of deionized water under strong stirring until a clear solution is obtained. Heat the solution if necessary. Then 13.6 ml of NaOH (0.265 g/ml) solution was added to the above-prepared solution, and 19.5 g of fumed silica was added to the above mixture under stirring until the mixture becomes homogeneous (it takes 30–60 min approx.). The mixture was transferred to an autoclave, which was then closed by tightening the cover and put into an oven at a temperature of 105°C for 2–4 days. The product was filtered off and extensively washed with deionized water to remove excessive NaOH until pH reaches 7 and dried. The dried product was calcined in an open crucible within an air oven at the temperature of 500°C for 12 h.

The MCM-41 sample was then washed with deionized water to remove impurities and dried for 24 h. The washed MCM-41 was soaked in 5% HCl solution for 24 h to further removal of any impurities and then washed again with deionized water until the pH reached near 7. The MCM-41 was filtered off and dried. Part of the sample (1 g) was immersed in 25 ml of $Cu(NO_3)_2$ solution of different concentrations of Cu^{2+} for 48 h. The impregnated MCM-41 was filtered off and dried. The sample was then calcined at 550°C for 18 h to remove the nitrate ligand. The Cu(II) impregnated onto MCM-41 was reduced to Cu(I) or copper by passing a pure hydrogen flow of 1 ml/s through the sample for 1 h at a temperature of 320°C, because Cu(II) does not help in generating hydroxyl radicals [4]. The Cu/MCM-41 catalyst is now ready for the reaction.

The photocatalytic activity of Cu/MCM-41 catalyst was examined in the degradation of phenol in water. The photoreactor was cylindrical with one UV light tube (Philips, 8 W, 365 nm) inserted in the center. Oxygen was bubbled from the bottom to the top with a flow rate of 0.1 m^3/h, which was enough to make a good suspension of catalyst. The total volume of the solution was 150 ml and the initial phenol concentration was 100 ppm. After mixing the catalyst (0.15 g) with the phenol solution for 30 min, the light was turned-on and 0.306 ml of 35% hydrogen peroxide (double the theoretical amount to completely oxidize phenol) was added into the solution. This was treated as the starting point of the reaction. The reaction temperature was 20°C. The concentration of the phenol was measured by the standard 4-aminoantipyrine colorimetric method.

3. Results and discussion

The original MCM-41 sample prepared was found to have a BET surface area of 1348 m^2/g, a pore diameter of 3 nm, and a pore volume of 0.626 cm^3/g. After impregnation, the copper loading on MCM-41 versus the Cu^{2+} concentration is shown in Fig. 1. As expected, the copper loading on MCM-41 support increase as Cu^{2+} concentration increase in the solution. After reduction, the copper on the support was found to be in the status of elemental form, as confirmed in the XRD analysis, shown in Fig. 2. The two peaks are the characteristic of metal copper. The peaks are higher as the copper loading on MCM-41 increases.

The prepared catalysts were then used in the photo-oxidation of 100 ppm phenol solution. The amount of solid catalyst used was 0.15 g in a 150 ml solution. Fig. 3 compares the photo-oxidation of

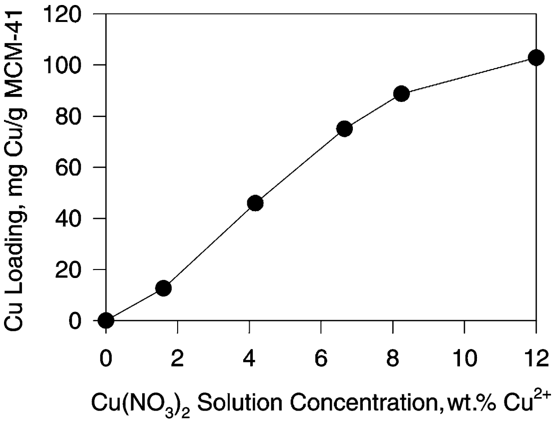

Fig. 1. Copper loading on MCM-41 versus the Cu^{2+} concentration in the solution.

phenol for the systems without any catalyst, with pure MCM-41, and with catalyst of 75 mg Cu/g MCM-41. In the following sections, the catalyst used refers to catalyst with a loading of 75 mg Cu/g MCM-41, unless specified. Without copper the oxidation of phenol by hydrogen peroxide is very slow, even with the help of UV light. This means that the generation of hydroxyl radicals from hydrogen peroxide by UV light is not adequate to maintain a fast reaction. The Cu/MCM-41 significantly accelerates the generation of hydroxyl radicals so that the oxidation process becomes much faster. About 70% removal of phenol can be achieved after 90 min of reaction at ambient temperature. There is little difference for the two curves of no catalyst and pure MCM-41. This points out that MCM-41 by itself does not have catalytic activity in the photo-oxidation of phenol. The active catalyst element is the copper immobilized onto MCM-41. There are small amount of Cu^+ and Cu^{2+} ions observed in the solution (~5 ppm) which indicates that a small amount of copper is dissolved into the solution.

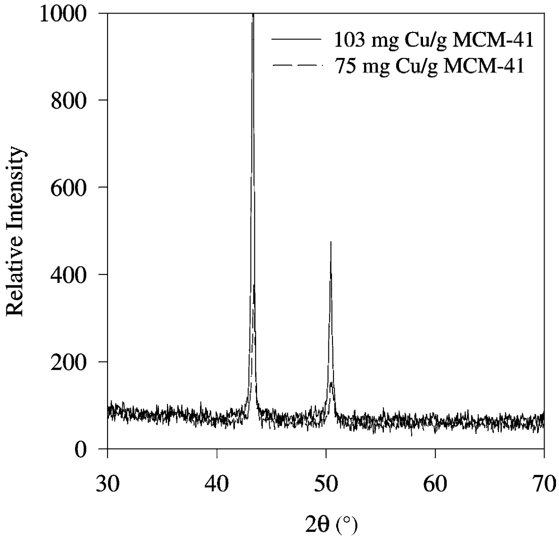

Fig. 2. XRD pattern of Cu/MCM-41.

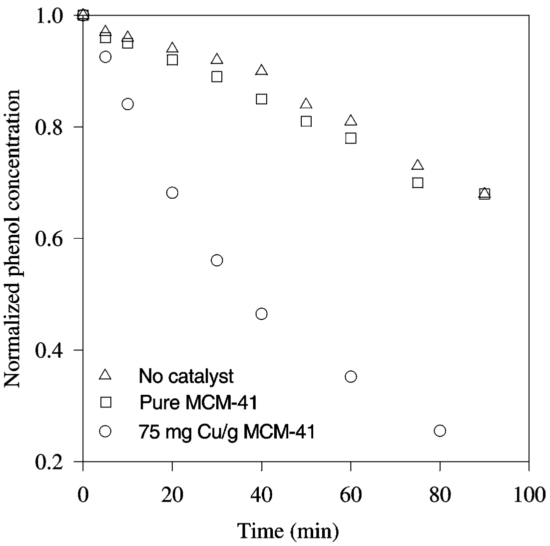

Fig. 3. Effect of Cu/MCM-41 on the photo-oxidation of phenol.

The effect of copper loading in MCM-41 on the photo-oxidation of phenol is shown in Fig. 4. Blank MCM-41 was used as the reference for zero copper loading. In general, the oxidation rate of phenol is enhanced as the copper loading is increased. This effect becomes less significant after the copper loading reaches 75 mg Cu/g MCM-41. At such high copper loadings, the copper immobilized onto MCM-41 may form large crystal particles so that the additional copper does not participate in the reaction because it is not on the surface. From the XRD result of Fig. 2, as the copper loading increases, the crystal grain size increases but the dispersion decreases.

The aqueous Cu^+ with H_2O_2 has been shown to be "Fenton-like", without the presence of UV light [7]. To see if the copper impregnated onto MCM-41 has the similar property, an experiment was carried out

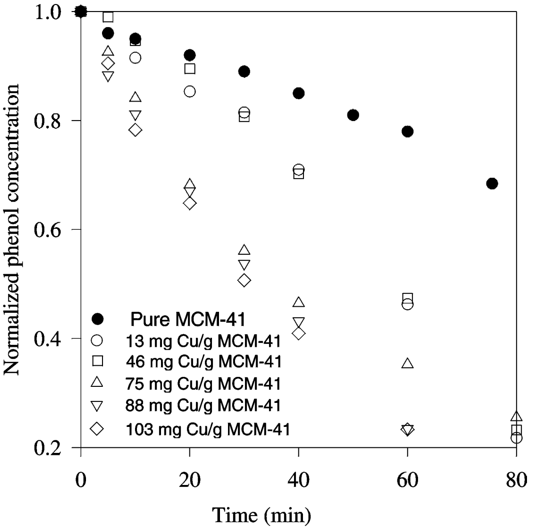

Fig. 4. Effect of copper loading in MCM-41 on the photo-oxidation of phenol.

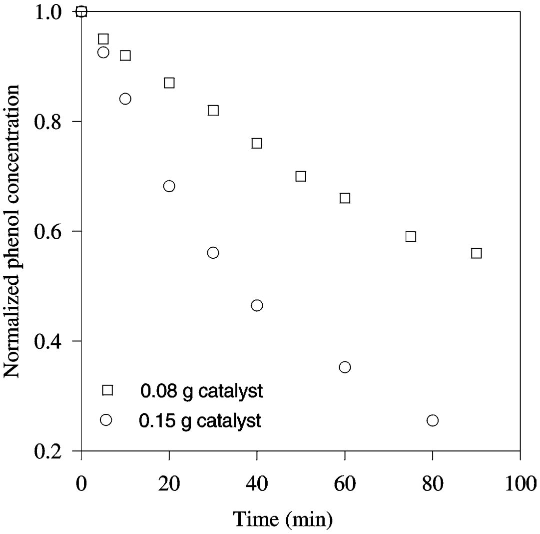

Fig. 6. Effect of catalyst dosage on the photo-oxidation of phenol.

using the catalyst of 75 mg Cu/g MCM-41 to oxidize phenol using H_2O_2 but without UV light. The result is shown in Fig. 5 together with that with UV light present. It is clear that without UV light the oxidation is negligible. This implies that the hydroxyl radicals generated by Cu/MCM-41 + H_2O_2 is very limited without the help of UV light. For the Cu/MCM-41 to be effective catalyst in generating hydroxyl radicals, the presence of UV light is necessary.

It should be pointed out that the catalyst loading in this study is relatively low (0.15 g Cu/MCM-41 in 150 ml phenol solution) for a photo-reaction system. By increasing the catalyst loading the reaction performance can be improved. Fig. 6 shows the effect

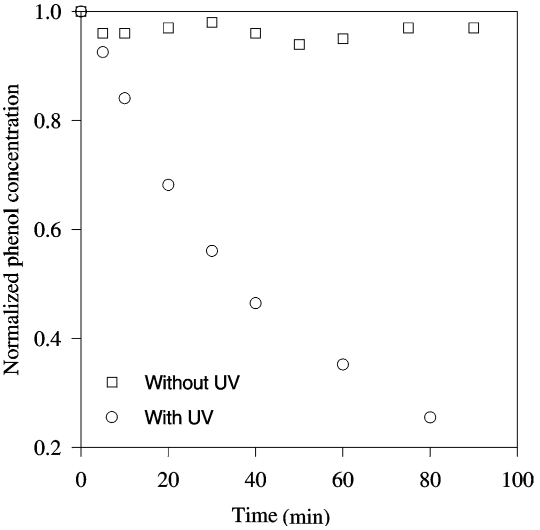

Fig. 5. Effect of UV on the oxidation of phenol.

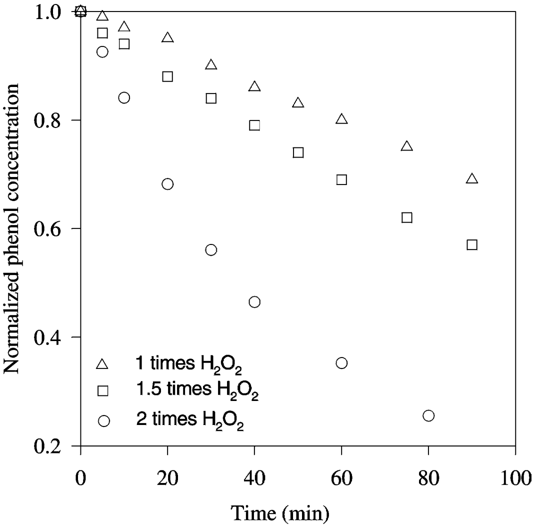

Fig. 7. Effect of hydrogen peroxide dosage on the photo-oxidation of phenol.

of catalyst dosage on the photo-oxidation of phenol. When the Cu/MCM-41 (75 mg/g) catalyst dosage is increased from 0.08 to 0.15 g, the removal rate of phenol increases from 44 to 75%.

Finally, the effect of the amount of hydrogen peroxide used on the photo-oxidation of phenol was studied and shown in Fig. 7. With the theoretical requirement of hydrogen peroxide (1 times) supplied, the removal of phenol is only 30% after 90 min of reaction. As the amount of hydrogen peroxide increases, the oxidation of phenol is improved. This means an excess amount of hydrogen peroxide is helpful to improve the oxidation.

4. Conclusions

To conclude, copper impregnated onto MCM-41 has the photocatalytic activity in the oxidation of phenol by hydrogen peroxide with the help of UV light. More than 70% of phenol can be oxidized within 90 min. A catalyst dosage of 1 g/l was found to be not adequate. The photo-oxidation of phenol can be enhanced by using more catalyst or adding more hydrogen peroxide. Without UV light, there is little reaction, which implies that, the Cu/MCM-41 catalyst functions as a photocatalyst in this system, which is helpful in the UV-aided generation of free radicals to initiate the reaction.

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