

Catalytic activity of Cu ion-exchanged Na · MCM-41 in the liquid-phase oxidation of 2,6-di-*tert*-butylphenol

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Abstract

The liquid-phase catalytic oxidation of 2,6-di-*tert*-butylphenol (BOH) was performed under mild reaction conditions using a Cu ion-exchanged Na · MCM-41 (Cu-Na · MCM-41) catalyst. 4,4'-Dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (H₂DPQ) and 3,3',5,5'-tetra-*tert*-butyl-4, 4'-diphenoquinone (DPQ) were obtained as the oxidation products. The addition of an inorganic base such as KOH onto the Cu-Na · MCM-41 catalyst or to the reaction solution was found to cause the increase in the oxidation activity. The oxidation activity of BOH in the presence of KOH in the reaction solution was greater than when using the K added Cu-Na · MCM-41 catalyst. The reaction scheme for the BOH oxidation was proposed, in which scheme the DPQ formation involves both a consecutive pathway via H₂DPQ intermediate and an oxidative dehydrogenation of a dimer formed by the C–C coupling of the corresponding phenoxy radicals, without H₂DPQ intermediate. To study the influence of the mesopore of the Na · MCM-41 on the oxidation of BOH, a comparably bulky molecule, Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) zeolite, whose pores are micro range in size, was attempted as a catalyst for the bulky phenol oxidation. The oxidation activity of the Cu-NaZSM-5 zeolite was found to be considerably lower than that of the Cu-Na · MCM-41 catalyst. The preference of the mesopore environment for the 2, 6-di-*tert*-butylphenol oxidation against the micropore counterpart was thus confirmed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cu ion-exchanged Na · MCM-41; Cu ion-exchanged NaZSM-5; Oxidation, 2,6-Di-*tert*-butylphenol; Dihydroxybiphenyl; Diphenoquinone; Pore-size selectivity

1. Introduction

Crystalline inorganic materials with a micropore structure, such as zeolites and pillared clay, have been utilized as adsorbents, molecular sieves, and catalysts. The application of the crystalline microporous materials to a catalyst

or its support has been limited to the catalytic reaction in which relatively small molecules participated because of a diffusion limitation and/or an inhibition from entering the molecules because the micropores are usually less than 10 Å [1,2]. More recently, mesoporous materials with uniform pores of more than 20 Å, high surface area, and heat resistances have been developed by separate groups [3–6]. Since then, many studies have been reported on the

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syntheses, the characterization, and the application to catalysts of these mesoporous materials such as MCM-41 [7–15]. The inorganic oxide with the uniform mesopores will be expected to offer a catalytic active field being applicable to sterically larger molecules. We have studied [16–19] the catalytic activity of Cu ion immobilized catalysts including Cu ion impregnated MCM-41 (Cu/MCM-41) in the liquid-phase oxidation of phenol and catechol derivatives in the presence of an inorganic base such as KOH. The catalytic behavior of the Cu/MCM-41 catalyst with that of Cu ion impregnated NaZSM-5 (Cu/NaZSM-5) was compared focusing on the difference in the pore size of both the oxide supports. Also, we have already reported [15] the synthesis of Cu ion-exchanged Na·MCM-41 (Cu-Na·MCM-41, Si/Al atomic ratio = 55) and attempted to utilize the Cu-Na·MCM-41 as a catalyst for liquid-phase oxidation of benzene to phenol.

In this paper, we report the catalytic activity of Cu ion-exchanged Na·MCM-41 (Cu-Na·MCM-41) in the liquid-phase oxidation of 2,6-di-*tert*-butylphenol and compare the catalytic activity with that of Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) catalyst. Also the oxidation activity of the Cu-Na·MCM-41 catalyst was compared with that of the Cu ion impregnated Na·MCM-41 (Cu/Na·MCM-41) counterpart. A plausible scheme for the BOH oxidation using the Cu-Na·MCM-41 catalysis is proposed.

2. Experimental

2.1. Catalysts

Na·MCM-41 was synthesized using $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ and $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N} \cdot \text{Br}$ as a source of Al atom and an organic template, respectively, by the hydrothermal method described elsewhere [19]. The resulting product was treated with 1 N NaNO_3 aqueous solution at 353 K for 2 h. After washing with de-ionized water and filtering off, and drying at ca. 393 K

overnight, the product was calcined at 773 K for 2 h in air flow. The XRD pattern obtained for the Na·MCM-41 showed four peaks at the region of the 2θ less than 10° , which peaks correspond to the hexagonal pore structure [4,5]. The Si/Al atomic ratio of the obtained Na·MCM-41 was 59.5. The BET surface area of the obtained Na·MCM-41 was $1030 \text{ m}^2/\text{g}$. Cu ion-exchanged Na·MCM-41 (Cu-Na·MCM-41) was prepared by the usual ion-exchange method at 353 K for 2 h using prescribed concentration of aqueous $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (Nacalai Tesque, guaranteed reagent) solution. The obtained Cu-Na·MCM-41 was filtered, washed with de-ionized water, dried at 393 K overnight, and calcined at 773 K for 5 h in air flow. K added Cu-Na·MCM-41 (K/Cu-Na·MCM-41) was prepared by an impregnation method using the prescribed concentration of ethanolic CH_3COOK (Nacalai Tesque, guaranteed reagent) solution. The K/Cu-Na·MCM-41 was dried at 393 K overnight and calcined at 773 K for 5 h in air flow. A Cu impregnated Na·MCM-41 (Cu/Na·MCM-41) was prepared by impregnating $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (Nacalai Tesque, guaranteed reagent) in ethanol, drying at 393 K overnight, and calcining at 773 K for 5 h in air flow. K and Cu co-impregnated Na·MCM-41 ((K-Cu)/Na·MCM-41) was prepared by simultaneously impregnating $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and CH_3COOK in ethanol, drying at 393 K overnight, and calcining at 773 K for 5 h in air flow. NaZSM-5 (Si/Al atomic ratio = 45) zeolite was synthesized according to a patent [20]. To prepare 100% Na ion-exchanged ZSM-5, the obtained NaZSM-5 zeolite was treated two times at 342–358 K for 1 h with an aqueous solution of 1 mol/l NaNO_3 . Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) zeolite was prepared by ion-exchanging with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in water at 353 K for 2 h, filtering off, drying at 393 K overnight, and calcining at 773 K for 5 h in air flow. K added Cu-NaZSM-5 (K/Cu-NaZSM-5) zeolite was prepared by impregnating CH_3COOK in ethanol and calcining at 773 K

for 5 h in air flow. The Si/Al ratios of Na · MCM-41 and NaZSM-5, and the Cu amounts supported on the Na · MCM-41 and the NaZSM-5 were measured using an atomic absorption spectrometer (Shimadzu type AA-630-01).

2.2. Liquid-phase oxidation of 2,6-di-*tert*-butylphenol

2,6-Di-*tert*-butylphenol (Nacalai Tesque, guaranteed reagent) was used without further purification. The reaction mixture of 0.5 mmol of 2,6-di-*tert*-butylphenol (BOH), 0.2 g of catalyst, and 12 cm³ of chloroform was reacted at 313 K for 24 h in air (1 atm) under magnetic stirring. A mixed solvent of 10 cm³ of chloroform and 2 cm³ of methanol was used when dissolving a K salt in the solvent. The analyses of the oxidation products were conducted using a Hitachi HPLC with an L-6200 intelligent pump and an L-2200 UV–VIS detector (column, GH-C18; moving phase, acetonitrile (Nacalai Tesque, a specified reagent for HPLC)). The amount of leached Cu ion during the oxidation was checked by measuring the Cu amount of the catalyst before and after the oxidation using an atomic absorption spectrometer (Shimadzu type AA-630-01).

3. Results and discussion

The oxidation products obtained in the present study were identified as 4,4'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (H₂DPQ) and 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (DPQ) [19]. No monomeric oxidation product such as benzoquinone derivatives [21] was detected under the present reaction conditions. The leaching of Cu ions from both the Cu supported Na · MCM-41 and the Cu supported NaZSM-5 catalysts was confirmed not to be detected during the liquid-phase oxidation of BOH under the reaction conditions studied here.

The dependence of the yields of the oxidation products on the reaction time (until 62 h) using K(1)/Cu(0.65)-NaMCM-41 (Cu content, 0.65 wt.%; K/Cu atomic ratio = 1) catalyst is illustrated in Fig. 1a. Further to see the detail in the initial stage of the oxidation, the time dependence of both product yields is illustrated enlarging the oxidation behavior until the reaction time of 8 h (Fig. 1b). The formation of each product had an induction period though the production of H₂DPQ had a shorter induction period than the counterpart of the DPQ forma-

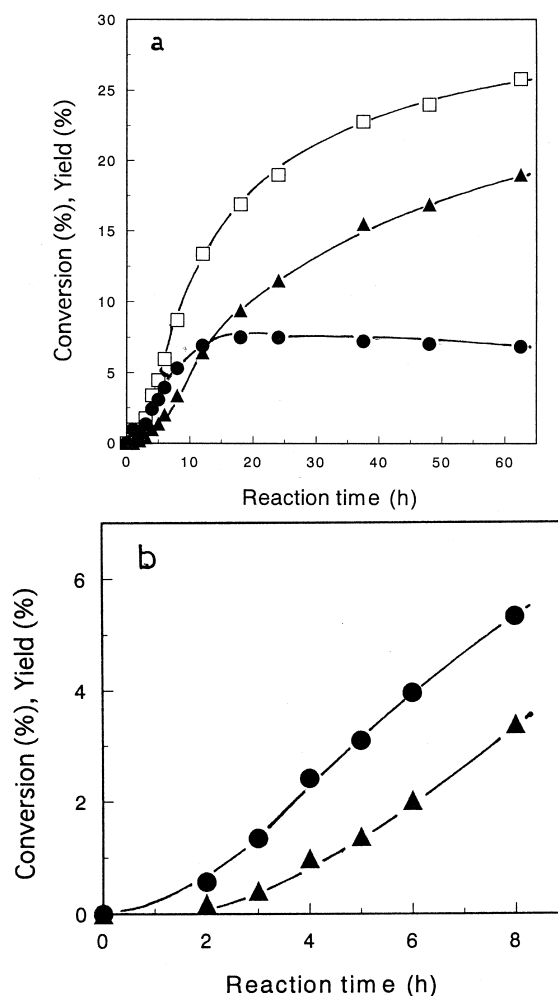


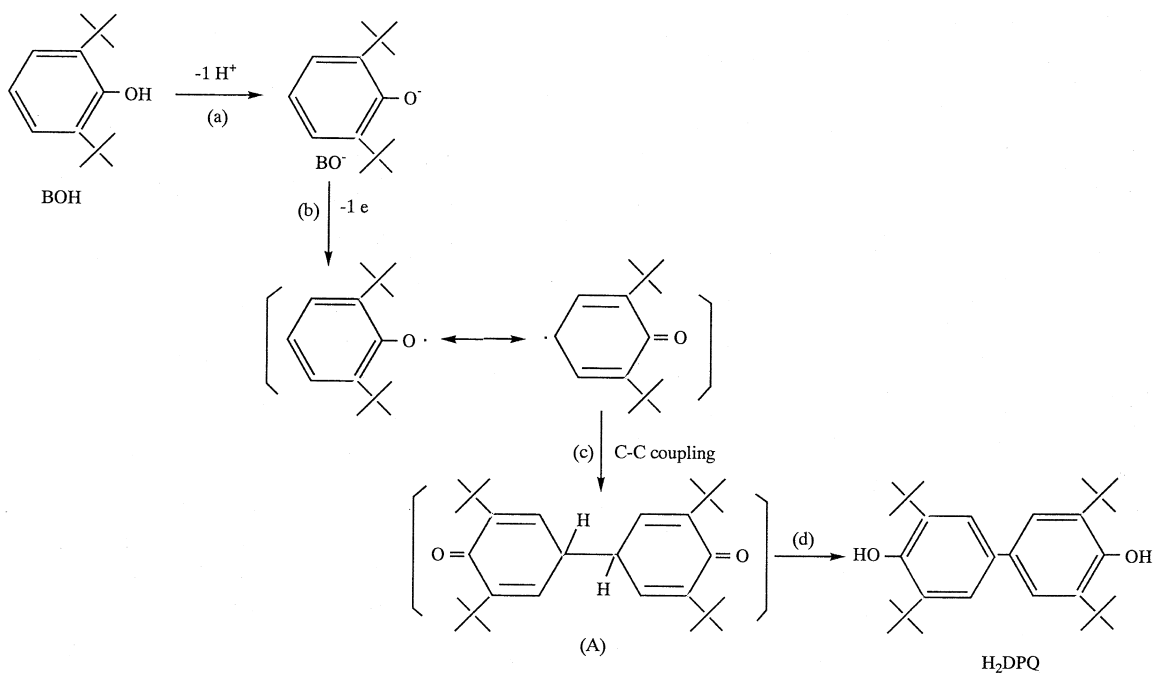
Fig. 1. Conversion and yields vs. reaction time in BOH oxidation catalyzed by K/Cu-Na·MCM-41. Catalyst, 0.2 g; BOH, 0.5 mmol; solvent, 5 cm³ CHCl₃; reaction temperature, 313 K; ●, yield of H₂DPQ; ▲, yield of DPQ; □, conversion.

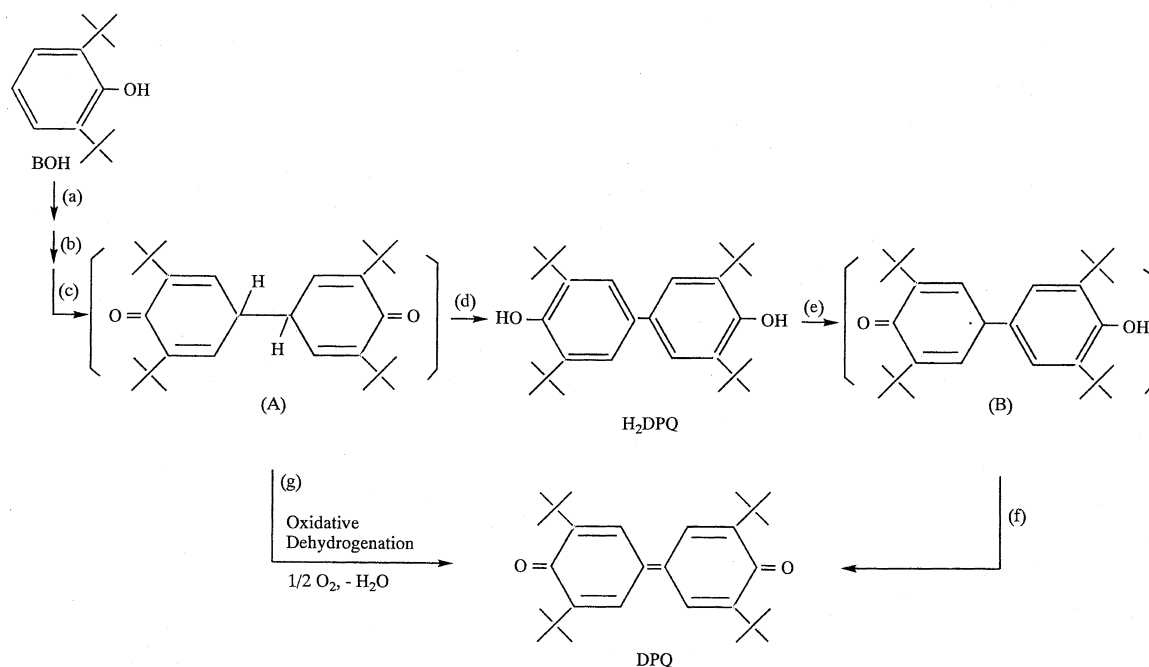
tion. The yield of H₂DPQ increased with the increase in the reaction time after the shorter induction period but tended to level off after a reaction time of ca. 10 h. The production of DPQ showed a prolonged induction period at the initial stage. After that, the yield of DPQ increased with increasing reaction time. The yield of DPQ tended to increase even at a reaction time of more than 60 h, differing from the behavior of the H₂DPQ yield, though the degree of the increase in the DPQ yield had a tendency to decrease.

According to the knowledge so far accumulated on the oxidation of phenol derivatives [22], the initial steps, through which steps a product H₂DPQ is yielded, of the oxidation of BOH will be depicted in Scheme 1: the corresponding phenoxy radical is generated through a one-electron transfer from the phenolate anion (BO⁻), which is formed by the dissociation of BOH, to Cu²⁺ ions on the catalyst. Alkalis being present in the catalytic system will cer-

tainly promote the formation of the phenolate anion. KOH dissolving in the bulk solution will be more effective for the dissociation of BOH to BO⁻ than the alkalis supported on the Cu-Na · MCM-41 catalyst. The C-C coupling of a resonance form with a high density of unpaired electron at *para*-position of the phenoxy radical will form a unstable dimer (A). The tautomeric rearrangement of the dimer will convert the dimer (A) to H₂DPQ.

The two plausible routes will be considered for the production of DPQ by the BOH oxidation (Scheme 2). First route (step (e) → (f)) is the one via H₂DPQ as an intermediate. Thus, DPQ will be formed through the sequential oxidation steps of the H₂DPQ yielded as illustrated in Scheme 1. The second route (step (g)) for DPQ production proceeds through the direct oxidative dehydrogenation of the dimer (A) produced by the C-C coupling reaction of the phenoxy radical. The second route must be noted not to include H₂DPQ intermediate in the way





Scheme 2.

of the DPQ production. The alkalis in the catalytic system will be able to promote both the routes (step (e) → (f), step (g)) for the production of DPQ. Thus, H₂DPQ will more easily receive a deprotonation and a one-electron transfer to form intermediate (B) in the presence of alkali and Cu²⁺ species, just as for the BOH oxidation (step (a) → (b)). Recently, the oxidative dehydrogenation of alcohols over the supported Cu catalysts has been reported [23–28] to be highly promoted by adding alkalis to the supported Cu catalysts. So that it is reasonable to think that the DPQ formation by the oxidative dehydrogenation of the dimer (A) (step (g)) can also be promoted by the presence of alkalis in the catalytic systems. Taking account for the longer induction period observed in the DPQ yield vs. reaction time curve (Fig. 1), the consecutive process having H₂DPQ as an intermediate (step (e) → (f)) is thought to be certainly a plausible route for the DPQ production. In this case, the curve profiles of the yields of both H₂DPQ and DPQ will be governed by the

relative ratio of the rate of H₂DPQ formation and the rate of step (e) → (f). The step (g), in which step DPQ is formed via the oxidative dehydrogenation of the dimer (A) and via no H₂DPQ intermediate, will be also possible in the present reaction system including Cu²⁺ and alkalis, as described previously. We propose the two routes (route (e) → (f) and route (g)) for DPQ production by the BOH oxidation using the Cu-Na · MCM-41 catalysts with and without alkalis, though the contribution of each route to the yield of DPQ cannot be quantitatively estimated.

The influence of the amount of Cu ion-exchanged on the Na · MCM-41 on the yields of the oxidation products was investigated under the condition of the added K/Cu ratio of 1 (Fig. 2). The yield of H₂DPQ increased with the increase in the supported Cu amount until ca. 2 wt.% and leveled off with a further increase in the Cu content. The yield of DPQ increased with increasing the Cu amount and passed through a maximum value as shown in Fig. 2.

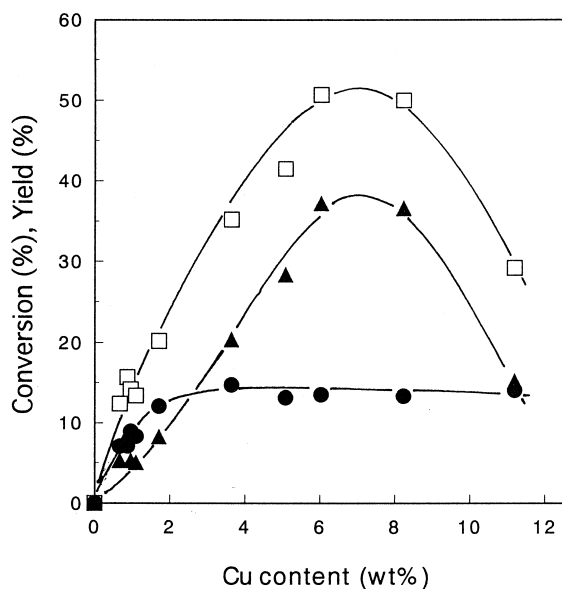


Fig. 2. Dependence of Cu content on conversion and yields in BOH oxidation catalyzed by K/Cu-Na·MCM-41. Catalyst, 0.2 g; BOH, 0.5 mmol; solvent, 5 cm³ CHCl₃; reaction temperature, 313 K; reaction time, 24 h; ●, yield of H₂DPQ; ▲, yield of DPQ; □, conversion.

The XRD pattern of 2θ of 2–6° of the K(1)/Cu(11)-Na·MCM-41 (Cu amount, 11 wt.%) was found to be considerably deteriorated. The decrease in the DPQ yield in the region of the higher Cu contents will be caused by the partial destruction of the regular hexagonal mesopores. The difference in the dependence of the yields of both H₂DPQ and DPQ on the Cu content will support the route (g) without H₂DPQ intermediate for the formation of DPQ as illustrated in Scheme 2.

The influences of the support method of Cu ions and the added K on the oxidation activity were investigated using Na·MCM-41 as a catalyst support (Table 1). The Cu ion-exchanged and the Cu impregnated Na·MCM-41 catalysts (Cu-Na·MCM-41 and Cu/Na·MCM-41) were found to give considerable conversions of BOH, even in the absence of the added alkali metal. The K added to Cu-Na·MCM-41 catalyst was found to promote the BOH oxidation though the effect was not so high under the present reaction conditions. The K and Cu co-impregnated Na·

MCM-41 ((K-Cu)/Na·MCM-41) catalyst had a lower oxidation activity for BOH than the Cu impregnated Na·MCM-41 (Cu/Na·MCM-41) without the added K catalyst, but we have no idea why the impregnated K inhibits the oxidation activity. As an added alkali species, CH₃COOK added to the reaction solution significantly promoted the BOH oxidation catalyzed by Cu-Na·MCM-41. This is due to the formation of the corresponding phenolate anion (Scheme 1, route (a)), which is more easily oxidized than the neutral BOH molecule [29].

The influence of the added K/Cu atomic ratio in the K/Cu(1)-Na·MCM-41 catalyst on the BOH oxidation was investigated at the reaction temperature of 313 K (Fig. 3). The yield of H₂DPQ increased with an increase in the added K/Cu atomic ratio, passed through a maximum at a ratio of around 2, and inversely decreased with the further increase in the ratio. The yield of DPQ exhibited similar behavior as the yield of H₂DPQ, except the DPQ yield had a maximum value at the K/Cu atomic ratio of ca. 0.2. Too much added K species is thought to cover the active Cu species and inhibit the access of the BOH molecule to the active Cu species. Fig. 4 illustrates the dependence of the added K/Cu atomic ratio on the selectivity of H₂DPQ and DPQ. The increase in the added K/Cu atomic

Table 1
Influence of supported method of Cu ions and added K on the oxidation activity^a

Catalyst	BOH conversion (%)	H ₂ DPQ yield (%)	DPQ yield (%)
Cu-Na·MCM-41	10.1	5.4	4.7
Cu/Na·MCM-41	13.3	7.7	5.6
(K-Cu)/Na·MCM-41	5.9	5.2	0.7
K/Cu-Na·MCM-41	14.3	9.0	5.3
Cu-Na·MCM-41 + CH ₃ COOK ^b	27.5	12.6	14.9

^aBOH, 0.5 mmol; catalyst (Cu, 1.0 wt.%, K/Cu atomic ratio, 1), 0.2 g; solvent, 12 cm³ of chloroform; reaction time, 24 h; reaction temperature, 313 K; reaction atmosphere, 1 atm of air.

^bSolvent, 10 cm³ of chloroform + 2 cm³ of methanol.

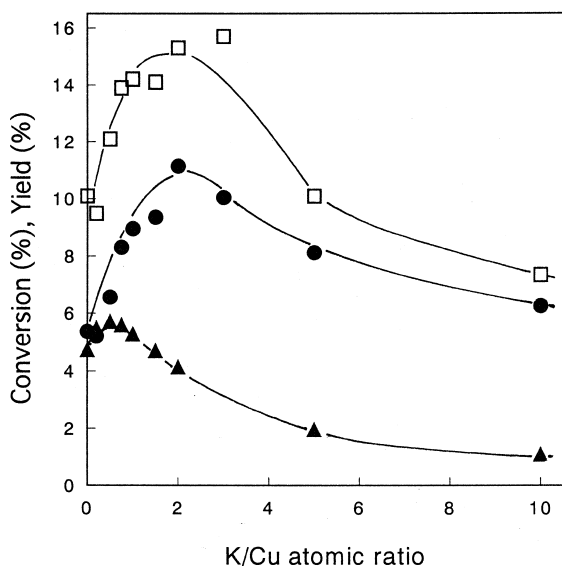


Fig. 3. Dependence of K/Cu atomic ratio on conversion and yields in BOH oxidation catalyzed by K/Cu-Na·MCM-41. Catalyst, 0.2 g; BOH, 0.5 mmol; solvent, 5 cm³ CHCl₃; reaction temperature, 313 K; reaction time, 24 h; ●, yield of H₂DPQ; ▲, yield of DPQ; □, conversion.

ratio caused the higher selectivity of H₂DPQ and lower selectivity of DPQ.

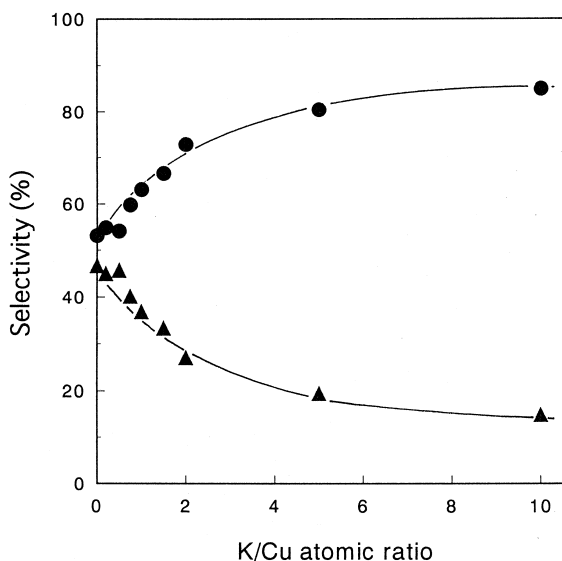


Fig. 4. Dependence of K/Cu atomic ratio on selectivities of H₂DPQ and DPQ in BOH oxidation catalyzed by K/Cu-Na·MCM-41. Catalyst, 0.2 g; BOH, 0.5 mmol; solvent, 5 cm³ CHCl₃; reaction temperature, 313 K; reaction time, 24 h; ●, selectivity of H₂DPQ; ▲, selectivity of DPQ.

The influence of the CH₃COOK added into the reaction solution, in place of impregnating the Cu-Na·MCM-41 catalyst, on BOH oxidation was investigated by the variation of the added K(in solution)/Cu atomic ratios (Fig. 5). At first, the catalytic activity for BOH oxidation of the Cu-Na·MCM-41 + CH₃COOK catalytic system was found to be much higher than that of the K/Cu-Na·MCM-41 catalyst from a comparison of the conversion of Figs. 3 and 5. The second feature of the Cu-Na·MCM-41 + CH₃COOK catalytic system compared with the K/Cu-Na·MCM-41 catalyst is that the yield of DPQ is considerably higher than that of H₂DPQ, particularly at the added K(in solution)/Cu atomic ratios greater than around 4 (high selectivity of DPQ). The yield of H₂DPQ passed through a maximum at the K/Cu ratio of ca. 1.5 and decreased with a further increase in the ratio. The CH₃COOK dissolved in the reaction solvent (10 cm³ CHCl₃ + 2 cm³ methanol) is thought to easily dissociate the BOH molecule to the corresponding phenolate anion (BO⁻) (Scheme 1, route (a)). The resulting BO⁻ will

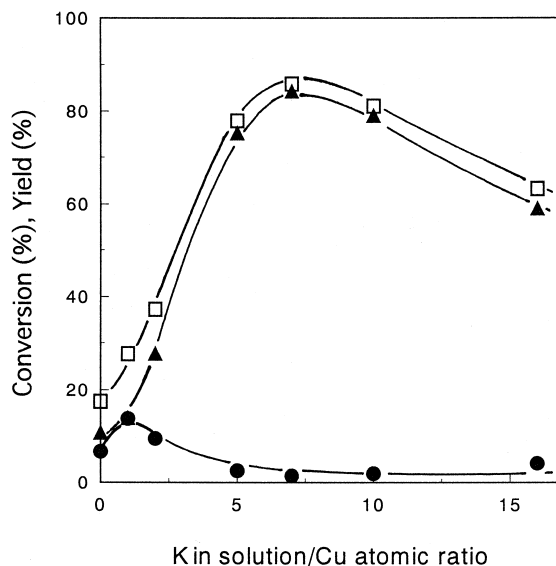


Fig. 5. Dependence of K in solution/Cu atomic ratio on conversion and yields in BOH oxidation catalyzed by Cu-Na·MCM-41. Catalyst, 0.2 g; BOH, 0.5 mmol; solvent, 5 cm³ CHCl₃ + 2 cm³ CH₃OH; reaction temperature, 313 K; reaction time, 24 h; ●, yield of H₂DPQ; ▲, yield of DPQ; □, conversion.

Table 2

Comparison of BOH oxidation catalyzed by K/Cu-Na · MCM-41 and K/Cu-NaZSM-5 catalysts^a

Catalyst	Cu Content (wt.%)	BOH (%) Conversion (%)	H ₂ DPQ yield (%)	DPQ yield (%)
K(1)/Cu-Na · MCM-41	1.0	14.3	9.0	5.3
	5.1	41.6	13.2	28.4
K(1)/Cu-NaZSM-5	1.0	0.5	0.5	0.0
	5.1	2.7	2.6	0.1

^aBOH, 0.5 mmol; catalyst (K/Cu atomic ratio, 1), 0.2 g; solvent, 12 cm³ chloroform; reaction time, 24 h; reaction temperature, 313 K; reaction atmosphere, 1 atm of air.

be oxidized to the corresponding phenoxy radical through a one-electron transfer by Cu²⁺ ions on the catalyst (Scheme 1, route (b)). The oxidative C–C coupling reaction of the resonance form with a high density of unpaired electron at *para*-position of the phenoxy radicals will cause the formation of the dimer (A) as illustrated in Scheme 1, route (c). The DPQ formation via the pathway without H₂DPQ intermediate (Scheme 2, route (g)) may occur using the Cu-Na · MCM-41 + CH₃COOK catalytic system because of the low yields of H₂DPQ.

To study the effect of the pore structure with meso size as a reaction field for comparatively bulky molecules, the liquid-phase oxidation of BOH catalyzed by Cu ion-exchanged Na · MCM-41 was compared using the Cu ion-exchanged NaZSM-5 catalyst, whose zeolite support has been known to possess only micropores. Table 2 shows the comparison of the catalytic activities between the K(1)/Cu-Na · MCM-41 and the K(1)/Cu-NaZSM-5 catalysts in the BOH oxidation. The BOH conversion catalyzed by K(1)/Cu-NaZSM-5 was found to be appreciably lower than that by the K(1)/Cu-Na · MCM-41 catalyst. The difference in the oxidation activity is thought to reflect the difference in the reaction field of NaZSM-5 and MCM-41 supports, thus the micro- and mesopores, because the other reaction conditions are kept substantially similar to each other. It is reasonable that the formation of sterically bulky molecules such as H₂DPQ and DPQ (both the minimum diameters, ca. 11 Å) from BOH (the minimum diameter, ca. 7 Å) is more easily carried out in the mesopore field (32 Å) of the

K(1)/CuNa · MCM-41 catalyst than in the micropore one (ca. 5 Å) of the K(1)/Cu-NaZSM-5 catalyst. We have already investigated [19] the liquid-phase adsorption of BOH on both MCM-41 (pore diameter, 31 Å) and NaZSM-5 (pore diameter, 5 Å) at 313 K. It has been found that the difference in the amount of BOH adsorption on both MCM-41 and NaZSM-5 was not so high, though the amount of BOH adsorption on the former was higher than on the latter support. These results suggest that the mesoporous support is preferable to the microporous one as a reaction field for forming a bulky reaction product, even if the reactant could access both pore sites.

4. Conclusions

2,6-Di-*tert*-butyphenol (BOH) was oxidized under a liquid-phase mild reaction condition by Cu ion-exchanged Na · MCM-41 (Cu-Na · MCM-41) catalyst to form 4,4'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (H₂DPQ) and 3,3',5,5'-tetra-*tert*-butyl-4, 4'-diphenoquinone (DPQ). The addition of alkali metal (as an alkali metal salt) onto the Cu-Na · MCM-41 catalyst or to the reaction solution caused the increase in the catalytic activity for BOH oxidation. The CH₃COOK added into the reaction solution largely promoted the formation of DPQ. A scheme including both a consecutive pathway via H₂DPQ intermediate and a pass involving the direct oxidative dehydrogenation of a dimer (Scheme 2, (A)) formed of the C–C coupling of the corresponding phenoxy radicals was pro-

posed for the DPQ formation. The K added Cu-Na·MCM-41 had considerably higher catalytic activity for the BOH oxidation than the K added Cu ion-exchanged NaZSM-5 (K added Cu-NaZSM-5). The preference of mesopores to micropores as a reaction field for the formation of sterically bulky products such as BOH was demonstrated from the comparison of the catalytic activities for the BOH oxidation catalyzed by the K added Cu-Na·MCM-41 catalyst with mesopores and the K added Cu-NaZSM-5 catalyst with micropores.

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