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Liquid-Phase Oxidation of 2,6-Di-*tert*-butylphenol with Cu-Impregnated MCM-41 Catalysts in the Presence of Alkali Metals

Hirofumi Fujiyama,* Ichitaro Kohara,* Keisuke Iwai,† Satoru Nishiyama,*
Shigeru Tsuruya,*,[1] and Mitsuo Masai‡

**Department of Chemical Science and Engineering, Faculty of Engineering, and †Division of Molecular Science, Graduate School of Science and Technology, Kobe University, Nada, Kobe, 657-8501, Japan; and ‡Department of Applied Physics and Chemistry, The Fukui University of Technology, Gakuen, 3-6-1, Fukui, 910 Japan*

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Mesoporous silicate MCM-41, with a uniform pore diameter of ca. 35 Å, was used as a support for impregnated Cu catalysts for liquid-phase oxidation of 2,6-di-*tert*-butylphenol (BOH) in the presence of a base such as KOH. The oxidation products were 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butyl-biphenyl (H_2DPQ) and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ). An alkali such as a potassium salt, which promotes the phenol oxidation activity of copper ion-impregnated MCM-41 (Cu/MCM-41) catalyst, was found to be more effective as an additive to the reaction solution than impregnation on the Cu/MCM-41 catalyst. The added alkali was found to play a role in generating the corresponding phenolate anion by dissolving a BOH molecule. H_2DPQ is formed through tautomerization of an intermediate dimer obtained by the C–C coupling of the corresponding phenoxy radicals. DPQ is formed via the consecutive oxidation of H_2DPQ and/or via the oxidative dehydrogenation of the intermediate dimer. The BOH molecules in the mesopores of Cu/MCM-41, rather than the BOH in bulk solution in the presence of $CuCl_2$, were found to favor H_2DPQ production. Cu/MCM-41 with added potassium [(K–Cu)/MCM-41] was much more active for phenol oxidation than Cu-impregnated NaZSM-5 with added potassium [(K–Cu)/NaZSM-5] or the corresponding NaY [(K–Cu)/NaY], each catalyst having only uniform micropores. This result indicates that the oxidation of sterically bulky BOH occurs mainly at the active sites in the mesopores and is difficult to carry out in the micropores of (K–Cu)/NaZSM-5 and (K–Cu)/NaY zeolites because of the steric bulkiness of the oxidation products, H_2DPQ and DPQ. The liquid-phase adsorption amounts of BOH on NaZSM-5 and NaY were found to be comparable to that on MCM-41. The shape selectivity by the oxidation products in the micropores of (K–Cu)/NaZSM-5 and (K–Cu)/NaY zeolites was thus suggested to inhibit the BOH oxidation activities of both catalysts, based on the results of the oxidation reaction and liquid-phase adsorption of BOH. © 1999 Academic Press

Key Words: **2,6-di-*tert*-butylphenol; oxidation; Cu/MCM-41; Cu/NaZSM-5; Cu/NaY; diphenoquinone; dihydroxylbiphenyl; alkali metals; shape selectivity.**

INTRODUCTION

Since Mobil's report (1, 2) on the syntheses of mesoporous silicates M41S, which is classified as MCM-41 (hexagonal prism structure), MCM-48 (cubic structure), and MCM-51 (sheet structure), many studies on the synthesis and characterization of the mesopore silicates and their counterparts with transition metals inserted into the tetrahedral framework of silica have been reported (3–8). In particular, MCM-41, which possesses one-dimensional uniform mesopores, the size of which can be controlled by selecting the template molecules, has been noted as a provider of a mesopore reaction field (9–14). The application of these mesopore materials to catalyst supports with a mesosize reaction field will be expected in liquid-phase fine chemical reactions including sterically bulky molecules.

We have been studying liquid-phase oxidation of phenol and/or catechol derivatives catalyzed by homogeneous copper complexes and heterogeneous copper-supported polymers (15). Through the study of the design and development of the copper catalyst for the oxidation of phenol derivatives, basic copper catalytic systems such as $CuCl_2$–KOH have been found (16, 17) to be effective for liquid-phase oxidation of phenol derivatives including phenols with sterically bulky substituent groups such as 2,6-di-*tert*-butylphenol using oxygen molecules as an oxidant under mild reaction conditions. The liquid-phase oxidation of 3,5-di-*tert*-butylphenol catalyzed by Ti- or V-incorporated mesoporous silicates has been reported (4, 13) using H_2O_2 or *tert*-butylhydroperoxide as an oxidant under various reaction conditions. We have already reported (14) the liquid-phase oxidation of benzene catalyzed by Cu-supported mesoporous silicates and their aluminosilicate counterparts using oxygen molecules and ascorbic acid as an oxidant and a reductant, respectively. Phenol has been produced by the direct oxygenation of benzene though the yield of produced phenol was rather low.

In this study, we report the liquid-phase oxidation of the titled phenol catalyzed by Cu-supported mesoporous

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[1] To whom correspondence should be addressed. Fax: +81–78–803–6171. E-mail: tsuruya@cx.kobe-u.ac.jp.

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silicates in the presence of alkali using oxygen molecules as an oxidant. The usefulness of the mesopore field in the reaction including the sterically bulky molecule is emphasized on the basis of the comparison of the oxidation activities of the Cu catalysts having mesopores and micropores. The high selectivity for dihydroxydiphenyl (H_2DPQ) derivative in the mesopore reaction field is shown in the comparison with a bulk solution as a reaction field. The role of added alkali on phenol oxidation is also discussed in terms of the reaction scheme of the phenol oxidation.

EXPERIMENTAL

Synthesis of MCM-41

MCM-41 was synthesized by a sol–gel method at room temperature in the atmosphere: tetraethyl orthosilicate [Nacarai Tesque, extra pure, 0.1 mol (20.83 g)] was added dropwise for 10 min with stirring to an aqueous ammonia solution (2.56%, 234 cm^3) containing dissolved hexadodecyltrimethylammonium bromide [Nacarai Tesque, guaranteed reagent, 0.012 mol (4.37 g)] as a template. The entire mixture was kept at room temperature for 24 h. The white precipitate produced was filtered off and washed under vacuum with warm (333–343 K) ion-exchanged water until the filtrate became neutral. The precipitate was dried at 393 K overnight, treated at 773 K for 1 h in a nitrogen flow (250 cm^3/min), and calcined at 773 K in an air flow (250 cm^3/min) to remove the template moieties.

Preparation of Cu-Impregnated and Cu–K-Coimpregnated Catalysts

MCM-41 (synthesized in our laboratory), NaZSM-5 [synthesized in our laboratory (18), Si/Al = 53], and NaY (Toso, Si/Al = 2.8) were used as supports. Cu-impregnated catalysts were prepared by impregnation with the prescribed amount of copper acetate dissolved in ethanol. Cu–K-coimpregnated catalysts were prepared using the ethanol solution with both dissolved copper acetate and potassium acetate. Cu-impregnated and Cu–K-coimpregnated catalysts were dried at 393 K overnight and calcined at 773 K for 5 h in an air flow. The standard impregnated amount of Cu was 1 wt%.

Preparation of Reduced Ru-Impregnated MCM-41

MCM-41 was poured into an ethanol solution containing $RuCl_3 \cdot 3H_2O$. After ethanol was evaporated to dryness with stirring, the resulting Ru-impregnated MCM-41 was dried at 393 K overnight, calcined at 673 K for 5 h, and reduced at 773 K for 5 h in a hydrogen flow. The amount of impregnated Ru was 3 wt%.

Liquid-Phase Adsorption of 2,6-Di-tert-butylphenol

A 0.2 g portion of support (MCM-41, NaZSM-5, NaY) was added to 20 cm^3 of chloroform solution containing 1 mmol of dissolved 2,6-di-*tert*-butylphenol (0.206 g). After magnetically stirring the whole system at 313 K for 24 h, the adsorbed amount of phenol was determined by measuring the amount of phenol remaining in the solution using HPLC (Hitachi L-4200).

Liquid-Phase Oxidation of 2,6-Di-tert-butylphenol

Oxidation of 2,6-di-*tert*-butylphenol (0.103 g, 0.5 mmol) was performed in 12 cm^3 of chloroform solvent including 0.2 g catalyst at 313 K under air atmosphere for 24 h using a magnetic stirrer. When an alkali salt was added to the reaction solution, a mixed solvent consisting of 10 cm^3 chloroform and 2 cm^3 methanol containing the homogeneously dissolved alkali salt was used, instead of pure chloroform solvent. To minimize the effect of the reactant and the products adsorbed on the catalyst, the reaction system, after the reaction, was centrifuged and immediately transferred to the HPLC analyses. The products were analyzed by HPLC (Hitachi L-4200) with a GC-C18 packed column using acetonitrile (degassed) as a carrier (1.0 cm^3/min). The amount of leached Cu or K during the oxidation was determined by measuring the amount of Cu or K in the catalyst, which was separated from the reaction solution by centrifugation followed by immediate filtration, before and after the oxidation using an atomic absorption spectrometer (Shimazu AA-630-01).

Synthesis of 3,3′,5,5′-Tetra-tert-butyl-4,4′-diphenoquinone

3,3′,5,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone was synthesized using a homogeneous $CuCl_2$–pyridine–KOH catalytic system according to the literature (16). The resultant reddish solid was recrystallized from methanol containing a small amount of chloroform [IR: strong C=O stretching peak at 1702 cm^{-1} (16); UV-VR: $\lambda_{max} = 430$ nm (2)].

Synthesis of 4,4′-Dihydroxy-3,3′,5,5′-tetra-tert-butylbiphenyl

4,4′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl was synthesized by catalytically reducing 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone. A 0.1-g sample (0.25 mmol) of the corresponding diphenoquinone, 0.1 g of 3 wt% reduced Ru-impregnated MCM-41 catalyst, and 5 cm^3 of chloroform solvent were added to a high-pressure stainless-steel reactor (Taiatsu Glass Co., 30 cm^3). After several hydrogen purges in the reactor, the reaction was conducted at 338 K for 24 h under 1.0 MPa hydrogen atmosphere. The resultant off-white solid product was analyzed by HPLC and obtained in almost 100% yield after centrifugation of the reaction mixture and evaporation of chloroform solvent [IR: no C=O stretching peak, a strong OH stretching peak at 3647 cm^{-1} (19); UV-VR: $\lambda_{max} = 270$ nm (2); LC-MS: 409 (parent dihydroxybiphenyl-2 H)].

RESULTS

The MCM-41 synthesized here had the same XRD pattern as that reported in the literature (1, 2). The physical properties of the obtained MCM-41 were as follows: XRD d_{100} spacing, 37.2 Å; pore diameter, 34.6 Å; wall thickness, 8.4 Å; BET surface area, 1023 m^2/g. The mechanical and thermal stabilities of MCM-41 are listed in Table 1. MCM-41 showed a relatively strong resistance to the calcination treatment at higher temperature but was not highly resistant to damage to its mechanical strength.

Through the present study, no oxidation products, such as monomer counterparts (benzoquinone and/or hydrobenzoquinone derivatives), other than two dimer products, 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H_2DPQ) and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ), were detected using the Cu catalysts supported on MCM-41 or ZSM-5 zeolite in the presence of alkali metal under the present reaction conditions.

Leaching of Cu species supported on MCM-41, NaY, and NaZSM-5 into the reaction solution was not detected during BOH oxidation under the reaction conditions attempted in this study.

Oxidation of 2,6-Di-tert-butylphenol

Figure 1 illustrates the time dependence of the yields of the oxidation products in the oxidation of 2,6-di-*tert*-butylphenol (BOH) catalyzed by the K–Cu-coimpregnated MCM-41 [(K–Cu)/MCM-41] system. The yield of H_2DPQ increased with the increase in reaction time from the initial stage, but the H_2DPQ yield tended to almost level off after the reaction time of around 10 h. On the other hand, DPQ was hardly detected in the initial stage of the oxidation; thus an induction period was observed in the production of DPQ.

TABLE 1

Mechanical and Thermal Properties of MCM-41

Applied pressure (kg/cm^2)	Calcination temperature (K)	Relative intensity of (100) diffraction peak	BET surface area (m^2/g)
None	773	100	1023
400	773	70	638
600	773	50	621
None	773	100	1023
None	1073	96	1023
None	1273	76	889

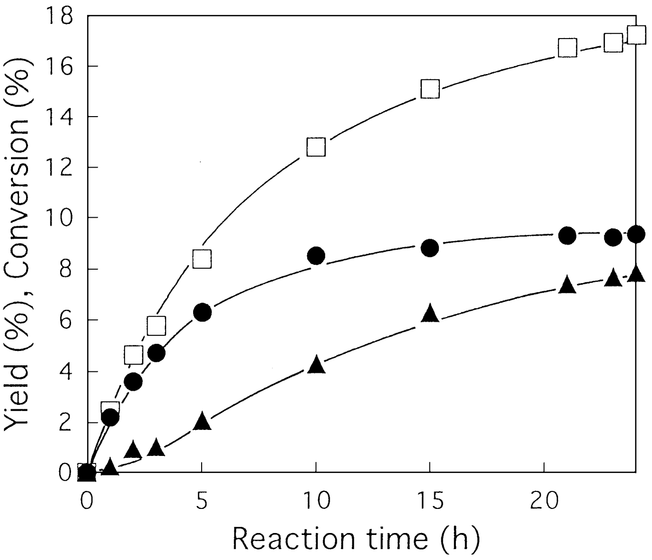


FIG. 1. Yield and conversion versus reaction time in BOH oxidation catalyzed by (K–Cu)/MCM-41. BOH, 5 mmol; catalyst, (K–Cu)/MCM-41, 0.2 g (Cu: 3.12×10^{-2} mmol); K/Cu atomic ratio, 1; reaction temperature, 313 K; solvent, 12 ml of chloroform. □, Conversion; ●, H_2DOQ yield; ▲, DPQ yield.

The relationship between reaction time and yield of both the products and the conversion of BOH using a basic $CuCl_2$ catalytic sytem ($CuCl_2$ + KOH) without a catalyst support is illustrated in Fig. 2. The yield of H_2DPQ passed through a maximum value at the reaction time of ca. 1 h and decreased with further reaction time. Differing from the supported

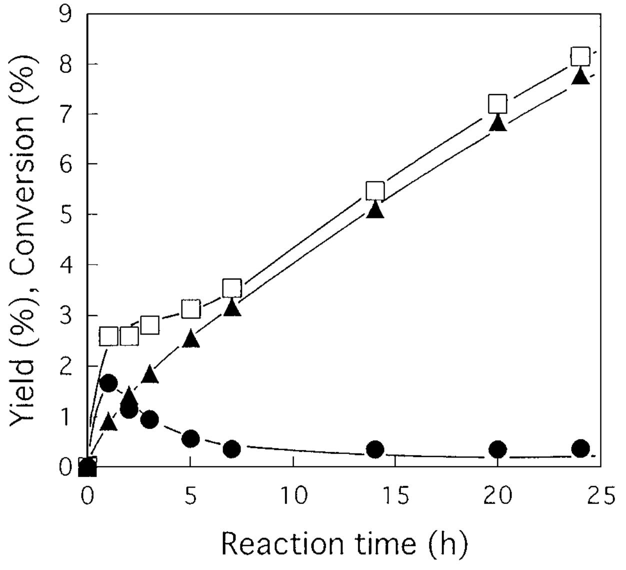


FIG. 2. Yield and conversion versus reaction time in BOH oxidation catalyzed by unsupported $CuCl_2$. BOH, 5 mmol; catalyst, $CuCl_2$, 3.12×10^{-2} mmol; KOH, 3.12×10^{-2} mmol; KOH (K)/Cu mole ratio, 1; reaction temperature, 313 K; solvent, 10 ml of chloroform + 2 ml of methanol. □, Conversion; ●, H_2DPQ yield; ▲, DPQ yield.

(K–Cu)/MCM-41 catalyst, DPQ was found to be produced almost selectively in a reaction time of more than 5 h using unsupported $CuCl_2$–KOH catalyst.

To investigate the cause of the difference in the time dependence of the oxidation products between the supported (K–Cu)/MCM-41 and the unsupported $CuCl_2$–KOH catalysts, oxidation of H_2DPQ, in place of the starting BOH, was carried out using both MCM-41 supported and unsupported Cu catalysts. The yields of DPQ catalyzed by both (K–Cu)/MCM-41 and $CuCl_2$–KOH catalysts were 58% and ca. 100% for a reaction time of 24 h, respectively. Thus the higher oxidation rate of H_2DPQ to DPQ catalyzed by the unsupported $CuCl_2$–KOH, in comparison with the supported (K–Cu)/MCM-41 catalyst, will explain the lower yield and selectivity of H_2DPQ (Fig. 2) over the prolonged reaction time. Also, the formation of 2,6-di-*tert*-butylphenolate, which will preferentially lead to DPQ as described later, is considered to be easier with the unsupported $CuCl_2$–KOH catalytic system, rather than with the (K–Cu)/MCM-41 catalyst, because of the presence of free KOH in the reaction solution.

Comparison of the Catalytic Activities of Cu-Supported Catalysts with Mesopores and Micropores

To investigate the influence of the difference between the meso- and microreaction fields on the oxidation of BOH, which has two sterically bulky substituents and a kinetic diameter (the minimum diameter of the molecule) of ca. 7 Å, we attempted to use NaZSM-5 and NaY zeolites as supports for the catalyst in place of MCM-41 (Table 2). The oxidation activities of both catalysts with a micropore support [(K–Cu)/NaZSM-5 and (K–Cu)/NaY] were found to be considerably lower than that of the (K–Cu)/MCM-41 catalyst. Because the kinetic parameter of both oxidation products, H_2DPQ and DPQ, is around 11 Å, it is difficult for both H_2DPQ and DPQ to be formed in the micropores of both zeolites by BOH oxidation. Diffusion of the starting material, BOH, into the micropores of the (K–Cu)/NaZSM-5 and (K–Cu)/NaY catalysts may also be considered to be restricted, in contrast to diffusion into the (K–Cu)/MCM-41 catalyst with mesopores.

TABLE 2

Effect of Supports with Mesopores and Micropores on BOH Oxidation[a]

Catalyst	Pore size of support (Å)	BET surface area of support (m^2/g)	BOH conversion (%)	H_2DPQ yield (%)	DPQ yield (%)
(K–Cu)/MCM-41	35	1020	17.8	11.0	6.8
(K–Cu)/NaZSM-5	5.5	360	0.4	0.4	0.0
(K–Cu)/NaY	7.4	750	0.2	0.2	0.0

[a] Catalyst, 0.2 g (Cu, 3.12×10^{-2} mmol); K/Cu atomic ratio, 1; reaction time, 24 h; reaction temperature, 313 K; solvent, 12 cm^3 of chloroform.

TABLE 3

Liquid-Phase Adsorption of BOH in the Supports with Mesopores and Micropores[a]

Support	Si/Al atomic ratio	Amount of adsorption (mmol/g support)
MCM-41	—[b]	0.93
NaZSM-5	53	0.88
NaY	2.8	0.36

[a] BOH, 1 mmol; support, 0.2 g; solvent, 20 cm^3 of chloroform; adsorption temperature, 313 K; adsorption time, 24 h.

[b] Al is not present.

Liquid-Phase Adsorption of 2,6-Di-tert-butylphenol (BOH)

To investigate the capacity of the support to accommodate the BOH molecule, the liquid-phase adsorptions of BOH on MCM-41, NaZSM-5, and NaY were measured at 313 K (Table 3). The amount of BOH adsorption on the MCM-41 support was found to be larger than those on the NaZSM-5 and NaY supports, but the difference in adsorption amounts of BOH was not so high. Thus the BOH molecules may be able to penetrate considerably into the micropores of the NaZSM-5 and NaY zeolites and to be accommodated in the micropores. The percentage of external surface area occupied in the total surface area of a support with high BET surface area is thought to be low. So the contributions of the external surface to liquid-phase adsorption using the three supports (MCM-41, NaY, and NaZSM-5) will be rather low and of similar extents, even if they could not be ignored. It is of interest to note that the amount of BOH adsorption on NaZSM-5 was higher than that on NaY, despite the smaller pore size of the former zeolite. This seems to be due in part to the higher hydrophobicity of the micropores in the NaZSM-5 zeolite because of its higher Si/Al atomic ratios than NaY.

Effect of the Added Alkali Metals on BOH Oxidation

The effect of the method of adding CH_3COOK on oxidation activity is shown in Table 4. At first, it must be noted that Cu/MCM-41 without added K was found to have catalytic activity for BOH oxidation though the oxidation activity was considerably low. K/MCM-41 in which only alkali metal, K, was impregnated had no catalytic activity for BOH oxidation. (K–Cu)/MCM-41 had higher oxidation activity than did Cu/MCM-41 without the added K. The catalytic system of Cu/MCM-41 + CH_3COOK, in which CH_3COOK is dissolved in the reaction solution rather than being impregnated into MCM-41, had higher oxidation activity than (K–Cu)/MCM-41. The higher concentration of

TABLE 4

Effect of the Addition Method of CH_3COOK on the Catalytic Activity of BOH Oxidation[a]

Run	Catalyst	K/Cu atomic ratio	BOH conversion (%)	H_2DPQ yield (%)	DPQ yield (%)
1	Cu/MCM-41	—	5.7	5.1	0.6
2	(K–Cu)/MCM-41	1	18.0	11.2	6.8
3	Cu/MCM-41 + CH_3COOK[b]	1	34.0	15.0	19.0
4	Cu/MCM-41 + CH_3COOK[b]	3	50.0	11.0	39.0
5	(K–Cu)/MCM-41 + CH_3COOK[b]	3	45.0	13.0	32.0
6	Cu/MCM-41 + BO^-K^+[c]	—	21.0	0.4	20.6

[a] Catalyst, 0.2 g (Cu, 3.12×10^{-2} mmol); reaction time, 24 h; reaction temperature, 313 K; solvent, chloroform 12 cm^3.

[b] Solvent, chloroform 10 cm^3 + methanol 2 cm^3.

[c] Isolated potassium di-*tert*-butylphenolate.

TABLE 5

Effect of KOH Added in the Reaction Solution on the Catalytic Activity of BOH Oxidation[a]

Run	Catalyst	K/Cu atomic ratio	BOH conversion (%)	H_2DPQ yield (%)	DPQ yield (%)
1	Cu/MCM-41	—	5.7	5.1	0.6
2	Cu/MCM-41 + KOH[b]	1	11.0	8.9	2.1
3	Cu/MCM-41 + KOH[b]	16	0.7	0.6	0.1
4	$CuCl_2$	—	4.8	0.2	4.6
5	$CuCl_2$ + KOH	1	13.0	1.0	12.0
6	$CuCl_2$ + KOH	16	10.0	1.5	8.5

[a] Cu, 3.12×10^{-2} mmol; reaction time, 24 h; reaction temperature, 313 K; solvent, chloroform 12 cm^3.

[b] Solvent, chloroform 10 cm^3 + methanol 2 cm^3.

CH_3COOK (higher K/Cu atomic ratio) caused higher BOH conversion. Oxidation of the corresponding isolated potassium phenolate of BOH was carried out using Cu/MCM-41 catalyst without added K (Table 4, run 6). Potassium phenolate was found to be oxidized almost selectively to DPQ with the Cu/MCM-41 catalyst without added K. One of the main roles played by the added alkali metal is to directly cause BOH to form the corresponding phenolate anion, which will be more easily oxidized than the neutral BOH molecule (16), in addition to the interaction of the added alkali metal with the Cu species supported on MCM-41, the interaction of which is considered to make oxidative dehydrogenation activity high (20–25). The DPQ selectivity (98%) of the Cu/MCM-41 + BO^-K^+ system (run 6) was considerably higher than that (38%) of the (K–Cu)/MCM-41 + BOH system (run 2), despite the similar conversions (18 and 21%, respectively) of both catalytic systems.

The effect of adding KOH to the reaction solution on BOH conversion and oxidation products is shown in Table 5, together with the data for unsupported $CuCl_2$ catalytic systems. Although the addition of KOH to the reaction solution caused an increase in BOH conversion (Table 5, run 2), the degree of the increase in BOH conversion was not as high as that with CH_3COOK addition (Table 4, run 2). Furthermore, too much KOH inversely caused a significant decrease in the conversion (Table 5, run 3). The XRD pattern of the used Cu/MCM-41 catalyst (Table 5, run 3) showed that the intensities of the diffraction peaks based on a hexagonal prism abruptly decreased. (Fig. 3b). Thus, the destruction of the mesopore structure caused by strong alkali in the reaction solution is considered to cause the disappearance of the catalytic activity for BOH oxidation. The Cu/MCM-41 catalyst without an added alkali and the unsupported $CuCl_2$ catalyst in the absence of an added alkali showed high selectivities for H_2DPQ and DPQ, respectively. H_2DPQ was thus found to be almost selectively synthesized, though the yield was not high, by supporting Cu on MCM-41 in the absence of alkalis, rather than using unsupported Cu ions. Figure 4 illustrates the influence of the K/Cu atomic ratio of the (K–Cu)/MCM-41 catalyst on the yields of both H_2DPQ and DPQ. Both yields had maximum values at a K/Cu ratio of around 1. Further addition of K caused decreases in both DPQ and H_2DPQ yields. The color of the (K–Cu)/MCM-41 catalyst was visually observed to vary from blue to off-white with an increase in K/Cu atomic ratio. High K/Cu ratios are thus considered to cause coverage of Cu species with the alkali and/or reduction of Cu(II) to Cu(I) through electron transfer from the alkali to Cu(II), variations of which in the

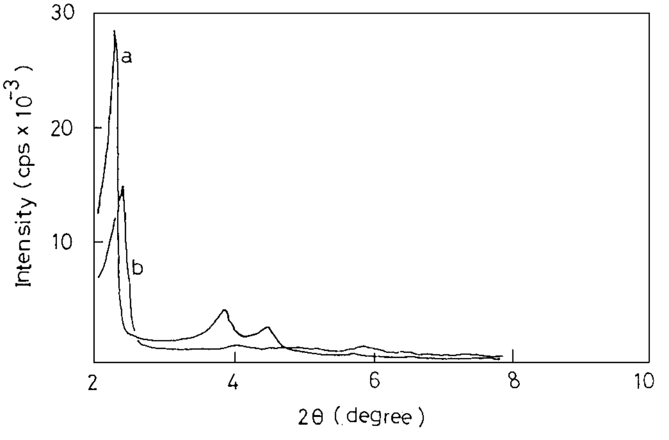


FIG. 3. XRD patterns of (a) Fresh Cu/MCM-41 catalyst (Cu: 3.12×10^{-2} mmol) and (b) Cu/MCM-41 catalyst (Cu, 3.12×10^{-2} mmol) used in BOH oxidation in the presence of methanolic KOH solution (KOH/Cu = 16) followed by calcination at 773 K for 5 h.

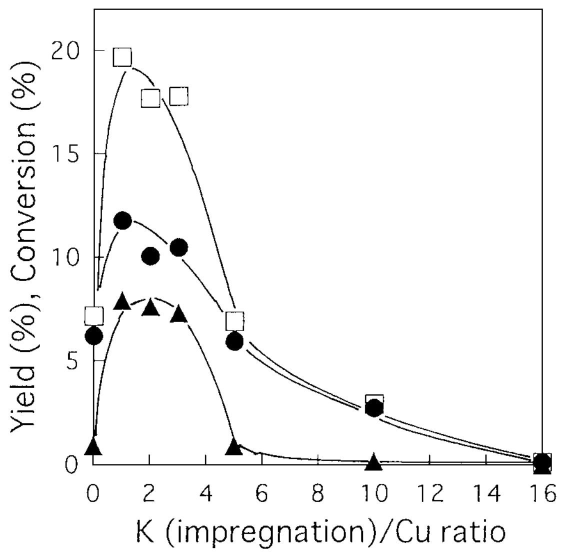


FIG. 4. Influence of K/Cu mole ratio on yield and conversion using (K–Cu)/MCM-41 catalyst. BOH, 5 mmol; catalyst, (K–Cu)/MCM-41, 0.2 g (Cu: 3.12×10^{-2} mmol); K/Cu mole ratio, 1; reaction temperature, 313 K; solvent, 12 ml of chloroform. □, Conversion; ●, H_2DOQ yield; ▲, DPQ yield.

catalyst will cause the catalytic activity for BOH oxidation to decrease.

The influence of K (as CH_3COOK) in the reaction solution to the Cu ratio on both H_2DPQ and DPQ yields using the Cu/MCM-41 catalyst is illustrated in Fig. 5. The yield of DPQ passed through a maximum value at a K/Cu atomic ratio of around 3, though the H_2DPQ yield was almost constant with the increase in K/Cu atomic ratio.

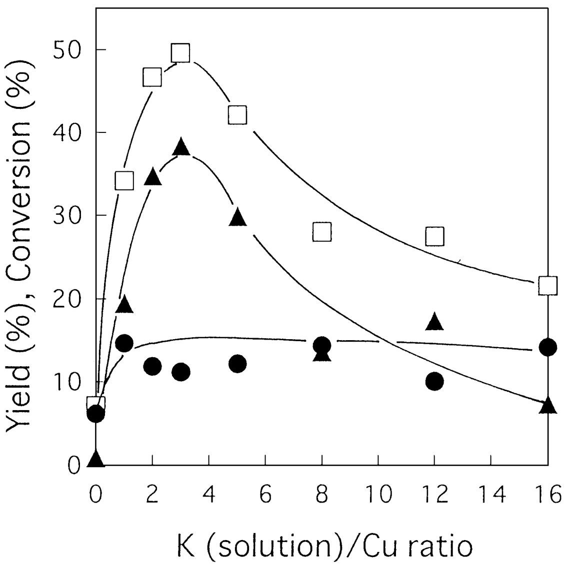


FIG. 5. Influence of K/Cu mole ratio on yield and conversion using unsupported $CuCl_2$ catalyst with methanolic CH_3COOK. BOH, 5 mmol; catalyst, Cu/MCM-41 (Cu: 3.12×10^{-2} mmol), 0.2 g; reaction temperature, 313 K; reaction time, 24 h; solvent, 10 ml of chloroform + 2 ml of methanol. □, Conversion; ●, H_2DOQ yield; ▲, DPQ yield.

We are now attempting the liquid-phase oxidation of BOH using Cu ion-exchanged Na · MCM-41 with added K (K/Cu–Na · MCM-41) as catalyst, in place of the Cu-impregnated MCM-41 with added K ((K–Cu)/MCM-41) counterparts studied here; the results will be reported elsewhere in the near future.

BOH Oxidation Catalyzed by Used (K–Cu)/MCM-41

BOH oxidation was attempted using used (K–Cu)/MCM-41 catalyst, in place of the fresh one, to investigate the durability of the catalyst under the present reaction conditions. Two used (K–Cu)/MCM-41 catalysts were utilized for the second BOH oxidation run (all the reaction conditions are same as those of the first run, except the catalyst). The first used catalyst [used (K–Cu)/MCM-41 (A)] was washed only with $CHCl_3$ after the filtration, and the second one [used (K–Cu)/MCM-41 (B)] was further calcined at 773 K for 5 h in air flow after washing with $CHCl_3$. Conversion of BOH using both the used catalysts were considerably lower than that using the fresh catalyst (Table 6). In particular, the decrease in the yield of DPQ was conspicuous in both used catalysts. There were hardly any differences in oxidation activity and selectivity between the used catalyst treated by only $CHCl_3$ washing and that treated with $CHCl_3$ washing followed by calcination, as evidenced in Table 6. To investigate the cause of the decrease in catalytic activity for BOH oxidation, the amounts of both Cu and K on used (K–Cu)/MCM-41 (A) and (B) were compared with those on the fresh catalyst. No change in the amounts of Cu supported on both the fresh and the used catalysts was detected as described previously, but the amounts of K on the used (K–Cu)/MCM-41 (A) and (B) catalysts were found to decrease to about 45% that on the fresh (K–Cu)/MCM-41 catalyst. The decrease in oxidation activity is thought to be brought about by leaching of the K during the first BOH oxidation run. It is of interest to note that the catalytic activity and the product selectivity of the used catalysts with lower-impregnated K (Table 6, runs 2 and 3) were almost comparable to those of the Cu/MCM-41 catalyst without added K (Table 5, run 1). The deactivating

TABLE 6

BOH Oxidation Catalyzed by Used (K–Cu)/MCM-41[a]

Run	Catalyst	BOH conversion (%)	H_2DPQ yield (%)	DPQ yield (%)
1	Fresh (K–Cu)/MCM-41	18.3	11.4	6.9
2	Used (K–Cu)/MCM-41 (A)[b]	3.7	3.5	0.2
3	Used (K–Cu)/MCM-41 (B)[c]	4.1	3.8	0.3

[a] Cu, 3.12×10^{-2} mmol; reaction time, 24 h; reaction temperature, 313 K; solvent, chloroform 12 cm^3.

[b] Washed with $CHCl_3$ before use as a used catalyst.

[c] Washed with $CHCl_3$ and calcined at 773 K for 5 h in air flow.

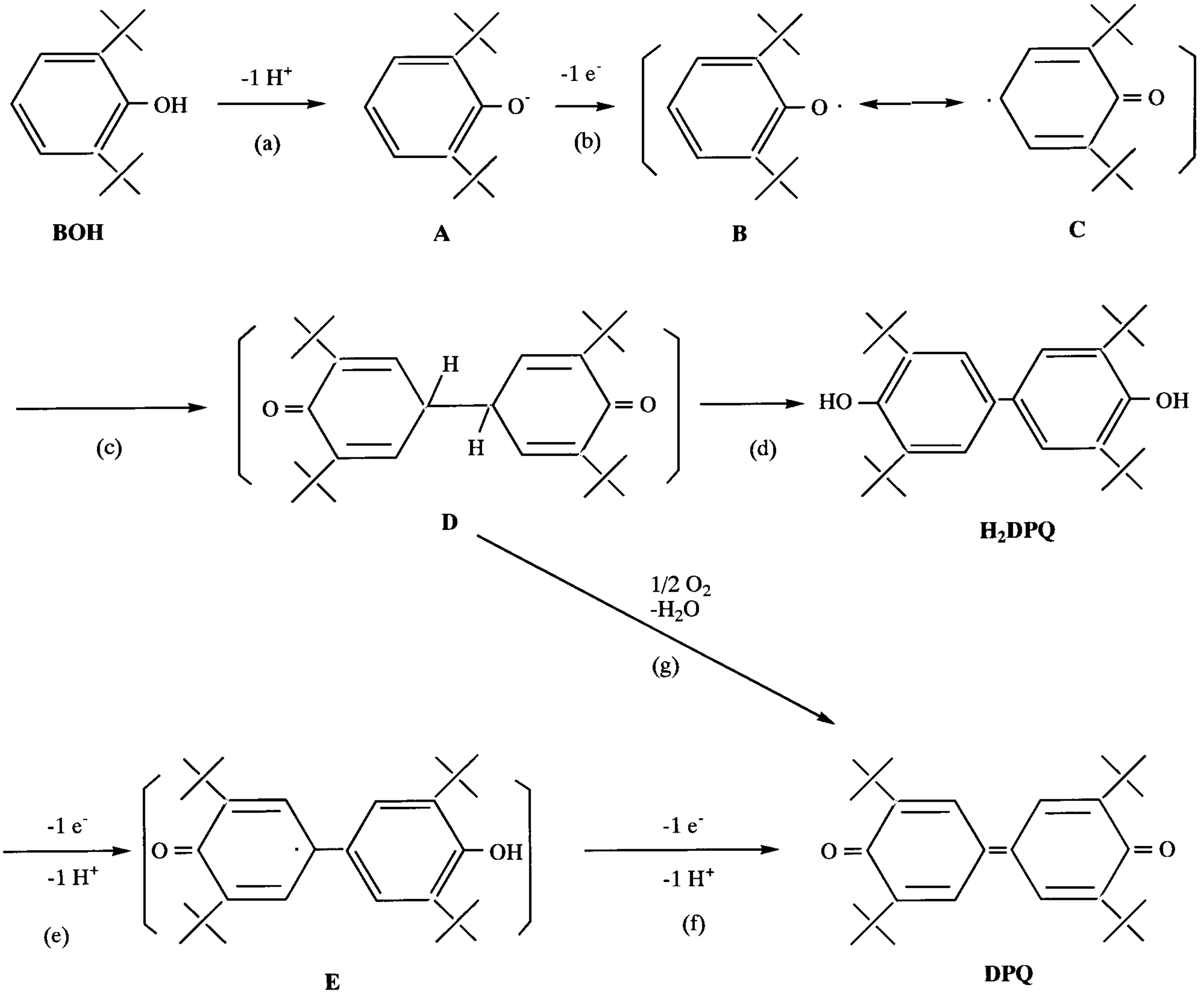
behavior of (K–Cu)/MCM-41 catalyst observed in the conversion-versus-reaction time curve after a reaction time of about 5 h (Fig. 1) is in part explained by the K leaching during the oxidation.

DISCUSSION

The oxidation of BOH using CuCl catalyst in acetonitrile in the presence of oxygen has been reported (26) to produce the corresponding *p*-benzoquinone at high catalyst to BOH ratios. However, the Cu/MCM-41, Cu/NaZSM-5, and K-added counterparts used in this study gave only dimeric oxidation products, H_2DPQ and DPQ, and not a corresponding monomeric benzoquinone. The selectivities for both benzoquinone and DPQ derivatives of BOH oxidation catalyzed by Co(salen) derivatives have been reported (27) to depend on the nature of axially coordinated ligand as well as on the solvent used. In particular, Mn(salen) in DMF solvent has been reported (27) to give DPQ almost selectively (more than 99%) in the BOH oxidation.

The scheme of formation of the dimeric oxidation products, H_2DPQ and DPQ, by the oxidative coupling reaction of 2,6-disubstituted phenol has been known (28) to be a consequent one in which DPQ is formed via H_2DPQ. Also, DPQ formation via the oxidative dehydrogenation of an intermediate obtained from the C–C coupling reaction of the corresponding phenoxy radicals has been reported (27, 29) in the oxidation of 2,6-disubstituted phenol catalyzed by Co(salen). Based on actual knowledge of the oxidation of phenol derivatives obtained so far, a plausible reaction path from BOH to both H_2DPQ and DPQ products is depicted in Scheme 1.

In a basic medium or the presence of alkali metal, BOH is easily deprotonated, giving the corresponding phenolate anion (A). The corresponding phenoxy radical (B, C) is formed via a one-electron transfer from the



SCHEME 1

phenolate anion (A) to Cu(II) ion. (The following oxidation of BOH is also possible: via at first a one-electron loss to form the corresponding cation radical followed by deprotonation to form the phenoxy radical.) This oxidation process proceeds more easily by dissolving an alkali such as CH_3COOK in the reaction medium, instead of being supported onto the MCM-41, which explains the higher activity of the Cu/MCM-41 + CH_3COOK system than the (K–Cu)/MCM-41 catalyst (Table 4, runs 2 and 3). The corresponding dimer (D) is formed through C–C coupling of the phenoxy radicals (C). The dimer (D) can easily rearrange to the more stable tautomer, product H_2DPQ. The product DPQ is obtained by two consecutive oxidation steps, each one involving both the withdrawal of an electron and deprotonation, to form species (E) first and then the product DPQ after the second oxidation step. The product DPQ can result through an alternative step (step g) via no H_2DPQ intermediate: the oxidative dehydrogenation of dimer (D) directly gives DPQ without H_2DPQ intermediate (29). The possibility of formation of DPQ by oxidative dehydrogenation of dimer (D) cannot be ignored in the presence of Cu catalysts and alkaline and in an O_2 atmosphere. The appearance of the induction period in the plots between the DPQ yield and reaction time using the (K–Cu)/MCM-41 catalyst (Fig. 1) is explained by considering DPQ to be formed through a consecutive step involving H_2DPQ as an intermediate. On the contrary, the unsupported $CuCl_2$ catalyst in the presence of dissolved KOH brought no induction period for the formation of DPQ as illustrated in Fig. 2, the results of which suggest that the production of DPQ can also occur via step g, in addition to the route passing through the H_2DPQ intermediate (steps d → e → f). Steps e and f are faster in basic medium or in the presence of alkalis. DPQ formation via the oxidative dehydrogenation of (D) (step g) is also enhanced in the presence of alkalis, based on the results (20–25) that the addition of alkali metals to supported Cu catalysts has considerably promoted the oxidative dehydrogenation of alcohols. From the Cu catalysts and the reaction conditions used in this study, it is reasonable to suppose that product DPQ is formed by two consecutive oxidation steps of H_2DPQ derived from (D) (route d → e → f) and also by the oxidative dehydrogenation of (D) (route g), though the contribution of each route for DPQ formation depends on the catalysts and the reaction conditions, and cannot be estimated quantitatively at the present stage.

The selectivity of H_2DPQ catalyzed by the Cu/MCM-41 + KOH system (Table 5, run 2) is considerably higher than that catalyzed by the $CuCl_2$ + KOH system (Table 5, run 5) in the comparison of the two BOH conversions with almost similar values. The results mean that the route e → f and/or route g are retarded using a MCM-41 support. One of the reasons may be that the mesopore field of the MCM-41 with hydrophobicity causes a lower concentration of KOH than in the bulk reaction medium, in which KOH promotes steps e, f, and also g. To see the influence of the mesoporous field itself, it is worthwhile to note that Cu/MCM-41 (Table 5, run 1) and unsupported $CuCl_2$ (Table 5, run 4) catalysts without added alkalis had catalytic activity for BOH oxidation and the selectivities for H_2DPQ and DPQ of both the catalysts were just opposite. Thus Cu/MCM-41 favored H_2DPQ formation; on the other hand, the oxidation product DPQ was preferentially obtained using unsupported $CuCl_2$ catalyst. The results seem to clearly indicate that the mesopores offers a reaction field substantially preferable for H_2DPQ formation in comparison with the bulk solution, though we explain the difference in selectivity. It must be noted from a synthetic chemical point of view that the catalytic Cu species in the mesopores of MCM-41 give higher selectivity for H_2DPQ formation, in contrast to the reaction field in the bulk solution, in which field DPQ was preferentially formed.

The catalytic activity of the (K–Cu)/MCM-41 catalyst in BOH oxidation was found to be considerably higher, compared with (K–Cu)/NaZSM-5 and (K–Cu)/NaY catalysts (Table 2). The difference in the catalytic activity of the BOH oxidation using the catalytic supports with different-sized pores indicates that the reaction field of the oxidation of BOH is mainly the interior of the mesopores or micropores, rather than the outer surface. The difference in catalytic activity caused by using Cu catalysts to which K is added supported by both mesopore and micropore supports is considered to be due to a kind of shape selectivity. On the other hand, the liquid-phase adsorption amount of BOH on the MCM-41 support was not very different from those on both the NaZSM-5 and the NaY supports (Tables 3), though the former support had a higher capacity for liquid adsorption of BOH than the latter two zeolite supports. The results of both BOH oxidation (Table 2) and liquid-phase adsorption of BOH (Table 3) suggest that the formation of sterically bulky H_2DPQ and DPQ (a kinetic parameter of 11 Å) and/or their transfers from the micropores to the reaction solution will be strongly restricted in the micropores of both zeolites, rather than the transfer of the reactant, BOH, into the micropores being restricted. Thus the shape selectivity, particularly the product restriction, is considered to be the main cause of the difference in oxidation activity between the MCM-41 and zeolite (NaZSM-5, NaY) supports.

In this study, we have not yet obtained information on the state of Cu impregnated on the MCM-41 support using various spectrometric methods. As an extension of the present study, Cu ion-exchanged MCM-41 (Cu–Na · MCM-41) was prepared using Na · MCM-41 (Si/Al atomic ratio, 59.5) as a support, and K-impregnated Cu–Na · MCM-41 (K/Cu–Na · MCM-41) has been used as a catalyst for the BOH oxidation (Table 7). BOH conversion and yields of both H_2DPQ and DPQ were comparable for the supported Cu catalysts prepared by both impregnation [(K–Cu)/MCM-41] and ion-exchange (K/Cu–Na · MCM-41) methods (K was supported by impregnation for the catalyst).

TABLE 7

BOH Oxidation Using Cu-Supported MCM-41 Catalysts Prepared by Both Impregnation and Ion-Exchange Methods[a]

Run	Catalyst	BOH conversion (%)	H_2DPQ yield (%)	DPQ yield (%)
1	(K–Cu)/MCM-41[b]	18.3	11.4	6.9
2	K/Cu–Na · MCM-41[c]	14.3	9.0	5.3

[a] Cu, 3.12×10^{-2} mmol; reaction time, 24 h; reaction temperature, 313 K; solvent, chloroform 12 cm^3, K/Cu atomic ratio, 1.

[b] Cu was impregnated followed by impregnation of K.

[c] Cu was ion-exchanged followed by impregnation of K.

The results imply that the state of Cu impregnated on the MCM-41 support with relatively low amount of Cu of 1 wt% may be similar to that of ion-exchanged Cu, the Cu ions of which are well dispersed on the mesoporous matrix.

CONCLUSIONS

Cu-impregnated MCM-41 with added alkali metal [(K–Cu)/MCM-41] was found to catalyze the liquid-phase oxidation of 2,6-di-*tert*-butylphenol (BOH) to form 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H_2DPQ) and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ). Both Cu-supported MCM-41 (Cu/MCM-41) and unsupported $CuCl_2$ catalysts without added alkalis were also found to have catalytic activity for BOH oxidation. The former catalyst favored H_2DPQ formation and the latter catalyst gave preferentially the DPQ product. In the presence of alkalis, the selectivities of H_2DPQ and DPQ greatly depended on the presence of the added alkali metal and/or the method of alkali metal addition. A scheme for BOH oxidation was proposed. At first the corresponding phenoxy radical was generated. H_2DPQ was thought to be formed due to a tautomeric rearrangement of a unstable dimer produced by the C–C coupling of the phenoxy radical generated. DPQ was proposed to be formed via the consecutive oxidation steps of H_2DPQ and/or via the oxidative dehydrogenation of the unstable dimer without passing through the H_2DPQ intermediate. Cu-impregnated NaZSM-5 with added alkali metal [(K–Cu)/NaZSM-5] and NaY [(K–Cu)/NaY] zeolites, which differed from the (K–Cu)/MCM-41 catalyst, were found to have hardly any catalytic activity for liquid-phase oxidation of BOH. The amounts of liquid-phase adsorption of BOH on NaZSM-5 and NaY supports, both of which have micropores, were found to be comparable to that on the MCM-41 support which has mesopores. These results indicate that the difference in BOH oxidation activities between Cu-supported catalysts with mesopores and those with micropores is governed by the shape selectivity in product restriction.

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