

# Catalytic Activities of $\text{CuSO}_4/\text{Al}_2\text{O}_3$ in Dehydrogenation of Arenes by Dioxygen

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The oxidation reactions of hydroquinones, 2-naphthols, or 2,6-di-*tert*-butylphenol efficiently occurred by catalysis with alumina-supported copper(II) sulfate to give the corresponding benzoquinones, 1,1'-bi-2-naphthols, and 4,4'-diphenoquinone, respectively, in good yields. The synthetic potentiality of the catalytic reactions was demonstrated by easy isolation of the final products using only filtration and solvent evaporation as well as by application to large-scale syntheses of the benzoquinones and binaphthols. The catalysis with alumina-supported copper(II) sulfate was also applied to the oxidative intramolecular coupling of 5,5'-diacenaphthene to the corresponding perylene compound.

## Introduction

Oxidative dehydrogenation reactions of arenes have been providing an important class of synthetic methods, particularly for the oxidation reactions of hydroxyarenes. For instance, the preparation of 1,1'-bi-2-naphthols has been conveniently achieved by the oxidative coupling of 2-naphthols using a variety of oxidants, *e.g.*,  $\text{FeCl}_3$ ,<sup>1,2</sup>  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,<sup>3</sup>  $\text{Mn}(\text{acac})_3$ ,<sup>4,5</sup> and  $\text{Cu}(\text{II})$ -amine complexes,<sup>6–8</sup> as stoichiometric reagents as well as by such catalyst systems as  $\text{CuCl}_2$ -amine- $\text{AgCl}$  combinations,<sup>9</sup>  $\text{CuCl}(\text{OH})$ -tetramethylethylenediamine complex under  $\text{O}_2$ ,<sup>10</sup> and solid  $\text{FeCl}_3$ .<sup>1</sup> Similarly, the preparative conversion of hydroquinones to quinones has been carried out with a wide variety of stoichiometric oxidants in homogeneous solution<sup>11</sup> and also with some catalysts.<sup>12–16</sup> While the oxidation of phenols very often gives complex mixtures, hindered phenols are readily oxidized to give discrete oxidation products depending upon the oxidants used as well as upon reaction conditions. A typical example is the oxidation of 2,6-di-*tert*-butylphenol under  $\text{O}_2$  that gives usually mixtures of the 1,4-benzoquinone and diphenoquinone, whereas the selective formation of the

latter has been achieved by using particular catalysts.<sup>13,14,17,18</sup>

In the oxidation reactions of hydroxyarenes, the use of homogeneous oxidants often results in low-yield formation of desired products accompanied by side reactions, thus bringing about difficulties in controlling the reactions as well as in separation of the products from reaction mixtures. In those cases, therefore, heterogeneous catalyst of the oxidation reactions should be advantageous, if suitable heterogeneous catalysts are available. A useful way for preparation of effective heterogeneous catalysts might be the insolubilized deposition of reagents on inorganic solid surfaces<sup>19,20</sup> that can be achieved without significant losses of activities of the reagents or even with activation of the reagents. From practical and environmental viewpoints, moreover, it is desirable that dioxygen can be used as the net oxidant to promote efficient catalytic cycles of the oxidation reactions without participation of oxygenation reactions.

In a previous paper,<sup>21</sup> we preliminarily reported that copper(II) sulfate supported on alumina efficiently catalyzes the oxidative coupling of 2-naphthols to the corresponding 1,1'-bi-2-naphthols under dioxygen. In the present paper, we wish to report details of the oxidative coupling reactions of 2-naphthols and also successful applications of this catalyst to the high-yield oxidation of hydroquinones, the selective oxidative coupling of 2,5-di-*tert*-butylphenol to the diphenoquinone, and the intramolecular oxidative cyclization of 5,5'-diacenaphthene to the corresponding perylene compound under dioxygen.

## Results

**1. Preparation of Supported Catalyst  $\text{CuSO}_4/\text{Al}_2\text{O}_3$  (SCAT).** The supported catalyst (SCAT) was easily obtained as sky blue powder as follows; commercially available neutral alumina was dispersed in an aqueous solution of  $\text{CuSO}_4$ , and then the mixture was evaporated to dryness at 150 °C under vacuum (eq 1). Unless otherwise noted, SCAT contains 10% (w/w)  $\text{CuSO}_4$  supported on neutral alumina.

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Other similar catalysts were also prepared by using such solid supports as acidic and basic alumina, Florisil, Celite, silica gel, and molecular sieves and by supporting  $\text{Cu}(\text{OAc})_2$  and  $\text{CuF}_2$  on neutral alumina. Although these catalysts were extensively investigated in all the oxidative dehydrogenation reactions shown below, their catalytic activities were significantly or much lower, in most cases, than those of SCAT. Therefore, details of the reactions using SCAT are described in this paper.

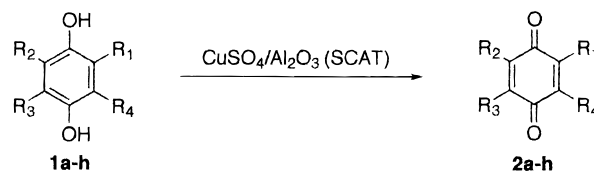
## 2. Oxidation of Hydroquinones to Quinones.

Hydroquinone (**1a**) was efficiently oxidized to 1,4-benzoquinone (**2a**) under air with a catalytic amount of SCAT. As a typical run, a slurry of **1a** (1 mmol) and SCAT (0.2 mmol in  $\text{Cu}(\text{II})$ ) in propyl acetate (10 mL) was heated at 100 °C for 8 h under bubbling air through the mixture. Analyses of the reaction by TLC (silica gel) and GLC showed the complete consumption of **1a** accompanied by the quantitative formation of **2a**. After conventional workup procedures, **2a** was obtained in  $\geq 95\%$  yield as the sole product. With a smaller amount of SCAT (0.05 mmol of  $\text{Cu}(\text{II})$ ), this reaction was comparably effected under similar conditions to give **2a** in 94% yield. On the other hand, the use of still smaller amounts of SCAT ( $\leq 0.03$  mmol of  $\text{Cu}(\text{II})$ ) led to incomplete conversions of **1a** and lower-yield formation of **2a** ( $\leq 65\%$ ), though the turnover numbers were higher ( $\geq 22$  mol of **2a** formed/mol of  $\text{Cu}(\text{II})$  used). It was found that such other solvents as hexanol, butyl ether, chlorobenzene, and nonane are much less favorable for the oxidation reaction than propyl acetate; yields of **2a** were  $< 33\%$ . It is of synthetic and mechanistic significance to note that the oxidation of **1a** did occur significantly, but much less efficiently, even under  $\text{N}_2$  with a catalytic amount of SCAT, while the absence of SCAT resulted in a negligible reaction under either air or  $\text{N}_2$ . Both dioxygen and SCAT are required for the efficient catalysis of the oxidation reaction, though dioxygen appears not to be directly responsible for the oxidation of **1a**. The yield of **2a** formed under  $\text{N}_2$  was increased with the amounts of SCAT used, *e.g.*, from only  $\sim 30\%$  with 0.2 equiv  $\text{Cu}(\text{II})$  to 97% with an excess amount of SCAT (6 mmol of  $\text{Cu}(\text{II})/1$  mmol of **1a**). This means that SCAT should be responsible for the oxidation of **1a**. Moreover, it should be noted that the oxidation of **1a** was not effected with  $\text{CuSO}_4$  powder or alumina powder alone nor with a mixture obtained by simple admixing of  $\text{CuSO}_4$  and alumina in powder.


We investigated the effectiveness of other catalysts in the coupling reaction of **1a** under similar reaction conditions. When  $\text{Cu}(\text{OAc})_2$  or  $\text{CuF}_2$  was used in place of  $\text{CuSO}_4$ , **2a** was obtained only in 46% or 57% yield each. Moreover, it was confirmed that the catalysts prepared from  $\text{CuSO}_4$  and other inorganic solids investigated are slightly or much less active than SCAT; yields of **2a** were 85% with acidic alumina, 90% with basic alumina, 32% with Florisil, 26% with Celite, 17% with silica gel, and 13% with molecular sieves-13X.

The catalysis of SCAT was effectively applied to the efficient oxidation of the other hydroquinones **1b–h** to the corresponding quinones **2b–h** under air (Scheme 1). Table 1 summarizes the results. In all the reactions, the products were isolated in excellent yields and in considerably high purities. Minimum amounts of SCAT required for the completion of the oxidation reactions were only 5 mol %  $\text{Cu}(\text{II})$  for **1a, b, g, h** and 10 mol %  $\text{Cu}(\text{II})$  for **1d–f** but significantly higher (30 mol %  $\text{Cu}(\text{II})$ ) for **1c**.

## Scheme 1



**Table 1.** SCAT-Catalyzed Oxidation of Hydroquinones **1a–h**<sup>a</sup>

entry	hydroquinones				$\text{CuSO}_4$ in SCAT mol%	quinones	Yield of <b>2</b> / <sup>b</sup>
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>			
1	<b>1a</b> : H	H	H	H	5	<b>2a</b>	94
2	<b>1b</b> : CH <sub>3</sub>	H	H	H	5	<b>2b</b>	94
3	<b>1c</b> : Cl	H	H	H	30	<b>2c</b>	92
4	<b>1d</b> : Ph	H	H	H	10	<b>2d</b>	95
5	<b>1e</b> : <i>t</i> -Bu	<i>t</i> -Bu	H	H	10	<b>2e</b>	93
6	<b>1f</b> : CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	10	<b>2f</b>	97
7	<b>1g</b> : CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	5	<b>2g</b>	98
8	<b>1h</b> : H			H	5	<b>2h</b>	97

<sup>a</sup> For reactions of **1a–h** (1 mmol) in propyl acetate (10 mL) at 100 °C under air bubbling for 8 h. <sup>b</sup> Isolated yields.

Similar procedures can be successfully applied to large-scale syntheses of **2**. For instance, a slurry of SCAT (8.78 g) and **1a** (11.01 g) in 1.0 L propyl acetate was heated at 100 °C for 20 h under bubbling air through the mixture. Filtration followed by conventional workup treatment gave  $\sim 9$  g of **2a** (83% yield). It was confirmed that the recovered SCAT turned brownish in color but still retained a partial catalytic activity, **2a** was formed in 32% yield by using the recovered SCAT without any reactivation treatment.

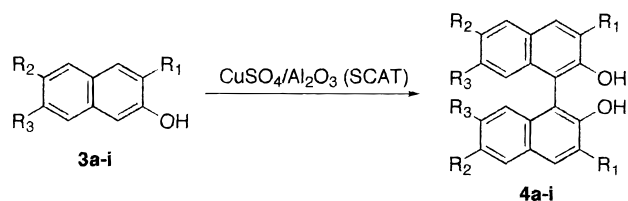
**3. Oxidative Coupling of 2-Naphthols.** The catalytic oxidative coupling of 2-naphthol (**3a**) to 1,1'-binaphthalene-2,2'-diol (**4a**) efficiently occurred in the presence of SCAT (Scheme 2). A slurry of **3a** (1 mmol) and SCAT (0.2 mmol in  $\text{Cu}(\text{II})$ ) in 10 mL chlorobenzene was heated at 140 °C for 8 h with bubbling air through the mixture. GLC analysis revealed the exclusive formation of **4a** with a negligible amount of byproducts at complete consumption of **3a**; neither naphthoquinone nor dinaphthoquinone was detected at all. After filtration followed by evaporation of the solvent, treatment of the product with active carbon gave pure **4a** in 97% yield based on **3a** used. It is, therefore, evident that the selective coupling of **3a** to **4a** occurred with no oxygenation of **3a** nor further oxidation of **4a**. This reaction was undertaken in other solvents, but the yields were significantly lower as follows; 62% in nonane, 77% in decalin, 59% in butyl ether, 63% in 2-heptanone, 85% in hexyl acetate, and 48% in hexanol.

The catalytic coupling reaction again requires the presence of both SCAT and dioxygen, because the formation of **4a** was much less efficient under an  $\text{N}_2$  atmosphere (only 14% yield) and was not observed in the absence of SCAT under either air or  $\text{N}_2$ . With an excess amount of SCAT (*e.g.*,  $\geq 2$  mol  $\text{Cu}(\text{II})/\text{mol}$  of **3a**), however, the selective coupling reaction of **3a** to **4a** occurred even under  $\text{N}_2$  as efficiently as the catalytic reaction under air, again suggesting that SCAT should be a requisite for the oxidative coupling of **3a** rather than air. It was confirmed that  $\text{CuSO}_4$  powder or alumina powder or a powder admixture of them is totally ineffective to the

**Table 2. SCAT-Catalyzed Oxidative Coupling of 2-Naphthols 3a–i<sup>a</sup>**

entry	2-naphthols	time/h	binaphthols	yield/%
1	<b>3a</b> : R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = H	8	<b>4a</b>	97
2	<b>3b</b> : R <sub>1</sub> = R <sub>3</sub> = H, R <sub>2</sub> = Br	2	<b>4b</b>	98
3	<b>3c</b> : R <sub>1</sub> = R <sub>3</sub> = H, R <sub>2</sub> = <i>t</i> -Bu	4	<b>4c</b>	98
4	<b>3d</b> : R <sub>1</sub> = R <sub>2</sub> = H, R <sub>3</sub> = OH	15	<b>4d</b>	93
5	<b>3e</b> : R <sub>1</sub> = R <sub>2</sub> = H, R <sub>3</sub> = OCH <sub>3</sub>	8	<b>4e</b>	97
6	<b>3f</b> : R <sub>1</sub> = OCH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = H	18	<b>4f</b>	41 <sup>b</sup> (94) <sup>c</sup>
7	<b>3g</b> : R <sub>1</sub> = CO <sub>2</sub> CH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = H	8	<b>4g</b>	trace (20) <sup>d</sup>
8	<b>3h</b> : R <sub>1</sub> = Br, R <sub>2</sub> = R <sub>3</sub> = H	8	<b>4h</b>	<i>e</i>
9	<b>3i</b> : R <sub>1</sub> = R <sub>3</sub> = H, R <sub>2</sub> = OH	8	<b>4i</b>	<i>f</i>

<sup>a</sup> For reactions of **3a–i** (1 mmol) with 10 wt % SCAT (0.2 equiv of CuSO<sub>4</sub>) in chlorobenzene (10 mL) at 140 °C under air bubbling. <sup>b</sup> Hexyl acetate was used as solvent. <sup>c</sup> At 160 °C for 8 h in hexyl acetate; CuSO<sub>4</sub>/**3f** = 2.0. <sup>d</sup> At 160 °C; CuSO<sub>4</sub>/**3g** = 2.0. <sup>e</sup> No reaction. **3h** was recovered in quantitative yield. <sup>f</sup> Complex mixture of products was obtained.

**Scheme 2**

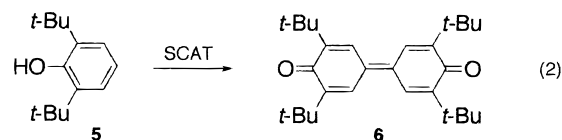
oxidative coupling of **3a** to **4a**. The adsorption of Cu(II) on alumina should be essential for this reaction.

Similarly, the catalytic coupling reactions of the other substituted 2-naphthols **3b–e** efficiently proceeded to give the corresponding binaphthols **4b–e** in excellent yields ( $\geq 93\%$ ) (Scheme 2). The reactions of 6-bromo- and 6-*tert*-butyl-2-naphthol (**3b,c**) were completed within 4 h, whereas a longer period of reaction was required for the completion of reaction in the case of either 7-hydroxy- or 7-methoxy-2-naphthol (**3d,e**). The coupling reaction of 3-methoxy-2-naphthol (**3f**) was much less efficient under similar reaction conditions but was effected by using an excess amount of SCAT (2 mol of Cu(II)/mol of **3f**) to give **4f** in 94% yield. The reactivity of 3-(methoxycarbonyl)-2-naphthol (**3g**) was negligibly low under the catalytic reaction conditions and still low even in a reaction using an excess amount of SCAT at 160 °C, where **4g** was formed only in 20% yield along with  $\sim 80\%$  recovery of **3g**. All the binaphthols were isolated and fully characterized by direct comparison of their physical properties with those of authentic samples. On the other hand, the reaction of 2,6-dihydroxynaphthalene (**3i**) under the catalytic conditions gave untraceable materials, while 3-bromo-2-naphthol (**3h**) remained unchanged upon heating at 160 °C in the presence of an excess amount of SCAT. The results are summarized in Table 2.

Large-scale reactions of **3a–g** can be easily achieved. As a typical run, a mixture of **3a** (14.4 g, 0.1 mol) and SCAT (35.1 g, 20 mmol in Cu(II)) in 1.0 L of chlorobenzene was heated at 140 °C for 8 h to give pure **4a** (13 g, 89% yield) after conventional workup followed by single recrystallization of the crude product. The recovered SCAT was dark-brownish in color, quite different from the initial sky-blue color. Nevertheless, it still retained a comparable, but slightly low, catalytic activity without any reactivation treatment, since a reaction of **3a** using the recovered SCAT under identical reaction conditions gave **4a** in 72% yield. Presumably, the color change might be mainly due to partial deposition of colored materials on the catalyst surface.

**4. Oxidative Coupling of 2,6-Di-*tert*-butylphenol to 3,3',5,5'-Tetra-*tert*-butyl-4,4'-diphenoquinone.** The SCAT-catalyzed oxidative coupling reaction was applied to some

phenols, among which only 2,6-di-*tert*-butylphenol (**5**) underwent the coupling reaction. A reaction of **5a** in the presence of SCAT (0.2 equiv of Cu(II)) in chlorobenzene was performed at 140 °C under bubbling air through the mixture for 8 h to give 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (**6**) in 94% yield (eq 2). When the coupling reaction of **5** in hexyl acetate as solvent, the best



solvent in the oxidation of hydroquinones **1** to quinones **2**, was carried out under similar reaction conditions, **6** was obtained in a slightly lower yield (88%). This reaction gave neither the corresponding biphenol nor benzoquinone at all, revealing a high chemoselectivity reminiscent of the laccase–O<sub>2</sub> system.<sup>22</sup> In the cases of 2,6-dimethylphenol and 2,6-dicyanophenol, the starting materials were mostly recovered, while parent phenol gave a complex mixture. Therefore, no further attempts were made to apply this reaction to other phenols.

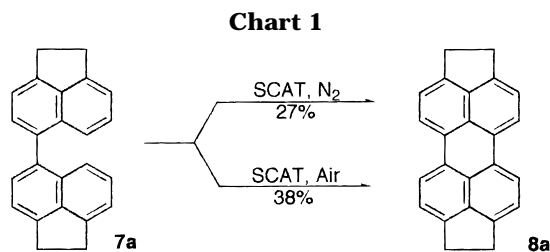
**5. Intramolecular Dehydrogenative Coupling of 5,5'-Diacenaphthene.** An easy access for synthesis of perylene compounds might be the intramolecular dehydrogenative coupling of 1,1'-binaphthalenes, since the starting compounds can be easily prepared from naphthalenes.<sup>23</sup> Among perylene compounds, perylenetetracarboxylic acid is of particular industrial importance, because it serves as a key synthetic intermediate for the production of perylene pigments.<sup>24</sup> From these viewpoints, we attempted the SCAT-catalyzed coupling reaction of 5,5'-diacenaphthene (**7a**) to the corresponding perylene **8a**, since the oxidation of **8a** to perylenetetracarboxylic acid can be readily achieved.

A slurry of **7a** (0.2 mmol) and SCAT (0.2 mmol in Cu(II)) in chlorobenzene (2 mL) was heated at 140 °C under N<sub>2</sub> or air for 8 h. GLC analysis of the solution revealed that 1,2,7,8-tetrahydrodicyclopenta[1,2,3-*cd*:lm]peryene (**8a**) was formed as the sole product at  $\sim 30\%$  conversion of **7a** under N<sub>2</sub> or  $\sim 40\%$  conversion under air (Chart 1). However, further increase in conversion of **7a** was not achieved even at higher reaction temperatures and/or by heating for a much longer period of reaction. Moreover, the use of greater amounts of SCAT led to formation of a complex mixture containing only a minor amount of **8a**. In order to isolate **8a**, we extensively performed

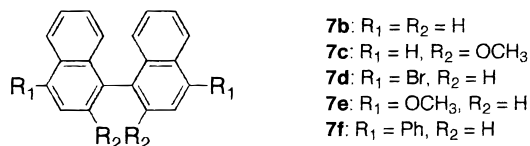
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**Chart 2. 1,1'-Dinaphthyl Derivatives That Do Not React with  $\text{CuSO}_4/\text{Al}_2\text{O}_3$  (SCAT)**

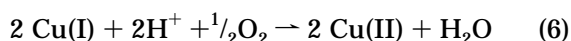
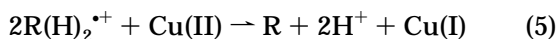
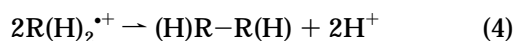
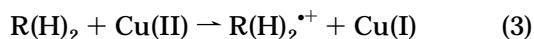


preparative HPLC as well as column chromatography of the reaction mixtures on either silica gel or alumina. However, all the attempts were unsuccessful to give only solid mixtures of **7a** and **8a**. Therefore, the identification of **8a** was performed by direct comparison of the GLC retention time and GC-mass spectra with those of an authentic sample.<sup>25</sup>

The SCAT-catalyzed cyclization was applied to such other 1,1'-binaphthalenes as parent 1,1'-binaphthalene **7b** and its 2,2'-dimethoxy, 4,4'-dibromo, 4,4'-dimethoxy, and 4,4'-diphenyl-substituted derivatives (**7c–f**). However, all these compounds were quantitatively recovered even after extensive reactions (Chart 2). The complete lack of reaction might be attributable to a mechanistic origin (*vide infra*).

### Discussion

**Mechanism.** Since the oxidative dehydrogenation reactions do not proceed in the absence of SCAT, the direct oxidant should be not dioxygen but SCAT. Presumably, the reactions might be commonly initiated by single electron transfer from a reactant molecule  $\text{R}(\text{H})_2$  to  $\text{Cu}(\text{II})$  of SCAT (eq 3) to generate the radical cation  $\text{R}(\text{H})_2^{\bullet+}$ , since a variety of  $\text{Cu}(\text{II})$  reagents are known as one-electron oxidant.<sup>26</sup> The subsequent processes should be complex, perhaps involving the coupling of  $\text{R}(\text{H})_2^{\bullet+}$  (eq 4) or the second one-electron oxidation (eq 5) followed by or coupled with deprotonation. All these processes would proceed on the catalyst surface. The support of  $\text{Cu}(\text{II})$  on alumina should be essential for the catalysis of the oxidative dehydrogenation reactions, since either  $\text{CuSO}_4$  or alumina or their solid admixture is totally ineffective as catalyst. Dioxygen may reactivate SCAT by the oxidation of  $\text{Cu}(\text{I})$  to  $\text{Cu}(\text{II})$  (eq 6), thus facilitating the efficient catalytic cycle for the oxidative dehydrogenation



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reactions, particularly in the cases of **1a–h**, **3a–e**, and **5**. Electrochemical investigation on the oxidation–reduction processes of hydroquinone–quinone couples<sup>27,28</sup> demonstrates that the net two-electron oxidation of hydroquinones to quinones proceeds through the initial one-electron oxidation followed by the sequential processes of the deprotonation of  $\text{R}(\text{H})_2^{\bullet+}$  and the deprotonation-coupled one-electron oxidation of semiquinone radical  $\text{R}(\text{H})^{\bullet}$  to  $\text{R}(\text{E})$  (ECEC mechanism). In the SCAT-catalyzed reactions,  $\text{R}(\text{H})_2^{\bullet+}$  formed on the SCAT surface should be in contact with alumina. This situation is certainly favorable for efficient proton transfer from  $\text{R}(\text{H})_2^{\bullet+}$  to alumina at the basic site as well as for the subsequent electron-proton transfer from  $\text{R}(\text{H})^{\bullet}$  to SCAT.

Mechanistic details of the oxidative coupling reactions of **3a–g**, **5**, and **7a** should be more complex, though the initiation process is probably one-electron oxidation of the reactants by  $\text{Cu}(\text{II})$ . The radical cations of **3a–g** and **5** formed on the SCAT surface might be readily deprotonated, as has been discussed for the oxidation of **1a–h**, to give the corresponding aryloxy radicals. On the SCAT surface, these radicals would be accumulated in concentration high enough to undergo the efficient radical coupling reactions at the 1-position of the naphthoxy radicals or at the 4-position of the 2,6-di-*tert*-butylphenoxy radical, reactive sites where free-spin densities are high. The initial product of **5** can be presumed to be the 4,4'-dihydroxybiphenyl, which would be spontaneously oxidized to **6** because of its higher susceptibility to the one-electron oxidation compared with the starting phenol. In the case of **7a**, the radical cation might undergo the intramolecular coupling followed by further oxidation to **8a**.

It is of interest to note that the substitution at the 3-position of 2-naphthol brings about lower reactivities (**3f,g**) or leads to the lack of reaction (**3h**) independently of the electron-donating or -withdrawing nature of the substituents. The substituents at the 3-position would sterically disfavor the adsorption of the reactants on the SCAT surface. Alternatively, the oxidation potential of **3h** would be too high to allow the initial one-electron oxidation by  $\text{Cu}(\text{II})$ , due to the electron-withdrawing effect of the bromo group. In the cases of **7b–f**, no reaction occurs at all independently of the substituents. Perhaps, the free spin in the radical cation of **7b–f** would be mostly localized on the substituted ring. As a result, free-spin densities on the unsubstituted ring where the coupling reaction must occur would be too low to allow the occurrence of any reaction.

### Conclusions

In this study, we have demonstrated that the new catalyst SCAT is potentially capable of catalyzing the dehydrogenation of hydroquinones to the quinones, the dehydrogenative coupling of 2-naphthols to the binaphthols, and the oxidation of 2,6-di-*tert*-butylphenol to the diphenoquinone under  $\text{O}_2$ . From industrial and synthetic viewpoints, it is of practical significance to note the following advantages in the use of SCAT: (1) The preparation of SCAT can be easily achieved by using the inexpensive reagents,  $\text{CuSO}_4$  and neutral alumina. (2) The oxidation reactions are exceptionally clean without

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significant contamination by oxygenation reactions and further oxidation reactions. (3) The final products can be readily isolated by filtration and subsequent evaporation of the solvent in most cases. (4) The catalytic activity of SCAT might be restored by appropriate reactivation treatment after oxidation reactions, since recovered SCAT retains partial catalytic activities. (5) The SCAT-catalyzed reactions appear to be free from possible environmental pollution, since no toxic reagent is involved and since SCAT can be quantitatively recovered with no leak of copper compounds.

Unfortunately, application of the SCAT catalysis to perylene compounds is limited to the inefficient oxidative cyclization of 5,5'-diacenaphthene to the corresponding perylene compound. This appears to reflect general limitations of the SCAT catalysis which would arise from steric and electronic requirements, *e.g.*, adsorption of the reactants on the SCAT surface without steric hindrance, lower oxidation potentials than the limit for one-electron oxidation by Cu(II) of SCAT, and reactivities of the radical cations for the follow-up processes. However, the present investigation suggests that the choice of metal ions and inorganic solids associated with improvements in preparation of supported catalysts might be able to open wide synthetic applicabilities of supported catalysts. Further investigation in this line is now in progress.

## Experimental Section

**General Methods.** Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. The preparation of 6-*tert*-butyl-2-naphthol (**5c**)<sup>29</sup> and 2,6-di-*tert*-butylhydroquinone (**1e**)<sup>30</sup> was performed as described in literature. 5,5'-Diacenaphthene (**7a**) was prepared by the oxidative coupling of acenaphthene using Pb(OAc)<sub>4</sub>.<sup>23</sup> Neutral alumina was purchased from ICN Bio-medicals (Woelm N-Super I) and used without any treatment. IR spectra were recorded on a JASCO A-202 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a JEOL JNM-GSX-400 spectrometer using TMS as internal standard. GC-MS and FD-MS spectra were recorded on a Shimadzu 9100-MK mass spectrometer. GLC analysis was carried out on a Shimadzu GC-8A flame ionization chromatography using a 50-mm × 0.25-mm capillary column of SE-54. Melting points were measured on a Yanagimoto micro melting-point apparatus and are uncorrected.

**Preparation of Copper(II) Sulfate Supported on Alumina (SCAT).** To a solution of copper(II) sulfate pentahydrate (7.8 g) in distilled water (200 mL) was added neutral alumina (50 g) at room temperature, and the suspension was stirred at this temperature for 30 min. After evaporation of water by using a rotary evaporator at 80 °C under reduced pressure (2 Torr), the resulting moist solid was then dried to dryness under vacuum (1 Torr) at 150 °C for 8 h and stored in a desiccator.

**General Procedure for SCAT-Catalyzed Oxidation of Hydroquinones under Air. 1,4-Benzoquinone (2a):** A 30-mL three-necked round-bottom flask was charged with SCAT (88 mg, 0.05 mmol), **1a** (0.110 g, 1.0 mmol), and propyl acetate (10 mL). A Teflon-coated stirring bar was added, and the mixture was stirred vigorously at 100 °C for 8 h under bubbling air through the mixture. The mixture was filtered, and the collected solid was washed with dichloromethane (10 mL × 4). Evaporation of the combined filtrate under reduced pressure left pure **2a** (0.102 g, 94%) as a yellow solid. The melting point and spectroscopic data of the product was identical with those of authentic benzoquinone: mp 115 °C (lit.<sup>16</sup> mp 115 °C).

**2-Methyl-1,4-benzoquinone (2b):** mp 69 °C (lit.<sup>16</sup> mp 68–69 °C).

**2-Chloro-1,4-benzoquinone (2c):** mp 55–56 °C (lit.<sup>16</sup> mp 54–55 °C).

**2-Phenyl-1,4-benzoquinone (2d):** mp 114 °C (lit.<sup>31</sup> mp 114–115 °C).

**2-Di-*tert*-butyl-1,4-benzoquinone (2e):** mp 66 °C (lit.<sup>12a</sup> mp 65–67 °C).

**2,3,5-Trimethyl-1,4-benzoquinone (2f):** mp 30–31 °C (lit.<sup>16</sup> mp 30–31 °C).

**2,3,5,6-Tetramethyl-1,4-benzoquinone (2g):** mp 110–112 °C (lit.<sup>16</sup> mp 111 °C).

**1,4-Naphthoquinone (2h):** mp 121–122 °C (Aldrich, mp 121–122 °C).

**Oxidation of 1a in the Absence of Air.** A 50-mL three-neck round-bottom flask was charged with SCAT (10.534 g, 6 mmol), **1a** (0.110 g, 1.0 mmol), and propyl acetate (20 mL). A Teflon-coated stirring bar was added, and the mixture was stirred vigorously at 100 °C for 8 h under N<sub>2</sub>. The mixture was filtered, and the collected solid was washed with dichloromethane (10 mL × 5). Evaporation of the combined filtrate under reduced pressure left pure **2a** (0.105 g, 97%) as a yellow solid.

**General Procedure for SCAT-Catalyzed Oxidative Coupling of 2-Naphthols under Air. 1,1'-Binaphthalene-2,2'-diol (4a):** A 30-mL three-necked round-bottom flask was charged with SCAT (0.351 g, 0.2 mmol), **3a** (0.144 g, 1.0 mmol), and chlorobenzene (10 mL). A Teflon-coated stirring bar was added, and the mixture was stirred vigorously at 140 °C for 8 h under bubbling air through the mixture. GLC analysis indicated the complete disappearance of **3a**. The mixture was filtered, and the collected solid was washed with dichloromethane (10 mL × 2) and then with acetone (10 mL × 2). Evaporation of the combined filtrate under reduced pressure left crude **4a** (0.142 g, 99%) as a brownish solid, which was further purified by treatment with active carbon to give colorless **4a** (0.138 g, 97%); mp 214–216 °C (lit.<sup>32</sup> mp 216–218 °C).

**6,6'-Dibromo-1,1'-binaphthalene-2,2'-diol (4b):** mp 208–209 °C (lit.<sup>33</sup> mp 198–199 °C).

**6,6'-Di-*tert*-butyl-1,1'-binaphthalene-2,2'-diol (4c):** mp 102–103 °C; *R*<sub>f</sub> 0.45 (SiO<sub>2</sub>, 2:1 hexane:acetone); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.38 (18 H, s), 5.0–5.1 (2 H, bs s), 7.12 (2 H, d, *J* = 8.59 Hz), 7.34 (2 H, d, *J* = 8.59 Hz), 7.39 (2 H, dd, *J* = 8.59 and 2.34 Hz), 7.81 (2 H, d, *J* = 2.34 Hz), 7.92 (2 H, d, *J* = 8.59 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 31.3, 34.5, 110.9, 117.6, 123.5, 124.0, 126.5, 129.5, 131.5, 131.6, 146.8, 152.5; IR (KBr) 3400, 2920, 1585, 1450, 1350, 1145, 820 cm<sup>-1</sup>; EI MS *m/z* (relative intensity) 398 (M<sup>+</sup>, 72), 383 (100), 365 (11), 184 (36), 156 (25), 57 (67). Anal. Calcd for C<sub>28</sub>H<sub>30</sub>O<sub>2</sub>: C, 84.4; H, 7.6. Found: C, 84.3; H, 7.7.

**2,2',7,7'-Tetrahydroxy-1,1'-binaphthyl (4d):** mp 131–132 °C (lit.<sup>7</sup> mp 111.0–113.0 °C; lit.<sup>34</sup> mp 151.0–152.0 °C).

**7,7'-Dimethoxy-1,1'-binaphthyl-2,2'-diol (4e):** mp 151–152 °C (lit.<sup>35</sup> mp 151–152 °C).

**3,3'-Dimethoxy-1,1'-binaphthyl-2,2'-diol (4f):** mp 264–265 °C; *R*<sub>f</sub> 0.45 (SiO<sub>2</sub>, 3:2 petroleum ether:acetone); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ 2.05 (6 H, s), 3.31–3.61 (2 H, bs s), 6.98 (2 H, dd, *J* = 8.23 and 1.49 Hz), 7.03 (2 H, ddd, *J* = 8.23, 8.23, and 1.49 Hz), 7.21 (2 H, ddd, *J* = 8.23, 8.23, and 1.49 Hz), 7.36 (2 H, s), 7.69 (2 H, d, *J* = 8.23 Hz); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ 30.6, 110.5, 115.8, 124.11, 124.18, 125.5, 127.4, 130.2, 130.8, 145.8, 147.3; IR (KBr) 3300 (s), 1680 (s), 1505 (s), 1450 (s), 1355 (m), 1285 (m), 1220 (s), 1095 (m), 1015 (m), 880 (m), 860 (m), 740 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>: C, 76.3; H, 5.2. Found: C, 76.1; H, 5.4.

**3,3'-Bis(methoxycarbonyl)-1,1'-binaphthyl-2,2'-diol (4g):** mp 276.0–277.0 °C (lit.<sup>7</sup> mp 276.0–278.0 °C).

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**Coupling of 3a in the Absence of Air.** To a 30-mL round-bottom flask were placed SCAT (3.51 g, 2.0 mmol), **3a** (0.144 g, 1.0 mmol), and chlorobenzene (10 mL). The mixture was stirred at 140 °C for 8 h under bubbling nitrogen, cooled down to room temperature, and then filtered. The collected solid was washed with dichloromethane (10 mL  $\times$  2) and then with acetone (10 mL  $\times$  2). Evaporation of the combined filtrate under reduced pressure left crude **4a** (0.133 g, 93%) as brownish solid, which was further purified by treatment with active carbon to give colorless **4a** (0.127 g, 89%).

**Large Scale Synthesis of 4a.** To a 2-L round-bottom flask were placed SCAT (35.11 g, 20 mmol), **3a** (14.42 g, 100 mmol), and chlorobenzene (1 L), and the mixture was stirred mechanically at 140 °C for 8 h under bubbling air through the mixture. The reaction mixture was cooled down to room temperature and filtered. The collected solid was washed with dichloromethane (100 mL  $\times$  2) and then with acetone (100 mL  $\times$  2). After evaporation of the combined filtrate, the brownish residue (14.17 g) was recrystallized from toluene to give colorless **4a** (12.74 g, 89%).

**The SCAT-Catalyzed Oxidative Coupling of 2,6-Di-*t*-butylphenol (5) under Air. 3,3',5,5'-Tetra-*tert*-butyl-4,4'-diphenquinone (6):** To a 30-mL three-necked round-bottom flask were placed SCAT (0.351 g, 0.2 mmol), **5** (0.206 g, 1.0 mmol), and chlorobenzene (10 mL), and the mixture was stirred with a Teflon-coated magnetic stirring bar at 140 °C for 8 h under bubbling air through the mixture. After filtration, the collected solid was washed with dichloromethane (10 mL  $\times$  2) and then with acetone (10 mL  $\times$  2). Evaporation of the combined filtrate under reduced pressure left **6** (0.2 g, 98%) as a brownish solid. The crude product was further purified

by treatment with active carbon to give light brownish **6** (0.19 g, 94%); mp 239–241 °C (lit.<sup>29</sup> mp 239–242 °C).

**Intramolecular Dehydrogenative Oxidative Coupling of 5,5'-Diacenaphthene (7a) to Perylene Derivative 8a.** To a 10-mL three-neck round-bottom flask was charged with SCAT (0.702 g, 0.4 mmol), **7a** (61 mg, 0.2 mmol), and chlorobenzene (2 mL). A Teflon-coated stirring bar was added, and the mixture was stirred vigorously at 140 °C for 8 h under bubbling air through the mixture. The mixture was filtered, and the collected solid was washed with dichloromethane (10 mL  $\times$  5). After evaporation of the combined filtrate, short column chromatography on SiO<sub>2</sub> gave a mixture of **7a** and perylene derivative **8a** in a ratio of 62:38 with no contamination of any other products as shown by GLC. Product **8a** was identified by comparison of GLC retention time and GC-MS analysis with an authentic sample.<sup>25</sup>

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**Supporting Information Available:** Characterization (<sup>1</sup>H and <sup>13</sup>C NMR, IR, and MS) of compounds **4b–f** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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