

Cu-substituted molecular sieves as liquid phase oxidation catalysts

Berryinne Chou, Jai-Long Tsai, Soofin Cheng *

Department of Chemistry, National Taiwan University, Roosevelt Road Section 4, Taipei 106, Taiwan, ROC

Received 6 August 2000; received in revised form 12 October 2000; accepted 15 January 2001

Abstract

Cu(II)-substituted molecular sieves were found to be efficient catalysts in liquid phase oxidation of aromatic compounds. CuAPO-5 was an efficient catalyst in hydroxylation of alkyl-substituted benzenes. For benzene itself as the reactant, a phenol selectivity of near 100% could be obtained using hydrogen peroxide as the oxidant at mild reaction conditions. Acetonitrile was the only effective solvent for this one-step oxidation of benzene to phenol. With the increase in steric hindrance of alkyl substitution on benzene, the oxidation reaction was driven toward benzylic oxidation instead of ring hydroxylation. However, the selectivities of the ring hydroxylation products were higher than those usually obtained in homogeneous radical reactions. On the other hand, Cu(II)-substituted MCM-41 of relatively larger pores was effective in catalyzing the oxidation of trimethylphenol to trimethylbenzoquinone at mild reaction conditions. The latter is an intermediate in manufacture of vitamin E. The optimal activity was obtained when MCM-41 was concomitantly substituted with small amounts of Cu(II) and Al(III). 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-substituted molecular sieve; Liquid phase oxidation; Catalyst; Benzene; Phenol; TMBQ

1. Introduction

The substitution of hetero-elements into the framework of molecular sieves was usually reported to create acidic sites, while the incorporation of transition metal elements, such as Ti, V, Cr, Mn, Fe and Co, endows sites for redox reactions. Ti-substituted molecular sieves, such as TS-1, Ti-beta and Ti-MCM-41, have attracted most of the

attention. They were reported to have remarkable redox catalytic activities, particularly in oxidation reactions with hydrogen peroxide as oxidant at mild reaction temperatures [1–5]. In contrast, very limited number of reports deals with Cu-substituted molecular sieves. In this paper, Cu(II)-substituted molecular sieves were prepared by hydrothermal reactions and the materials were examined as catalysts in liquid phase oxidation of aromatic compounds.

The hydroxylation of aromatic hydrocarbons to phenols and phenol derivatives with H₂O₂ was reported to proceed readily over Ti- and V-substituted microporous zeolites of MFI and MEL

* Corresponding author. Tel.: +886-2-236-380-17; fax: +886-2-236-363-59.

E-mail address: chem1031@ccms.ntu.edu.tw (S. Cheng).

crystalline structures [6,7]. Phenol is an important compound for industry and pharmaceuticals. The annual world production in 1996 had reached 4.9×10^6 tons [8]. Although a direct oxidation process of benzene to phenol would be the most economical route, until now only the indirect manufacturing processes have been operated. The reason resides in that the oxidation capability of phenol is higher than that of benzene and the selectivity of one-step oxidation of benzene into phenol is generally not high. For example, liquid phase oxidation of benzene using Ti- or V-containing zeolites as catalysts and hydrogen peroxide as the oxidants also generated some deep oxidation side products such as *p*-benzoquinone and hydroquinone [9,10]. In the present study, a near 100% selectivity and 30% yield of phenol could be achieved with Cu(II)-substituted $\text{AlPO}_4\text{-5}$ under proper reaction condition.

Trimethylbenzoquinone (TMBQ) is a key intermediate in making vitamin E [11]. The latter is expected to have a constantly increasing demand in pharmaceutical and food industry in the coming decade [12]. In the literature, various catalysts and oxidants have been declared in the oxidation of trimethylphenol (TMP) to TMBQ [13–21]. 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. In the present study, we found Cu(II)-substituted MCM-41 to be an efficient catalyst for this reaction.

2. Experimental methods

2.1. Synthesis of Cu(II)-substituted $\text{AlPO}_4\text{-5}$ molecular sieve

The material was prepared by hydrothermal method. The molar composition in the synthesis gel was $\text{Al}:\text{P}:\text{Cu} = 1:1:0.01\text{--}0.04$. 5.5 g of pseudo-boehmite (73.5% Al_2O_3 , Condea Vista, Catapal® A Alumina) 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 adding desired amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Hanawa) 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 to remove the template.

2.2. Synthesis of Cu, Al-substituted 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 ($\sim 14\%$ NaOH, $\sim 27\%$ SiO_2) in 15 g water. To another flask was charged in 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 $\text{SiO}_2:(0\text{--}0.05)\text{Al}_2\text{O}_3:(0\text{--}0.05)\text{CuO}:0.48\text{CTMA}^+:0.67\text{TPA}^+:0.39\text{Na}_2\text{O}:0.29\text{H}_2\text{SO}_4:50\text{--}110\text{H}_2\text{O}$. The gel mixture was stirred for two days at room temperature and then transferred to polypropylene bottles and statically heated at 100°C for seven 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.

The elemental contents of the samples were analyzed with ICP-AES (Allied Analytic System, Jarrell-Ash, Model IC AP 9000). The Cu(II) containing $\text{AlPO}_4\text{-5}$ was dissolved with 37% HCl and that of MCM-41 was dissolved with HF solution. Temperature-programmed reduction (TPR) of Cu-containing samples was carried out in a fixed bed reactor. In the experiment, ~ 0.1 g sample in powder form was packed in a quartz tube of 0.8 mm I.D. The sample was pre-treated in nitrogen for 30 min at 200°C, and cooled to ambient tem-

perature. A 10% H₂/N₂ mixed gas with a flow rate of 30 ml/min was used as the reducing agent. The temperature was programmed to rise from 50°C to 800°C with a heating rate of 10°C/min. TCD was used as the detector.

2.3. Catalyst testing

A batch reactor, which composed of a three-neck flask connected with a reflux condenser and a thermometer, was used for catalytic reactions. In alkyl-benzene oxidation, 0.2 g aluminophosphate molecular sieve in powder form was suspended in a mixture of 1 g alkyl-benzene and 2.3 g acetonitrile. After heating the mixture to 60°C under stirring, 2.5 g of 35% H₂O₂ (Acros Organics) solution was added. The products obtained after 3 h reaction period were analyzed with a HP5980-5973 GC-MS. The conversions were calculated based on the mole numbers of aromatic reactants lost after the reaction relative to the original mole number of the aromatic reactants. The yields of the products were calculated based on the mole number of products formed relative to the original mole number of aromatic reactants. The selectivity of a specific product was calculated by dividing the yield with the conversion. The areas obtained from gas chromatograph were calibrated relative to toluene, which was added into the product as internal standard. In the toluene oxidation reaction, *o*-xylene was used as the internal standard.

In oxidation of 2,3,6-trimethylphenol, a 0.2 g portion of the catalyst suspended in solvent 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 for 20 min. The liquid products were separated with a Rtx-1 capillary column and detected by an FID detector in a Shimadzu GC-14 chromatography. Toluene was used as an internal standard to calculate the TMP conversion and TMBQ yield. The gas products were separated with a Carboxen 1000 packing column and detected by a TCD detector in a Shimadzu GC-8A chromatography.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. CuAPO-5

Pure AlPO₄-5 (with the structure type code AFI) crystalline phase was obtained when Cu/(Al+P) molar ratio of up to 2% was incorporated into the synthesis gel of AlPO₄-5. Table 1 summarizes the BET surface area and the chemical composition of the samples determined by ICP-AES. Generally speaking, the metal contents in the crystals are proportional to but lower than those added into the gels. As the metal content increases, the difference between the amount added in the gel and that incorporated into the crystal increases. These results suggest that there are limitations in the amount of hetero-elements being incorporated into the crystals. The other important point shown in Table 1 is that the Al/P molar ratios analyzed by ICP-MS are less than 1 for all the CuAPO-5 samples, implying that most of the Cu(II) ions are likely substituted the Al tetrahedral sites instead of

Table 1
The chemical compositions and surface areas of AlPO₄-5 with different Cu loadings

Cu loading ^a (%)	BET S.A. (m ² /g)	Gel			Solid ^b		
		Cu	Al	P	Cu	Al	P
0	290	0 (0%)	1 (50%)	1 (50%)	0 (0%)	1 (50.25%)	0.99 (49.75%)
0.5	270	0.01 (0.50%)	1 (49.75%)	1 (49.75%)	0.008 (0.38%)	1 (48.36%)	1.06 (51.26%)
1	272	0.02 (1.00%)	1 (49.50%)	1 (49.50%)	0.017 (0.81%)	1 (47.92%)	1.07 (51.27%)
2	273	0.04 (1.96%)	1 (49.02%)	1 (49.02%)	0.032 (1.53%)	1 (47.80%)	1.06 (50.67%)

Values in parentheses are molar percentages of metal species.

^a Analyzed with ICP-MS.

^b Cu/(Al+P) molar ratio in the synthesis gel.

Table 2
Lattice parameter of $\text{AlPO}_4\text{-5}$ with different Cu loadings

Cu loading ^a	<i>a</i> , <i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
0	13.614 (0.004)	8.484 (0.005)	1361.8
0.5%	13.637 (0.002)	8.491 (0.002)	1367.5
1%	13.681 (0.013)	8.445 (0.014)	1368.9
2%	13.654 (0.005)	8.486 (0.005)	1370.1

Values in parentheses are the standard deviations.

^a Cu/(Al+P) molar ratio in gel.

P on the framework. Table 1 also shows that $\text{AlPO}_4\text{-5}$ has higher surface area than those incorporated with copper, but the differences are negligible.

Table 2 shows the variation in lattice parameters of $\text{AlPO}_4\text{-5}$ with different Cu loadings. It was found that the unit cell volume increases with the Cu loading. This is one of the evidences that Cu(II) ions are probably incorporated in the framework. The fluctuation of the unit cell axes as Cu loading increases implies that the lattice is distorted.

The TPR of CuAPO-5 was carried out and the results were compared with those of the impregnated and physically mixed samples. Fig. 1 shows that the reduction of CuAPO-5 starts at $\approx 225^\circ\text{C}$ and the peak maxima appear at 300°C and 280°C for 1% and 2% CuAPO-5, respectively. For the impregnated sample, which was prepared with $\text{Cu}(\text{NO}_3)_2$ solution, the reduction starts at a lower temperature and the peak is sharper than CuAPO-5. The peak maximum appears at 240°C , which is much lower than CuAPO-5. These results imply that the impregnated sample is much easier to be reduced than CuAPO-5 and the Cu species in CuAPO-5 should be in the framework. For the physically mixed sample, the reduction peak is broad and covers a wide temperature range of $\approx 200^\circ\text{C}$. That is due to the relatively large particles of CuO used for physical mixture.

3.1.2. CuMCM-41

The chemical compositions of the MCM-41 samples substituted with Cu(II) and Al(III) were tabulated in Table 3. Again, the metal contents in the crystals, based on the M/Si molar ratios, are proportional to but lower than those added into the gels. Exception was found on Al-substituted

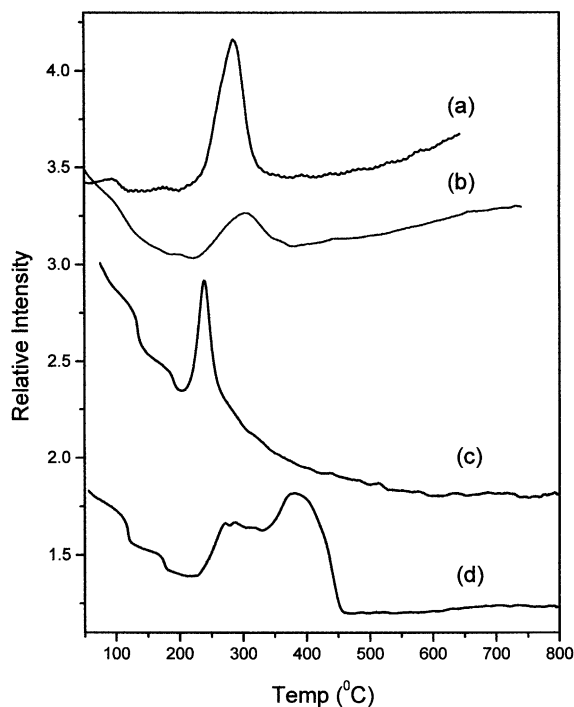


Fig. 1. TPR of Cu containing $\text{AlPO}_4\text{-5}$: (a) 2%CuAPO-5, (b) 1%CuAPO-5, (c) 1%Cu/ $\text{AlPO}_4\text{-5}$ (imp), and (d) 1%CuO/ $\text{AlPO}_4\text{-5}$ (phys-mix).

Table 3
Compositions and symbols of Cu, Al-MCM-41

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

^a Analyzed by ICP-AES.

samples of low loading. The Al/Si molar ratios in the solids were slightly higher than those in gels.

Table 4
Surface area and pore size of Cu, Al-MCM-41

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

That was attributed to that 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.

The physical properties of the MCM-41 samples incorporated with different amounts of cations are given in Table 4. It can be seen that the BET surface areas of these samples were in the range of 871–1034 m²/g. The nitrogen adsorption–desorption isotherms of Cu,Al-substituted MCM-41 samples showed 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 cm³/g were obtained. A slight decrease in the surface area and pore volume was observed only when relatively large amount of Cu(II) and Al(III) ions were incorporated in MCM-41.

3.2. Catalytic reactions

Most of the Cu(II)-substituted molecular sieves were catalytic active for one-step oxidation of benzene to phenol with hydrogen peroxide as the oxidant, and in particular the aluminum phosphate molecular sieve AlPO₄-5 doped with Cu(II) ions gave the optimal effect. The liquid phase reactions were extremely sensitive to the oxidant and solvent used. Table 5 shows that by selecting suitable reaction conditions, product containing predominantly phenol could be obtained. The CuAPO-5 prepared by hydrothermal method has higher catalytic activity than that prepared by impregnation or copper ions presented in oxides or

Table 5
Benzene oxidation catalyzed by different Cu containing catalysts

Catalyst	Conversion (%) ^a	Phenol	
		Yield (%)	Selectivity (%)
AlPO ₄ -5	0	0	–
1%CuAPO-5	28	28	~100
1%Cu/AlPO ₄ -5 (imp)	54	9	17
1%CuAPO-5 (re-generated) ^b	18	18	~100
CuO ^c	78	8	10
Cu ₂ O ^d	66	4	6
Cu(NO ₃) ₂ solution ^e	13	6	46

Reaction conditions: 60°C, 3 h; catalyst, 0.2 g; benzene, 1.0 g; acetonitrile, 2.3 g; H₂O₂, 2.5 ml.

^a Conversions were based on benzene.

^b The used sample was regenerated by calcination at 550°C for 8 h.

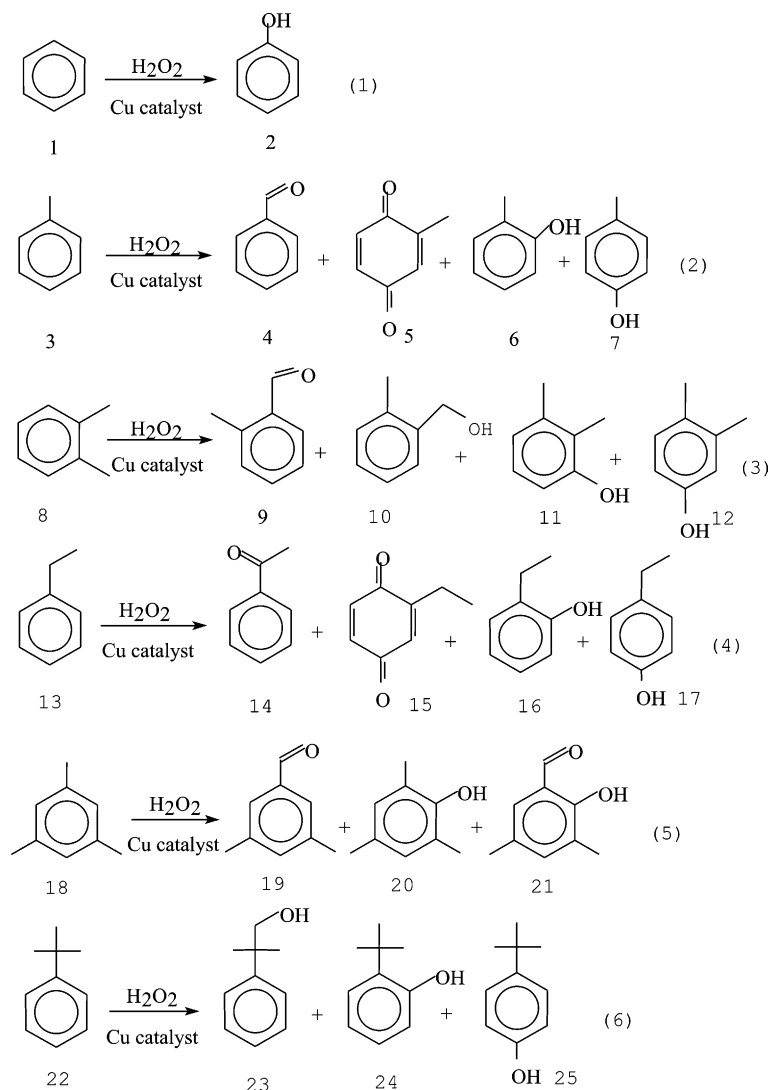
^c CuO 2.65 × 10⁻³ g.

^d Cu₂O 2.38 × 10⁻³ g.

^e Same Cu molar numbers as that in 1%Cu-APO-5.

solutions. The conversions shown in the table were based on benzene. The H₂O₂ conversion over CuAPO-5, determined by iodide titration with starch indicator, was found about a half of that of benzene. Since the mole ratio of benzene/H₂O₂ to start with was 1/2, this result implies that little amount of H₂O₂ decomposed through disproportionation during the reaction. The reaction mechanism was examined by adding 4-methyl-2, 6-*t*-butylphenol, which is a radical scavenger, of equal equivalents as benzene into the reaction system. The phenol yield decreased dramatically from 28% to 2%, indicating that the reaction was through radical intermediates.

For alkyl-substituted benzene, the benzene ring hydroxylation is competed by benzylic oxidation if benzylic hydrogen is present. In solution reaction, the benzylic oxidation is usually favored to ring hydroxylation due to the formation of thermally stable benzylic radicals as intermediates in the former reaction. Scheme 1 shows the reaction products obtained in the oxidation of various alkyl-substituted benzenes. The product distributions shown in Table 6 were very different from what should be observed through homogeneous radical reactions in solutions. High selectivities of



Scheme 1. Reaction products in liquid phase oxidation of alkylbenzenes over CuAPO-5.

products from benzene ring hydroxylation are seen. Moreover, the conversion and the selectivity of ring hydroxylation products decrease when more or bulkier alkyl groups are present. For *t*-butylbenzene with a bulky substitution group, although the conversion is low, the selectivity of ring hydroxylation is relatively high comparing with other alkyl-substituted benzenes. That is because no benzylic hydrogen is present on this bulky molecule. The decrease in conversion with the increase in bulkiness of the substitution on the

benzene ring implies that the benzene reactants must be adsorbed on the surface active sites before hydroxylation reaction occurred.

The phenol selectivity in benzene oxidation reaction was found to be influenced by reaction temperature and the amount of catalyst used. Table 7 shows that phenol conversion increases with reaction temperature. In the temperature range of 40–70°C, phenol was almost the exclusive product. As the temperature was raised to 80°C, most of the benzene was vaporized and the phenol

Table 6
Different alkyl-substituted benzene oxidation over 1%CuAPO-5

Reactant	Conversion (%)	Product yield (%)				^a Selectivity (%)
Benzene ^b (1)	28	28 (2)				~100
Toluene (3)	14	3.8 (4)	0.6 (5)	7.0 (6)	2.5 (7)	72.1
<i>o</i> - xylene (8)	8.9	3.8 (9)	0.6 (10)	2 (11)	2.2 (12)	47.2
Ethylbenzene (13)	9.6	4.6 (14)	0.6 (15)	2.6 (16)	1.8 (17)	45.8
1,3,5-trimethyl-benzene (18)	6.7	4.6 (19)	1.2 (20)	1.0 (21)		32.8
<i>t</i> - butyl-benzene (22)	1.8	0.3 (23)	0.3 (24)	1.2 (25)		83.3

Reaction conditions: 60°C; reactant:acetonitrile:H₂O₂ = 1.0 g:2.3 g:2.5 ml; reaction duration 3 h.

^a Selectivities of products from benzene ring hydroxylation.

^b Italic numbers are the compounds designated in Scheme 1.

Table 7
Temperature effect on benzene oxidation

Temperature (°C)	Conversion (%)	Phenol	
		Yield (%)	Selectivity (%)
25	0	0	–
40	16	16	~100
50	24	24	~100
60	28	28	~100
70	30	30	~100
80	88	2	2.5

Reaction condition: 1%CuAPO-5 0.2 g; Benzene 1.0 g; acetonitrile 2.3 g; H₂O₂ 2.5 ml; reaction duration 3 h.

Table 8
Benzene oxidation with different amount of 1%CuAPO-5

Catalyst weight (g)	Conversion (%)	Phenol	
		Yield (%)	Selectivity (%)
0.1	17	17	~100
0.2	28	28	~100
0.3	46	35	76

Reaction condition: 60°C; Benzene 1.0 g; acetonitrile 2.3 g; H₂O₂ 2.5 ml; reaction duration 3 h.

yield was very low. Table 8 shows the effect of the catalyst amount. The conversion was almost proportional to the amount of catalyst used. However, the phenol selectivity decreases if too much of the catalyst was used. The generation of secondary oxidation products, such as catechol and hydroquinone accounts for this observation.

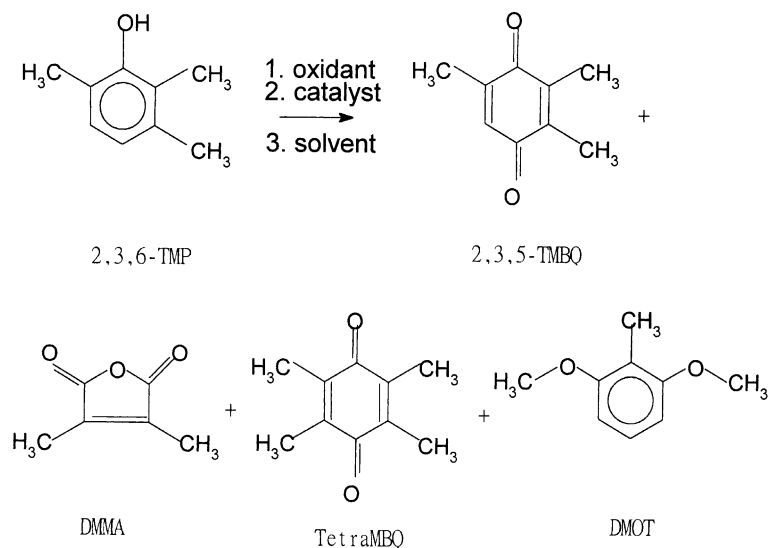
In the oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethylbenzoquinone, various Cu(II)-sub-

stituted molecular sieves were examined as the catalysts. Table 9 shows that mesoporous MCM-41 gives the highest TMBQ selectivity in comparison with other microporous molecular sieves, such as ZSM-5 and AlPO₄-5. The main liquid products obtained in this reaction are shown in Scheme 2. Besides, CO and CO₂ were also detected in the gas products. CuAPO-5 molecular sieve

Table 9
TMP oxidation over various Cu(II) containing catalysts

Catalysts	Conversion (%)	TMBQ	
		Yield (%)	Selectivity (%)
1%CuAPO-5	85	20	24
2%CuAPO-5	85	30	36
1%CuZSM-5	32	0	0
Cu-ZSM-5 (exchange)	61	0	0
2%CuMCM-41	52	28	54
2%Cu, 2%AlMCM-41	64	47	73
2%Cu, 3%AlMCM-41	74	34	46
2%Cu, 5%AlMCM-41	78	21	27
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 ₂ O ₃	35	0	0
Cu(NO ₃) _{2(aq)}	65	5.3	8.2

TMP:H₂O₂:CH₃CN = 1:1:3; reaction period = 20 min.



Scheme 2. Reaction products in liquid phase oxidation of TMP over CuMCM-41, where DMMA is dimethylmaleic anhydride and DMOT is dimethoxytoluene.

gave high TMP conversion but the TMBQ selectivity was relatively low. On the other hand, no TMBQ was formed over Cu-ZSM-5 prepared either by co-precipitation or ion-exchange. These results are elucidated by that the reaction is restricted by the relatively small pore diameters of ZSM-5 and $\text{AlPO}_4\text{-5}$.

The optimal TMBQ selectivity was observed over MCM-41 concomitantly substituted with Cu(II) and small amounts of Al(III). When the MCM-41 sample impregnated with $\text{Cu}(\text{NO}_3)_2$ solution was used as the catalyst, very low yield of TMBQ was observed. The activity was greatly improved by co-impregnation of Al(III) species, with either NaAlO_2 or $\text{Al}_2(\text{SO}_4)_3$ solution. However, the TMBQ yields were still less than half of the values obtained over the co-precipitated samples. In another experiment, an aqueous $\text{Cu}(\text{NO}_3)_2$ solution containing the same molar number of Cu(II) as that in sample 2%Cu, 2%AlMCM-41 was used as the catalyst. Very low yield and selectivity of TMBQ were observed. It clarified that the catalytic activity of Cu, Al-MCM-41 was not due to Cu(II) ions leaching into the solution. When 0.2 g of Al_2O_3 fine powders was used as the catalyst, no TMBQ was detected in the products. These results imply that well-dispersed Cu(II) on

the framework is the active center on Cu-MCM-41 in 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. However when too much Al(III) was substituted on MCM-41, although the TMP conversion increased, the TMBQ yield decreased. This phenomenon was attributed to that Al(III) would compete with Cu(II) for the sites exposed on the surface but Al(III) was not the catalytic active center for oxidation.

The liquid phase TMP oxidation reaction was extremely sensitive to the oxidant and solvent used. Table 10 shows the effect of solvent and oxidant over 2%Cu, 2%AlMCM-41. With H_2O_2 as the oxidant, benzaldehyde gave the highest TMP conversion and TMBQ selectivity among the solvents used, which included ethanol, acetaldehyde, acetonitrile and benzaldehyde. 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

Table 10

Effect of solvent and oxidant in TMP oxidation over 2%Cu, 2%AlMCM-41 catalyst

Solvents	Oxidant	Reaction period	Conversion (%)	TMBQ	
				Yield (%)	Selectivity (%)
C ₂ H ₅ OH	H ₂ O ₂	20 min	2.0	0	0
CH ₃ CHO	H ₂ O ₂	20 min	68.0	1.3	1.9
CH ₃ CN	H ₂ O ₂	20 min	63.7	46.7	73.3
CH ₃ CN	TBHP	20 min	97.8	83.2	85.1
CH ₃ CN	O ₂	6 h	17.3	0	0
Ph-CHO	H ₂ O ₂	20 min	87.0	68.7	78.9
Ph-CHO	TBHP	20 min	98.0	87.5	89.3
Ph-CHO	O ₂	2 h	43.2	22.3	51.6
Ph-CHO	O ₂	4 h	71.4	40.9	57.3
Ph-CHO	O ₂	6 h	82.4	44.6	54.1

TBHP: tert-butylhydroperoxide; reaction temperature = 60°C.

in 20 min. Another advantage of using benzaldehyde solvent is that oxygen gas could be used as the oxidant, although the reaction proceeded slower 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 benzoic peracid, was detected in the products. Therefore, the benzoic acid, which is the oxidation product of benzaldehyde, probably performed as a co-catalyst in the oxidation reaction.

Acknowledgements

Financial supports from National Science Council and China Petroleum Corporation, Taiwan are gratefully acknowledged. The authors also thank Condea Vista, Inc. for free supply of pseudo-boehmite. The assistance of Chih-Chang Chen and Yu-Jen Lin in TPR studies is also acknowledged.

References

- [1] T. Blasco, M.A. Cambor, A. Corma, J. Pérez-Parienté, *J. Am. Chem. Soc.* 115 (1993) 11806.
- [2] D.C. Huybrechts, L.D. Bruycker, P.A. Jacobs, *Nature* 345 (1990) 240.
- [3] J.S. Reddy, P.A. Jacobs, *J. Chem. Soc., Perkin Trans. 1*, 22 (1993) 2665.
- [4] T. Tatsumi, N. Jappar, *J. Catal.* 161 (1996) 570.
- [5] R. Bhaumik, T. Tatsumi, *J. Catal.* 176 (1998) 305.
- [6] B. Notari, *Stud. Surf. Sci. Catal.* 37 (1987) 413.
- [7] P.R. Hari Prasad Rao, A.V. Ramaswamy, P. Ratnasamy, *J. Catal.* 137 (1992) 225.
- [8] K. Weissermel, H.J. Arpe, *Industrial Organic Chemistry*, 3rd ed., VCH Publishers, New York, 1997, p. 347.
- [9] J. Sudhakar Reddy, S. Sivasanker, P. Ratnasamy, *J. Mol. Catal.* 71 (1992) 373.
- [10] A.V. Ramaswamy, S. Sivasanker, P. Ratnasamy, *Micro. Mater.* 2 (1994) 451.
- [11] P. Schudel, H. Mayer, O. Isler, in: W.H. Sebrell Jr., R.S. Harris (Eds.), *The Vitamins*, Academic Press, New York, vol. 5, 1972, p. 165.
- [12] C. Mercier, P. Chabardes, in: M.G. Scaros, M. Prunier (Eds.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1994, p. 213.
- [13] M. Shimizu, H. Orita, T. Hayakawa, K. Takehara, *Tetra. Lett.* 30 (1989) 471.
- [14] O.A. Kholdeeva, A.V. Golovin, R.I. Maksimovskaya, I.V. Kozhevnikov, *J. Molec. Catal.* 75 (1992) 235.
- [15] D. Michelet, US Patent no. 3910967 (1975).
- [16] S. Ito, K. Aihara, M. Masakatsu, *Tetra. Lett.* 24 (1983) 5249.
- [17] J.G.A. Bitter, R.J. Maas, J.H. Scheeman, US Patent no. 4250335 (1981).
- [18] T. Gessner, US Patent no. 5712416 (1998).
- [19] F. Thoemel, W. Hoffmann, US Patent no. 4491545 (1985).
- [20] T. Isshiki, T. Yui, M. Abe, M. Jono, H. Uno, US Patent no. 4828762 (1989).
- [21] U. Hoercher, B. Bockstiegel, P. Grafen, H. Laas, US Patent no. 5041572 (1991).
- [22] D. Michelet, M. Razoutz, US Patent no. 3927045 (1975).