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Synthesis of TMBQ using Cu(II)-substituted MCM-41 as the catalyst

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Abstract

Mesoporous MCM-41 molecular sieves substituted with various amounts of Cu(II) and Al(III) were synthesized by the hydrothermal method. The resultant materials were characterized by XRD, XANES, surface area and pore size measurement, EPR and ^{27}Al solid state NMR. The Cu(II)-substituted MCM-41 was found to be an efficient catalyst in the oxidation of trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ) at mild reaction conditions. The latter is an intermediate in the manufacture of Vitamin E. The optimal activity was obtained when MCM-41 was concomitantly substituted with small amounts of Cu(II) and Al(III). The liquid phase reactions were extremely sensitive to the oxidant and solvent used. With acetonitrile as solvent, hydrogen peroxide and *tert*-butyl hydrogen peroxide were effective oxidants but with benzaldehyde as solvent, oxygen gas was also an effective oxidant. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cu(II)-substituted MCM-41; Liquid phase oxidation; Trimethylphenol; Trimethylbenzoquinone

1. Introduction

The discovery of mesostructures of M41S family by the researchers of Mobil in 1992 has attracted much attention [1,2]. Among them, MCM-41 of uniform hexagonal arranged tunnel-shaped pores with pore diameter ranging between 20–100 Å is most studied. The high surface area and highly ordered uniform mesopores make it a potential candidate for applications in catalytic conversions of bulky molecules encountered in the cracking of heavy crude oil or the manufacture of fine chemicals and pharmaceuticals [3] as well as in adsorption and host-guest chemistry [4,5]. The Ti-substituted MCM-41 has been synthesized; it shows potential in oxidation of bulky molecules which cannot enter the micropores of TS-1 or Ti-β [6–8]. In contrast, only a very limited number of reports deal with Cu-substituted mesoporous molecular sieves [9]. In this work, Cu(II)-substituted MCM-41 was prepared by hydrothermal reaction and the material was found to be an efficient catalyst in liquid phase oxidation of trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ).

TMBQ is a key intermediate in making Vitamin E [10]. The latter is expected to experience constantly increasing demand in the pharmaceutical and food industries in the coming decade [11]. In the literature, various catalysts and oxidants have been declared in the oxidation of TMP to TMBQ. The disclosed catalysts included organic and inorganic acids [12–14], $RuCl_3$ [15], complexes of cobalt, iron and manganese [16,17], and solutions of cupric halides/alkaline

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halides [18–20]. The effective oxidants used in the literature included percarboxylic acids [17], organic hydroperoxides, hydrogen peroxide [12,15], Tl(III) compounds [14], manganese dioxide [21], and oxygen gas [15,18–20]. Most of these systems were homogeneous phase reactions, and the process may be improved by using stable heterogeneous catalysts to achieve easier work-up. Toward this direction, a carbon-supported heteropoly anion (HPA) was examined as a catalyst [22]. However, leaching of HPA during the reaction was the drawback. Recently, Ti-substituted $AlPO_4$-5 molecular sieve was reported to be an effective catalyst in oxidation of alkyl substituted phenols to give the corresponding benzoquinone using H_2O_2 as oxidant and acetic acid as solvent [23]. However, carboxylic acids were reported to be the catalysts for this reaction [14], and acetic acid which was used as the solvent in most of the declosed processes, could also catalyze the reaction to some extent [23]. In the present study we found that Cu-substituted MCM-41 could efficiently catalyze the reaction with various oxidants in acid free solvents. Moreover, it was found that the catalytic activity was enhanced when a small amount of Al(III) was also incorporated in the framework of MCM-41.

2. Experimental methods

2.1. Synthesis of Cu-substituted molecular sieves

2.1.1. MCM-41

Cetyltrimethylammonium (CTMA) bromide was used as the surfactant template. The hydrothermal crystallization procedure was modified by adding tetrapropylammonium (TPA^+) bromide salt to the synthesis gel to increase the hydrothermal stability of the resultant MCM-41 material [24]. In a small flask, a required amount of $NaAlO_2$ in 15 g water was mixed with 5.33 g sodium silicate solution (∼14% NaOH, ∼27% SiO_2) in 15 g water. To another flask was charged 4.25 g CTMABr and 2.13 g TPABr and 45 g water. The latter solution and a desired amount of copper(II) nitrate dissolved in a minimum amount of water were added to the silicate-containing flask. With stirring, the pH of the mixture was adjusted to 9.5–10 using diluted sulfuric acid. The molar ratio of the final gel composition is SiO_2:(0-0.05)Al_2O_3:(0-0.05)CuO:0.48$CTMA^+$:0.67-TPA^+:0.39Na_2O:0.29H_2SO_4:50-110H_2O. The gel mixture was stirred for 2 days at room temperature and then transferred to polypropylene bottles and statically heated at 100°C for 7 days under autogeneous pressure. The final solid material obtained was washed with plenty of water, dried and calcined (heating rate 1°C/min) at 560°C for 6 h.

2.1.2. $AlPO_4$-5

Cu-substituted $AlPO_4$-5 molecular sieves were prepared by hydrothermal method. The molar composition in synthesis gel was Al:P:Cu = 1:1:0.02–0.04. 5.5 g of psudoboemite (73.5%Al_2O_3 VISCA) was hydrolyzed with 15 g of H_2O. Phosphoric acid (9.2 g, 85% Janssen) was diluted with 10 g of water and added to the Al source under stirring. After addition of the desired amount of $Cu(NO_3)_2 \cdot 3H_2O$ (Hanawa) dissolved in 5 g of water, 4.2 g triethylamine (Janssen) was added. The precursor gel was transferred to an autoclave and heated in static condition for 48 h at 200°C. The resultant crystals were washed and dried at 100°C followed by calcination at 550°C for 8 h.

2.1.3. Characterization

XRD patterns were recorded in the 2θ range 1.5–10° using a Scintag X1 diffractometer with Cu Kα radiation operated at 30 mA and 40 kV. The pore structures of MCM-41 samples were analyzed by nitrogen physical adsorption at liquid N_2 temperature using a Micromeritics ASAP 2100 system. Prior to the experiments, samples were outgassed at 300°C for about 6–8 h under vacuum (10^{-3} Torr). The elemental contents in bulk were determined by ICP-MS (ELAN 5000) on the HF dissolved samples. The EPR spectra were measured using a Bruker ESP 300 X-band spectrometer. The g value was determined using DPPH as the standard. The ^{27}Al MAS NMR spectra were measured using a Bruker MSL-500 spectrometer with zirconia rotors spun at 12 kHz. Data were acquired at 130.32 MHz, 1 μs pulse width and 0.3 s recycle delay. The chemical shifts are given in ppm, using 3 M $AlCl_3$ aqueous solution as the standard. The Cu K-edge X-ray absorption spectra were obtained in the transmissoin mode at the Synchrotron Radiation Research Center, Hsinchu, Taiwan. The ion chambers which were used for measuring the incident and transmitted photon intensities were filled with a mixture of nitrogen and helium, and argon and helium gases, respectively. The photon energies were calibrated using the known absorption edge of Cu foil.

2.1.4. Catalytic reactions

The catalytic activities of the Cu,Al-MCM-41 molecular sieves in oxidation of 2,3,6-trimethylphenol (TMP) were examined using a batch reactor which was composed of a three-neck flask connected with a reflux condenser and a thermometer. A 0.2 g portion of the catalyst suspended in solvent containing 1 g of TMP was heated to 60°C and then the oxidant was introduced into the system. Hydrogen peroxide (35%, Acros Organics), *tert*-butyl hydrogen peroxide (70%, Acros Organics) and oxygen (a flow rate of 20 ml/min) were used as the oxidants. The reaction was operated under atmospheric pressure. The liquid products were separated with a Rtx-1 capillary column and detected by a FID detector in a Shimadzu GC-14. Toluene was used as an internal standard to calculate the TMP conversion and TMBQ yield.

3. Results and discussion

3.1. Catalyst characterization

The chemical compositions of the metal-substituted MCM-41 samples determined by ICP-MAS are tabulated in Table 1. Generally speaking, the metal contents in the crystals based on the M/Si molar ratios are proportional to but lower than those added into the gels. Exceptions were found for Al-substituted samples of low loading. The Al/Si molar ratios in the solids were slightly higher than those in gels. That was because Si in gel was not completely precipitated. It is also noticeable that the amount of Al(III) incorporated in the solids seem to increase when Cu(II) is also present. Fig. 1 compares the ^{27}Al solid state MAS NMR spectra of the Al-MCM-41 samples with and without Cu. For the samples incorporated with both Al(III) and Cu(II), a single peak which appeared around 56 ppm implies that the Al(III) ions are in a tetrahedral environment. However, for the sample incorporated with Al(III) only, there is an additional small peak appearing at 0 ppm which corresponds to octahedral-coordinated Al or the extra-framework Al. These results indicate an interesting phenomenon that the concomitant presence of Cu(II) helps Al(III) substitution into the framework of MCM-41.

Table 1
Compositions and symbols of Cu,Al-substituted MCM-41

Catalyst symbol	Cu/Si atomic ratio (%)		Al/Si atomic ratio (%)	
	In gel	In solid[a]	In gel	In solid[a]
MCM-41	0	0	0	0
0Cu1Al	0	0	1	1.29
0Cu2Al	0	0	2	2.16
0Cu5Al	0	0	2	3.31
1Cu0Al	1	0.72	0	0
1Cu1Al	1	0.78	1	0.92
1Cu2Al	1	0.83	2	1.35
2Cu0Al	2	1.65	0	0
2Cu1Al	2	1.71	1	1.44
2Cu2Al	2	1.74	2	1.71
2Cu5Al	2	1.79	5	4.70
3Cu3Al	3	2.68	3	2.73
5Cu2Al	5	4.74	2	1.83
5Cu3Al	5	4.67	3	2.84
5Cu5Al	5	4.49	5	4.68

[a] Analyzed by ICP-MAS.

In order to examine the nature of copper species incorporated in MCM-41, the Cu K-edge X-ray absorption spectra of the co-precipitated sample 2Cu1Al (Fig. 2A) were compared with that of Cu(II) ion-exchanged 1%Al-MCM-41 (Fig. 2B). CuO, Cu_2O and Cu foil were used as references for +2, +1 and 0 oxidation states, respectively, and their spectra are shown in Fig. 2C. Before reduction, the Cu K-edge spectra of 2Cu1Al and ion-exchanged sample were similar, and both edge energies were close to that of CuO, implying that the Cu species in both samples were in +2 oxidation state. After reduction with 10% H_2/Ar flow at 200°C for 15 min, the spectrum and the edge position were not much changed for ion-exchanged sample, while the co-precipitated sample 2Cu1Al had a small shoulder which appeared around 8983 keV. When the reduction temperature was raised to 300°C, the ion-exchanged sample was reduced to copper metal and its spectrum was almost the same as that of copper foil. In contrast for the co-precipitated sample 2Cu1Al, the copper species were not completely reduced and the spectrum was a mixed pattern of those of Cu(II) and Cu(I). These results confirmed that the Cu(II) ions substituted in MCM-41 were not in the ion-exchange sites but were more likely in the framework. The counter ions in

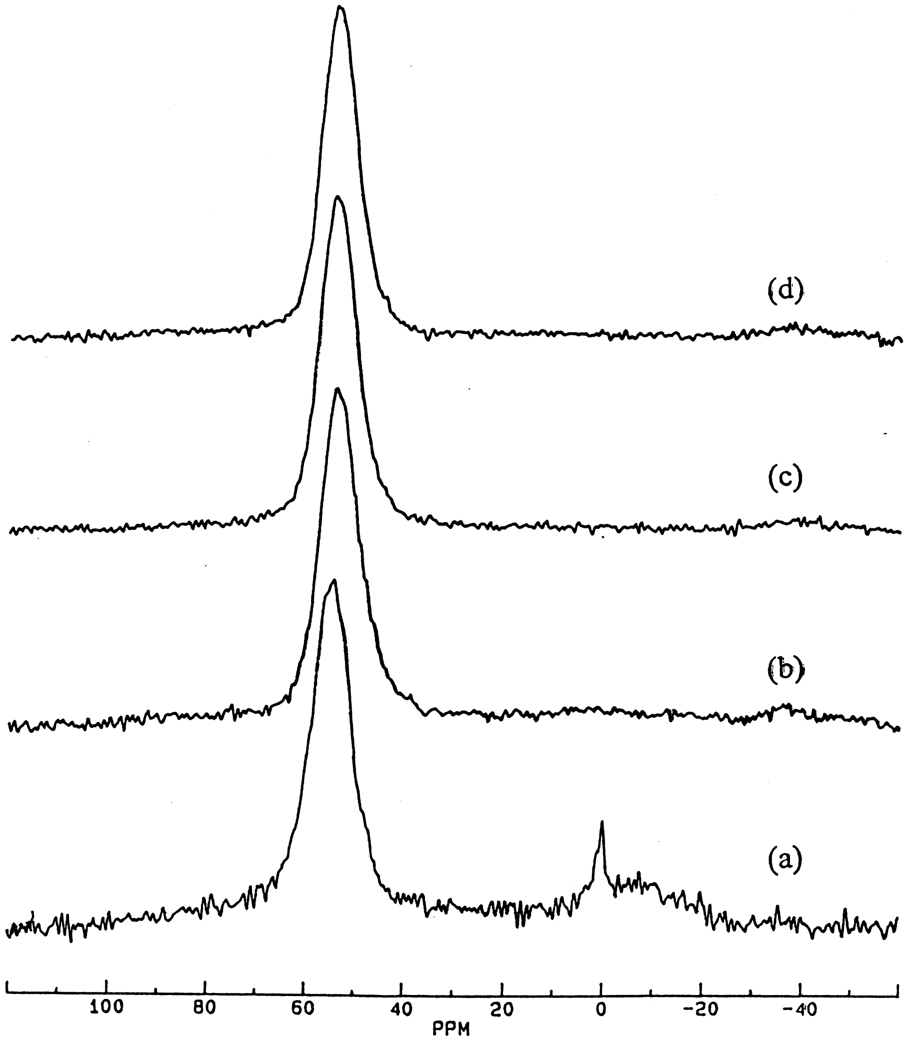

Fig. 1. ^{27}Al solid state MAS NMR spectra of MCM-41 containing 2%Al and various amounts of Cu(II): (a) 0%, (b) 1%, and (c), (d) 2% (from different batches).

extra-framework of MCM-41 to balance the charge caused by Cu(II) and Al(III) substitution might be Na^+ ions or protons. The former are abundant in sodium silicate, and protons are generated by the decomposition of $CTMA^+$ template during calcination.

The XRD patterns in Figs. 3 and 4 show that the hexagonal-arranged structure of MCM-41 was little affected by the incorporation of Cu(II) and Al(III) ions. However, the long range order of the structure was disturbed and the X-ray diffraction peaks broadened with the increase in metal content. For comparison, impregnated samples were also prepared by wetting calcined MCM-41 with solutions of $Cu(NO_3)_2$ and $NaAlO_2$ or $Al_2(SO_4)_3$, followed by drying and calcination. The XRD patterns of the impregnated samples, in contrast, showed no broadening of the peaks. These results are considered evidence that most of the Cu(II) and Al(III) ions introduced in the synthesis gel and co-precipitated with silicon oxide were in the framework of MCM-41.

Fig. 5 compares the EPR spectra of the MCM-41 samples containing 1%Cu and 2%Al prepared by

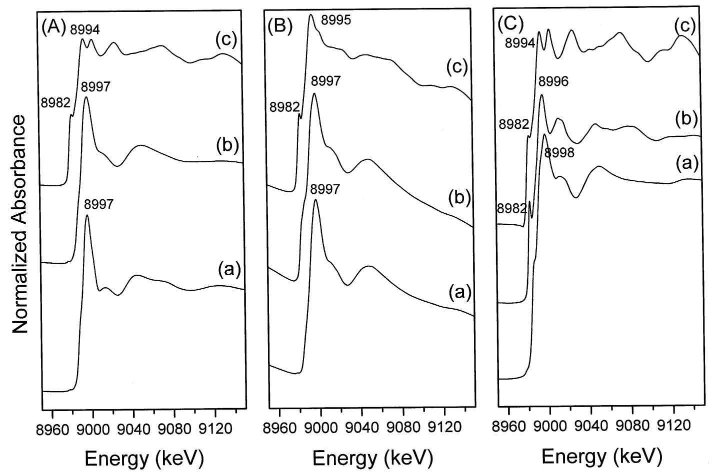

Fig. 2. Cu K-edge X-ray absorption spectra of (**A**) Cu(II)-exchanged 1%Al-MCM-41, (**B**) calcined 2%Cu,1%Al-MCM-41: (a) before reduction, and reduction with 10% H_2/Ar at (b) 200°C, (c) 300°C and (**C**) references: (a) CuO, (b) Cu_2O and (c) Cu foil.

co-precipitation and impregnation, respectively. The spectra taken at ambient temperature show a broad peak at $g = 2.193$ for the co-precipitated sample but no peak other than that of DPPH at $g = 2.0036$ for the impregnated sample. When cooling the samples to liquid N_2 temperature, the broad peak of the co-precipitated sample was greatly intensified and split into several peaks which were assigned as

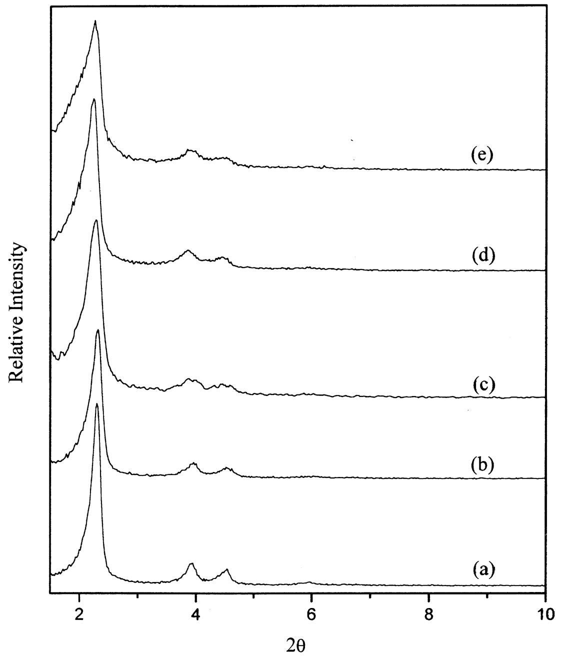

Fig. 3. XRD patterns of calcined MCM-41 containing 3%Al and various amounts of Cu(II): (a) 0%, (b) 1%, (c) 2%, (d) 3%, and (e) 5%.

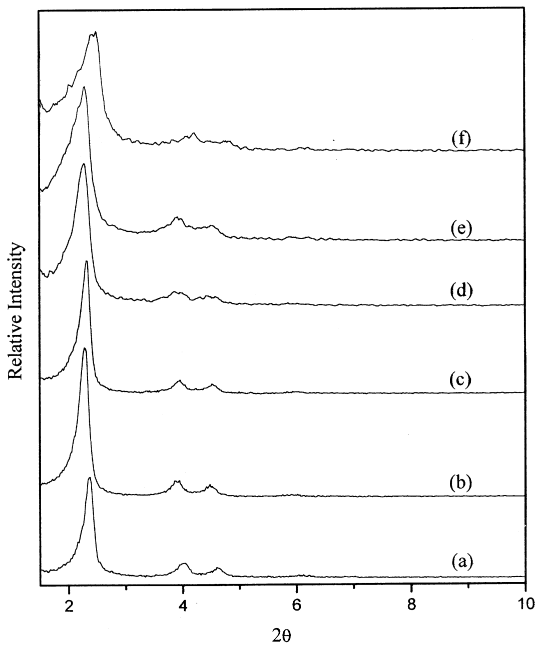

Fig. 4. XRD patterns of calcined MCM-41 containing 2%Cu and various amounts of Al(III): (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 5%, and (f) 10%.

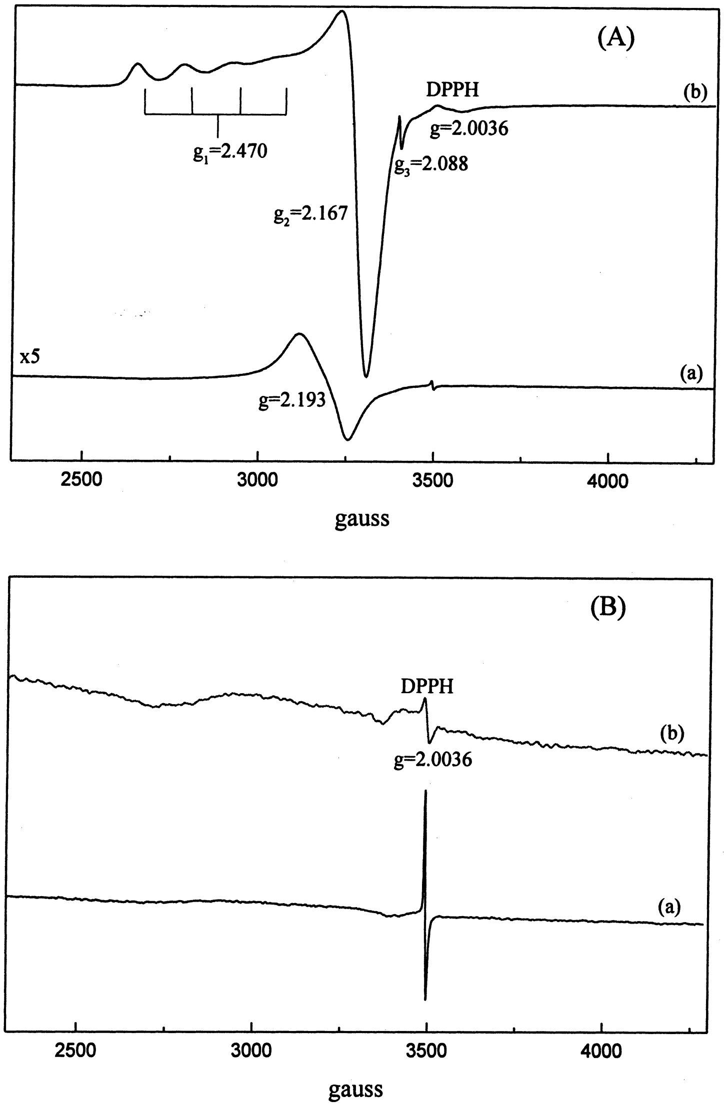

Fig. 5. EPR spectra of 1%Cu,2%Al-MCM-41 prepared by (A) co-precipitation and (B) impregnation; spectra taken at (a) RT and (b) liquid N_2 temperature.

$g_1 = 2.470$, $g_2 = 2.167$ and $g_3 = 2.088$. In addition, hyperfine splitting of the g_1 peak into four peaks due to electron-nucleus ($I = 3/2$ for Cu) spin interaction is clearly seen. In contrast, the impregnated sample still did not show obvious peaks. These results are elucidated by the explanation that Cu(II) ions on an impregnated sample are aggregated in the form of copper oxide where the distances between Cu(II) ions are so close that the EPR signals are broadened out by the strong spin-spin interaction. On the other hand, the Cu(II) ions in the co-precipitated sample are relatively well dispersed in the framework of MCM-41 with anisotropic coordination environment.

The physical properties of the MCM-41 samples incorporated with different amounts of cations are given in Table 2. It can be seen that the BET surface areas of these samples were in the range of 871–1034 m^2/g. The nitrogen adsorption–desorption isotherms of

Table 2
Surface area and pore size of Cu,Al-substituted MCM-41

Catalyst	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
MCM-41	1034	2.4	0.918
1Cu0Al	979	2.4	0.846
2Cu0Al	943	2.4	0.779
2Cu1Al	1006	2.6	0.914
2Cu2Al	999	2.4	0.874
2Cu3Al	948	2.4	0.799
2Cu5Al	907	2.4	0.757
3Cu0Al	913	2.4	0.766
3Cu3Al	925	2.4	0.774
5Cu3Al	873	2.5	0.745
5Cu5Al	871	2.6	0.745

several of the Cu,Al-substituted MCM-41 samples are shown in Fig. 6. A very narrow distribution of the mesopores with average pore diameter around 2.4–2.6 nm and the pore volume in the range of 0.745–0.918 cm^3/g were obtained. A slight decrease in the surface area and pore volume was observed only when relatively large amounts of Cu(II) and Al(III) ions were incorporated in MCM-41.

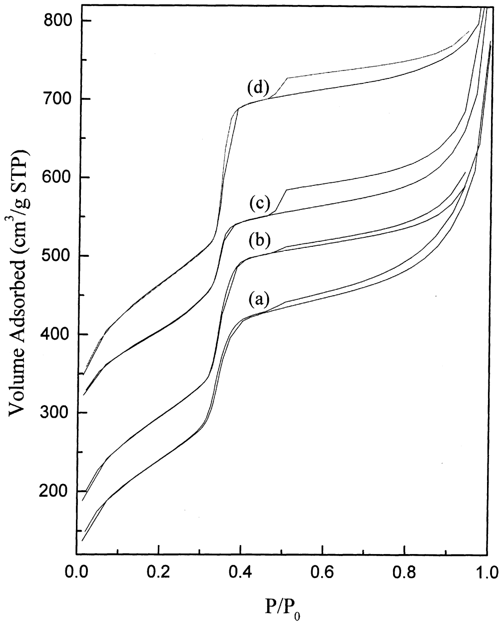

Fig. 6. N_2 adsorption–desorption isotherms of Cu,Al-MCM-41 samples (a) 5C3A, (b) 3C3A, (c) 2C10A, and (d) 2C2A.

Table 3
Effect of oxidant and solvent molar ratios in TMP oxidation[a]

Reactant: H_2O_2:CH_3CN	Conversion (%)	TMBQ	
		Yield (%)	Selectivity (%)
1:1:3	64	47	73
1:1:1	59	41	70
1:0.5:3	54	38	70
1:0.5:1	27	6	22

[a] 0.2 g 2%Cu,2%Al-MCM-41 as catalyst, 1 g TMP, reaction period 20 min.

3.2. Catalytic activities

In oxidation of 2,3,6-TMP to 2,3,5-TMBQ, Cu,Al-substituted MCM-41 samples were found to be efficient catalysts when H_2O_2 was used as oxidant and CH_3CN as solvent at temperatures around 60°C. In an effort to minimize the amount of solvent used, Table 3 shows the results of varying the molar ratio of reactant:oxidant:solvent using sample 2Cu2Al (MCM-41 substituted with 2%Cu and 2%Al) as the catalyst. TMP conversions greater than 50% and TMBQ selectivities around 70% were obtained except for the very viscous mixture of TMP:H_2O_2:CH_3CN = 1:0.5:1. The by-products found in the gas phase were CO and CO_2, and those in liquid phase included 2,3-dimethylmaleic anhydride, tetramethyl benzoquinone and some polymeric compounds. The TMP conversion and TMBQ yield were higher when larger amounts of oxidant and solvent were used. Although large amounts of solvent lowered the concentrations of the reactants, the TMP:H_2O_2:CH_3CN ratio of 1:1:3 was the optimal condition in order to achieve good dispersion of the catalyst powders and thorough mixing of the liquid-solid phases. Therefore, this ratio was used for the later experiments hereafter.

The reaction pattern as a function of time course is shown in Table 4. In 20 min, the TMP conversion reached 64% and TMBQ yield was 47%. The latter reached a maximum after 40 min then decreased with time course. Because several of the by-products were formed through the secondary reactions of the TMBQ product, 20 min reaction period was used in the experiments hereafter in order to achieve maximum TMBQ selectivity.

The effects of Cu and Al contents in MCM-41 on the catalytic activity are demonstrated in Table 5.

Table 4
Effect of reaction period in TMP oxidation[a]

Reaction period (min)	Conversion (%)	TMBQ	
		Yield (%)	Selectivity (%)
20	64	47	73
30	80	50	63
40	81	58	72
60	82	51	63

[a] Catalyst: 2%Cu,2%Al-MCM-41.

MCM-41 itself has little catalytic activity in the reaction. Cu-substituted MCM-41 samples were active in TMBQ formation while Al-substituted samples only converted TMP to some products other than TMBQ. The catalytic activity of CuMCM-41, however, was found to enhance when a small amount of Al was also incorporated. Fig. 7 shows that there is an optimal amount of Al content to achieve the maximum TMP conversion and TMBQ yield. The maximum TMP conversion was obtained over the 2%Cu-MCM-41 catalyst also containing 5%Al while the maximum TMBQ yield was achieved over the catalyst containing 2%Al.

The effect of varying Cu content in the 3%Al-MCM-41 catalyst was somewhat different. Fig. 7 shows that an abrupt increase in TMP conversion from 23 to 75% and TMPQ yield from 0 to 24% was observed when 1%Cu was also incorporated. Then, the TMP conversions flattened out and stayed almost unchanged when the Cu content varies from 1 to 5% while TMBQ yield reached a maximum over the 2%Cu sample. These results demonstrate again that Cu(II) on the framework is the active site for the catalytic oxidation of TMP to TMBQ. The role of Al(III) in the reaction is unclear. It is suspected that the small amount of Al(III) present on the framework may increase the polarity of the MCM-41 framework and facilitate the absorption of TMP onto the catalyst surface. Too much Al(III) would, however, compete with Cu(II) for the sites exposed on the surface.

Table 5
Effect of Cu and Al contents in TMP oxidation[a]

Catalysts	Conversion (%)	TMBQ	
		Yield (%)	Selectivity (%)
MCM-41	1.1	0	0
0Cu1Al	19	0	0
0Cu2Al	23	0	0
0Cu10Al	45	0	0
1Cu1Al	65	17	27
1Cu2Al	69	19	28
2Cu0Al	52	28	54
2Cu0Al (uncalc)	30	7	24
2Cu1Al	61	41	67
2Cu2Al	64	47	73
2Cu2Al (uncalc)	41	11	27
2Cu10Al	63	17	27
2Cu20Al	60	11	19
2Cu2Al (regenerated)	59	43	72

[a] Reactant:H_2O_2:CH_3CN = 1 : 1 : 3; reaction period 20 min.

Table 5 also compares the catalytic activities of Cu,Al-MCM-41 samples before and after calcination. The uncalcined catalyst gave TMP conversion and TMBQ yield much lower than the calcined catalyst. Therefore, the catalytic reaction should proceed mainly inside the pores of MCM-41 molecular sieve. Furthermore, for the purpose of examining any leaching of the metal ions into the solvent during the reaction, a used catalyst was regenerated by separation from the reaction mixture and calcination at 560°C for 6 h to burn off any surface coking species. Table 5 shows that the catalytic activity of the regenerated catalyst was close to that of the original catalyst. The slight decrease in conversion and TMBQ yield were attributed to the loss of some catalyst powders during the regeneration and transfer process.

Table 6 compares the catalytic activities of Cu,Al-MCM-41 samples prepared by co-precipitation with those prepared by impregnation. The MCM-41 sample impregnated with $Cu(NO_3)_2$ solution gave very low yield of TMBQ. The latter was greatly improved by co-impregnation of Al(III) with either $NaAlO_2$ or $Al_2(SO_4)_3$ solution. However, the TMBQ yields were still less than half of the values obtained over the co-precipitated samples. When 0.2 g of Al_2O_3 fine powders was used as the catalyst, no TMBQ was detected in the products. In another experiment, an aqueous $Cu(NO_3)_2$ solution containing the same molar number of Cu(II) as that in sample 2C2A was used as the catalyst. Very low yield and selectivity of TMBQ were observed, implying that the catalytic activity of Cu,Al-MCM-41 was not due to Cu(II) ions leaching into the solution. These results confirm that well-dispersed Cu(II) on the framework is the active

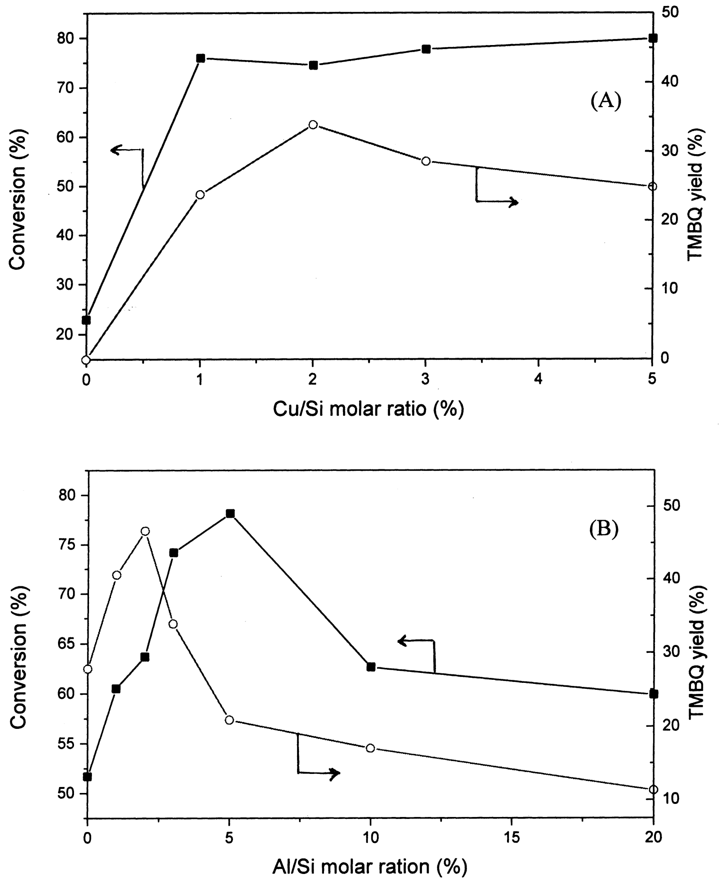

Fig. 7. Effect of (A) Cu content in 3%Al-MCM-41 and (B) Al content in 2%Cu-MCM-41 in TMP catalytic oxidation: (■) TMP conversion, and (○) TMBQ yield.

Table 6
TMP oxidation over various Cu(II) containing catalysts[a]

Catalysts	Conversion (%)	TMBQ	
		Yield (%)	Selectivity (%)
2%Cu-MCM-41	52	28	54
2%Cu,2%Al-MCM-41	64	47	73
2%Cu-MCM-41-imp	53	4.3	8.1
2%Cu,2%Al-MCM-41-imp with $NaAlO_2$	56	23	41
2%Cu,2%Al-MCM-41-imp with $Al_2(SO_4)_3$	65	17	27
Al_2O_3	35	0	0
$CU(NO_3)_{2(aq)}$	65	5.3	8.2
1%Cu-ZSM-5	32	0	0
Cu-ZSM-5 (exchange)	61	0	0
1%CuAPO-5	85	20	24
2%CuAPO-5	85	30	36

[a] Reactant:H_2O_2:CH_3CN = 1 : 1 : 3; reaction period 20 min.

Table 7
Effect of solvent and oxidant in TMP oxidation over catalyst 2%Cu,2%Al-MCM-41[a]

Solvents	Oxidant	Rxn period	Conversion (%)	TMBQ Yield (%)	TMBQ Selectivity (%)
C_2H_5OH	H_2O_2	20 min	2.0	0	0
CH_3CHO	H_2O_2	20 min	68	1.3	1.9
CH_3CN	H_2O_2	20 min	64	47	73
CH_3CN	TBHP[a]	20 min	98	83	85
CH_3CN	O_2	6 h	17	0	0
Ph-CHO	H_2O_2	20 min	87	69	79
Ph-CHO	TBHP	20 min	98	88	89
Ph-CHO	O_2	2 h	43	22	52
Ph-CHO	O_2	4 h	71	41	57
Ph-CHO	O_2	6 h	82	45	54

[a] TBHP: *tert*-butylhydroperoxide.

center on Cu-MCM-41 in catalytic oxidation of TMP to TMBQ.

The catalytic activities of other Cu-substituted molecular sieves were also examined. Table 6 shows that no TMBQ formation was obtained over Cu-ZSM-5 prepared either by co-precipitation or ion-exchange. For Cu-incorporated $AlPO_4$-5 molecular sieve, some activities in TMBQ formation were observed, yet the selectivities were relatively low. These results are elucidated by noting that the reaction is restricted by the relatively small pore diameters of ZSM-5 and $AlPO_4$-5.

The liquid phase TMP oxidation reaction was extremely sensitive to the oxidant and solvent used. Table 7 shows the effect of solvent and oxidant over MCM-41 incorporated with 2%Cu and 2%Al. With H_2O_2 as the oxidant and among the solvents used including ethanol, acetaldehyde, acetonitile and benzaldehyde, benzaldehyde gave the highest TMP conversion and TMBQ selectivity while no activity or very little TMBQ was formed in ethanol or acetaldehyde. The activities in both acetonitrile and benzaldehyde were markedly enhanced if *tert*-butylhydroperoxide (TBHP) was used as the oxidant instead of H_2O_2. A 98% TMP conversion and higher than 85% TMBQ selectivity were obtained in 20 min. Another advantage of using benzaldehyde solvent is that oxygen gas could be used as the oxidant, although the reaction proceeded more slowly and the TMBQ selectivity was not as high as with other strong oxidants. In this system, benzaldehyde solvent was considered to participate in the oxidation reaction through the formation of benzoic peracid which is considered a strong oxidant. Although the latter was not observed, a small amount of benzoic acid which should be the precursor of peracid was detected in the products.

4. Conclusions

Cu(II)-incorporated MCM-41 was an efficient catalyst for partial oxidation of trimethylphenol to trimethylbenzoquinone in non-acidic solvents under mild reaction conditions. The product TMBQ is an important intermediate for making Vitamin E in industry. Well dispersed Cu(II) on the framework of MCM-41 was found to be the active center for the catalytic reaction. The catalytic activity was enhanced when a small amount of Al(III) was also incorporated in the framework. The meso-porous structure of MCM-41 was important for this reaction involving relatively large molecules, and the oxidation reaction proceeded mainly inside the pores of MCM-41. The stability of the Cu,Al-MCM-41 catalysts was high. The regenerated catalyst retained similar activity to that of the original catalyst. The liquid phase reaction was extremely sensitive to the oxidant and solvent used. A 98% TMP conversion and higher than 85% TMBQ selectivity were obtained in 20 min when acetonitrile or benzaldehyde was the solvent and *tert*-butylhydroperoxide was the oxidant. Different from Ti- or V-substituted molecular sieves, oxygen gas could also be an effective oxidant with Cu,Al-MCM-41 catalyst. In this case, benzaldehyde was the only effective solvent among the solvents studied, and the reaction was slower and TMP conversion and TMBQ selectivity were lower than those obtained with other strong oxidants such as H_2O_2 and TBHP.

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