

Clean syntheses of phenoquinones and diphenoquinones from phenols catalyzed by alkali-modified M-Mg-Al hydrotalcites (M=Cu, Fe, Ru, Ni, V, and Pd) in the presence of molecular oxygen

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The oxidative coupling of phenols to diphenoquinone using alkali-modified M-Mg-Al-CO₃ hydrotalcites (M = Cu, Fe, Ru, Ni, and Pd) was studied in the presence of molecular oxygen. The reaction of 2,6-di-*tert*-butylphenol catalyzed by K/M-Mg-Al-CO₃ hydrotalcites selectively gave 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone over 97 % yield. In addition, the K/Fe-Mg-Al hydrotalcite was applicable to the oxidative coupling of phenols and naphthols having the bulky alkyl group at 2 and/or 6 positions to the corresponding biphenyldiols and diphenoquinones. The above oxidation system has following advantages; (1) use of O₂ as an ultimate oxidant, (2) non-polluting and reusable catalyst, and (3) simple work-up procedures.

Key words: hydrotalcite, phenoquinones, diphenoquinones, oxidative coupling, molecular oxygen

1. INTRODUCTION

Diphenoquinones have been recently utilized as a photosensitizer based on their unique characters¹. The oxidative coupling of phenols using stoichiometric inorganic oxidants is one of the conventional methods for an industrial production of diphenoquinones. From an environmental points of view, catalytic method using molecular oxygen as a "green" oxidant is urgently required. Typical examples are copper(II) complexes coupled with a strong base such as KOH.

Tsuruya *et al*² reported K-modified Cu-MCM-41 (mesoporous silicate) as a solid catalyst for the oxidative coupling of phenols. The product yield, however, resulted in only 40 %, and the catalyst could not be recyclable. We have developed highly-functionalized catalysts based on the cation-exchange property of hydrotalcite³, consisted of a positively charged Brucite-layer and interlayer of CO₃²⁻ species⁴. Especially, alkali-modified Cu-Mg-Al-CO₃ hydrotalcites acted as efficient and recyclable catalysts for the oxidative coupling of 2,6-di-*tert*-butylphenol (DBP) to 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TBDPQ)⁵. Here, we report the excellent catalysis of alkali modified-hydrotalcites exchanged with Pd, Ru, V, Ni, and Fe which are effective metals for the oxidative dehydrogenation of alcohols to carbonyl compounds⁶, not only for the coupling of DBP but also for the oxidative coupling of

other phenols and naphthols under an O₂ atmosphere.

2. EXPERIMENTAL

2.1 Reagents and Apparatus

2,6-Di-*tert*-butylphenol (Tokyo Kasei Kogyo Co.), 2,6-di-isopropylphenol, 2-methyl-1-naphthol (Aldrich Chemical Co.), 1-naphthol, 3,7-dimethyl-3-octanol, FeCl₃, MgCl₂·6H₂O, AlCl₃·H₂O, K₂CO₃ and KOH (Wako Chemical Co.) were all analytical grade and used without further purification. The oxidation products were analyzed by HPLC using an internal standard (2,4,6-trimethylbenzene). HPLC analyses were performed on SHIMADZU LC-10ADvp equipped with UV-VIS detector and Shim-pack CLC-ODS column at 30°C using CH₃CN as an eluent (λ = 220 nm).

2.2 Preparation of Catalysts

The hydrotalcite was prepared according to the modified method in the literatures^{3,4}. In a typical preparation of K/Fe-Mg-Al-CO₃, FeCl₃ (12.9 mmol), MgCl₂·6H₂O (129.6 mmol), and AlCl₃·6H₂O (43.2 mmol) were dissolved in 120 mL of distilled water. A 120 mL of an aqueous solution of K₂CO₃ (224.0 mmol) and KOH (390.0 mmol) was slowly added to the above solution, then the mixture was heated at 65 °C for 18 h with vigorous stirring. The obtained crystal was filtered, washed two times with distilled water (75 mL) and dried at 100 °C for 15 h to give 12.8 g of Fe-Mg-Al-CO₃. This

Fe-hydrotalcite (12.0 g) was impregnated in aqueous 1 M KOH solution (120 mL) for 2 h, followed by filtration, washing, and drying, to afford a whitish gray powder of K/Fe-Mg-Al-CO₃.

2.3 The oxidation of 2,6-Di-*tert*-butylphenol

A typical oxidative coupling of DBP is as follows. Into a 50mL four-necked flask were placed 1.24 g of DBP (6 mmol), 1.20 g of K/Fe-Mg-Al-CO₃ (K: 0.9 mmol) and *o*-xylene (15 mL). The reaction mixture was vigorously stirred at 130 °C for 10 h under an O₂ atmosphere. The hydrotalcite was removed by filtration and the amount of 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TBDBQ) was determined by HPLC analysis. TBDPQ was isolated by column chromatography on silica gel using solvent (*n*-hexane:EtOAc=4:1).

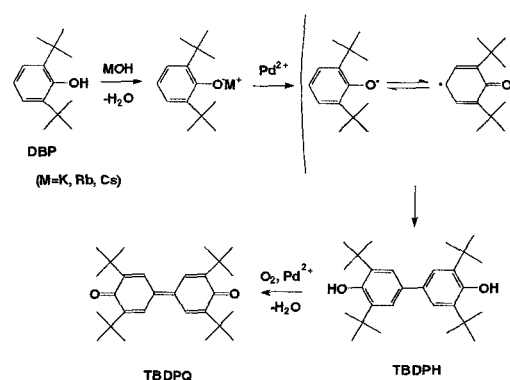
2.4 Regeneration of Catalyst

The used Fe-hydrotalcite, 1.20 g, was washed with methanol and impregnated for 2 h in 20 mL of aqueous 1 M KOH solution, followed by filtration. The used catalyst was washed again with distilled water and dried at 100 °C. The catalyst was then subjected to the oxidative coupling reaction of DBP.

3. RESULTS AND DISCUSSION

The oxidation of DBP was carried out using hydrotalcites modified with various metals and alkalines in the presence of molecular oxygen, which is summarized in Table I. Major products were 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TBDPQ) and 3,3',5,5'-tetra-*tert*-butyl-4,4'-biphenyldiol (TBDPH) (Scheme I). The activity and selectivity of K-modified M-Mg-Al-CO₃ hydrotalcite catalysts (M = Cu, Fe, Ni, Ru, V, and Pd) were extremely high (entries 1, 2, 5, 6, 7 and 8). In the case of alkali-free M-Mg-Al-CO₃ hydrotalcites, the yield of TBDPQ was quite low (entries 13 and 14). Notably, Ru-Mg-Al-CO₃ hydrotalcites modified with K, Cs, and Rb acted as highly active catalysts for the oxidative coupling of DBP to TBDPQ (entries 6, 11, and 12). On the other hand, the metal-free hydrotalcites were not effective for this coupling reaction (entries 15-19). Therefore, a combination of transition metals and alkali metals, *i.e.* K, Cs, and Rb, is necessary to achieve efficient oxidative coupling of DBP to TBDPQ using molecular oxygen. Further, the spent K/Fe-Mg-Al-CO₃, as well as the K/Cu-Mg-Al-CO₃⁵, could be reused while keeping its high catalytic activity and selectivity for the above oxidation (entries 3 and 4).

The K/Fe-Mg-Al-CO₃ hydrotalcite was applied to the oxidation of other phenols and naphthols under an O₂ atmosphere. The results are summarized in Table II. The reaction of 2,6-di-isopropylphenol (DIP) for 40 h gave 3,3',5,5'-tetra-isopropyl-4,4'-biphenyldiol in 82 % yield together with the formation of 3,3',5,5'-tetra-isopropyl-



Scheme I

Table I Aerobic oxidation of 2,6-di-*tert*-butylphenol (DBP) catalyzed by various hydrotalcites in the presence of molecular oxygen^a

Entry	Catalyst	DBP Conv. /% ^b	Yield /% ^b	
			TBDPH	TBDPQ
1	K/Cu-Mg-Al-CO ₃	99	0	99(96) ^c
2	K/Fe-Mg-Al-CO ₃	99	0	98(93) ^c
3	K/Fe-Mg-Al-CO ₃ ^d	99	2	97(93) ^c
4	K/Fe-Mg-Al-CO ₃ ^e	99	1	97(94) ^c
5	K/Ni-Mg-Al-CO ₃	98	0	98
6	K/Ru-Mg-Al-CO ₃	99	0	98
7	K/V-Mg-Al-CO ₃	99	1	97
8	K/Pd-Mg-Al-CO ₃	100	0	98
9	Na/Ru-Mg-Al-CO ₃	19	11	5
10	Na/V-Mg-Al-CO ₃	32	19	12
11	Cs/Ru-Mg-Al-CO ₃	99	0	98
12	Rb/Ru-Mg-Al-CO ₃	100	1	98
13	Cu-Mg-Al-CO ₃	21	7	13
14	Ru-Mg-Al-CO ₃	22	9	11
15	Li/Mg-Al-CO ₃	10	2	8
16	Na/Mg-Al-CO ₃	16	11	5
17	K/Mg-Al-CO ₃	28	22	6
18	Rb/Mg-Al-CO ₃	9	2	7
19	Cs/Mg-Al-CO ₃	9	2	7

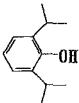
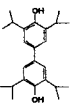
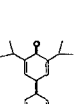
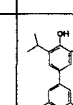
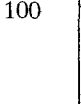
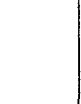


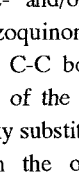
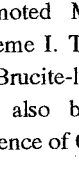
^aReaction conditions; 2,6-di-*tert*-butylphenol (1.24 g, 6 mmol), catalyst (1.20 g), *o*-xylene (15 mL), O₂ flow, 130 °C, 10 h.

^bConversion and yield were determined by HPLC using an internal standard method.

^cA value in parenthesis is an isolated yield.

^dReuse-1. ^eReuse-2.

Table II Aerobic oxidation of phenols catalyzed by K/Fe-hydrotalcite^a

Entry	Materials	Reaction time / h	Material Conv./ % ^b	Products	Yield (%) ^d
20		40	100		82
					9
21 ^c		40	100		77
					11
22		42	100		69
23		10	100		56 ^e

^aReaction conditions; Phenol or Naphthols (6 mmol), catalyst (1.20 g), *o*-xylene (15 mL), O₂ flow, 130 °C.

^bConversion and yield were determined by HPLC using an internal standard method.

^cUsing K/Cu-hydrotalcite. ^dIsolated yield.

^eYield was based on mixture of *o*-alkylnaphthol and *p*-alkylnaphthol obtained after alkylation of 1-naphthol as starting material.

4,4'-diphenylquinone in 9 % yield (entry 20). The almost same product distribution was obtained in the case of the K/Cu-Mg-Al-CO₃ hydrotalcite catalyst (entry 21). The rate of oxidation of DIP was slower than that of DBP. In contrast to DBP oxidation, the biphenyldiol was the major product in the oxidation of DIP.

The K/Fe-Mg-Al-CO₃ hydrotalcite could oxidize 2-methyl-1-naphthol to afford naphthoquinone as a main product (entry 22). 2-(1-Ethyl-1,5-dimethyl)-1-naphthol was converted to the corresponding dinaphthoquinone in 56 % yield (entry 23). Further, the corresponding

benzoquinone was obtained in 30 % yield as a major product in the oxidation of 2,6-dimethylphenol⁷. Oxidation of phenols and naphthols with methyl group at 2- and/or 6-position gave the corresponding 1,4-benzoquinones and 1,4-naphthoquinones, respectively. The C-C bond formation preferentially occurs in the case of the oxidation of phenols and naphthols having bulky substituents at 2- and/or 6-position.

In the oxidative coupling of DBP using alkali-modified M-Mg-Al-CO₃ catalysts, *e.g.* K/Pd-Mg-Al-CO₃, it seems that K⁺ promotes the deprotonation of DBP to afford a K-phenolate species, which is subsequently oxidized by Pd^{II} to generate radical intermediates of carbon-carbon coupling. A stability of the intermediate might be affected by the kinds of substituents at 2- and/or 6-positions. A resultant Pd^I is reoxidized to Pd^{II} by molecular oxygen. We proposed a catalytic cycle of this DBP oxidation using the alkali-promoted M-Mg-Al-CO₃ hydrotalcite as shown in Scheme I. The transition metal cations immobilized in the Brucite-layer efficiently oxidize the phenolate anion, and also biphenyldiols to diphenylquinones in the presence of O₂.

4. CONCLUSION

The highly active and recyclable heterogeneous catalysts for the oxidative coupling of DBP to TDBPQ using molecular oxygen as an oxidant were developed by modification of M-Mg-Al-CO₃ hydrotalcites (M = Cu, Fe, Ru, Ni, V, and Pd) with alkali metals. Especially, K/Fe-Mg-Al-CO₃ could also oxidize substituted-phenols and naphthols to the corresponding biphenyldiols and diphenylquinones. This functionalized hydrotalcite serves as a practical catalyst for the production of useful diphenylquinones. The present oxidation system has the following advantages; (1) use of O₂ as an ultimate oxidant, (2) non-polluting and cheap catalyst, (3) reusability of the solid catalysts, and (4) simple work-up procedures.

5. REFERENCES

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[7] The byproducts were polymeric compounds.

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