

Mechanistic Study of Oxidative Aromatization Using Activated Carbon–Molecular Oxygen System in the Synthesis of 2-Arylbenzazoles: Focus on the Role of Activated Carbon

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Nineteen activated carbons, including sixteen tailor-made and three commercially available ones, were employed to investigate their role in the one-pot synthesis of 2-arylbenzazoles starting from 2-aminophenol, 1,2-diaminobenzene, or 2-aminobenzenethiol, and aldehyde via oxidative cyclization of intermediate phenolic Schiff base promoted by the activated carbon–molecular oxygen system. Tailor-made activated carbons were prepared from wood, coconut shell, and coal by the steam activation method or the chemical activation method. All activated carbons were characterized to clarify their properties, such as metal contaminants, specific surface area, porosity, and surface functionality. After examining their effects on reactivity in the oxidative aromatization, we found that the essential role of activated carbon in this oxidation system is concerned not with metal contaminants, specific surface area, pore volume, mean pore diameter, and surface oxygen groups evolving as CO_2 at 900 °C but with surface oxygen groups evolving as CO during heating at 900 °C, such as carbonyl groups on the surface of activated carbon. Additionally, in the synthesis of 2-arylbenzoxazole, it was found that activated carbon would also promote the cyclization of the intermediate Schiff base.

Benzazole ring moieties are often found in compounds that exhibit a variety of biological activities, including antitumor, antimicrobial, and antiviral properties.[1] In the case of 2-substituted benzoxazoles, three general methods are available for their synthesis. One is the coupling of 2-aminophenols with carboxylic acid derivatives catalyzed by strong acids or requiring microwave conditions.[2] Recently, the palladium-catalyzed coupling reactions of bromo- or iodobenzene with benzimidazole or benzoxazole were reported.[3] Another method is the oxidative cyclization of phenolic Schiff bases derived from the condensation reaction of 2-aminophenols with aldehydes. In the last reaction, various oxidants, such as DDQ,[4] $Mn(OAc)_3$,[5] $PhI(OAc)_2$,[6] $Th^+ClO_4^-$,[7] $BaMnO_4$,[8] NiO_2,[9] and $Pb(OAc)_4$,[10] have been used. However, stoichiometric or excess amounts of all these oxidants were required. Therefore, a more efficient process is strongly desired.

In response to those requirements, we developed practical and environmentally friendly one-pot syntheses of 2-arylbenzoxazoles.[11] The reactions proceeded smoothly, starting from 2-aminophenols and aldehydes under oxygen atmosphere in the presence of activated carbon using xylene as solvent. Although several dehydrogenation reactions using activated carbon as catalyst have been employed in the vapor-phase reaction of ethanol[12] and ethylbenzene,[13] ours is the first approach to the synthesis of functional molecules using activated carbon as catalyst in the liquid phase. The present activated carbon–molecular oxygen system is also applicable to the syntheses of anthracenes,[14] pyridines,[15] pyrazoles,[15] and indoles[16] by oxidative aromatization of the corresponding dihydro compounds. Benzylic oxygenation reaction of alkylarenes[17] and oxidation of secondary benzylic alcohols[18] to corresponding ketones were also performed. In this article, we will report the mechanism of this activated carbon–molecular oxygen system in the synthesis of 2-arylbenzoxazoles, with focus on the role of activated carbon.

Results and Discussion

A variety of functionalized 2-arylbenzoxazoles, 2-arylbenzimidazoles, and 2-arylbenzothiazoles were synthesized in high yields in a one-pot reaction using the activated carbon–molecular oxygen system (Scheme 1 and Table 1).[11,19] The use of activated carbon available from Tokyo Chemical Industry Co., Ltd., Shirasagi KL (Japan EnviroChemicals, Ltd.), and Darco® KB (Aldrich Inc.) are recommended. During the course of detailed study of this reaction, we found that the activated carbons had different reactivities. Therefore, we investigated the reaction mechanism, particularly the role of activated carbon.

Rate-Determining Step. To investigate which reaction step in Scheme 1 was promoted by activated carbon, several experiments were performed. First, time courses of the starting material benzaldehyde ($R^2 = H$ in **2** in Scheme 1), the intermediate 2-(benzylideneamino)phenol ($R^1 = R^2 = H$ in **3a**), and the product 2-phenylbenzoxazole ($R^1 = R^2 = H$ in **5a**) were measured by ^1H NMR analysis (Figure 1). Reactions were carried out using 0.5 mmol of 2-aminophenol ($R^1 = H$ in **1a**), 0.5 mmol of benzaldehyde ($R^2 = H$ in **2**), and 50 mg of activated carbon (Darco® KB) in *p*-xylene-d_{10} (2 mL) at 120 °C under oxygen atmosphere. Anthracene (0.1 mmol) was used as an internal standard to estimate the yield of the product by

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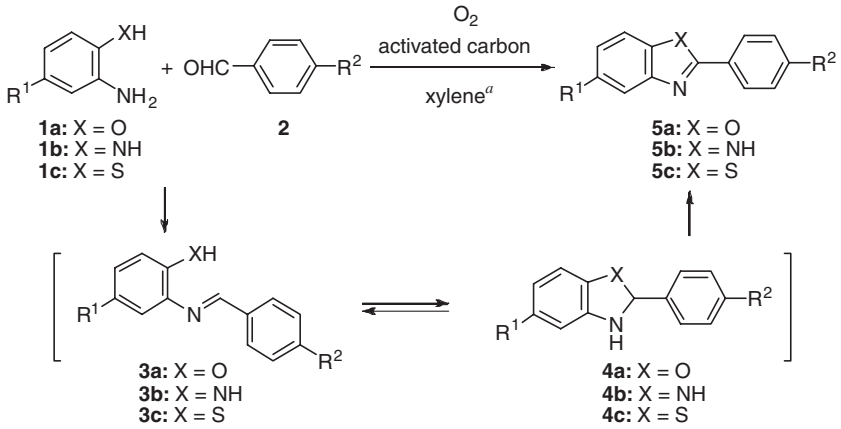
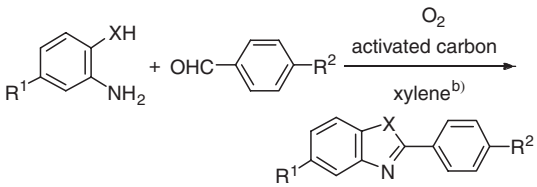


[a] *o*-, *m*-, *p*-xylene mixture.

Scheme 1. One-pot synthesis of 2-arylbenzazoles.

Table 1. One-Pot Synthesis of Various 2-Arylbenzazoles[a)]



Entry	X	R^1	R^2	Temp/°C	Time/h	Yield/%[c)]
1	O	H	H	120	4	78[d)]
2	O	H	CH_3	120	4	79[d)]
3	O	H	OCH_3	120	4	76[e)]
4	O	H	Cl	120	6	88[e)]
5	O	H	CN	120	4	87
6	O	H	NO_2	120	4	86
7	O	CH_3	H	120	4	82[d)]
8	O	NO_2	H	120	24	82
9	O	NO_2	OCH_3	120	29	67
10	O	NO_2	Cl	120	21	83
11	NH	H	H	120	2	79
12	NH	H	CH_3	120	3	60
13	NH	H	OCH_3	120	2	72
14	NH	H	Cl	120	2	67
15	NH	H	NO_2	120	2	72
16	S	H	H	50	3	79
17	S	H	CH_3	50	3	82[d)]
18	S	H	OCH_3	50	3	81[d)]
19	S	H	Cl	50	4	72
20	S	H	CN	50	4	82
21	S	H	NO_2	50	4	86

a) The ratio of 2-aminophenol, 1,2-diaminobenzene, and 2-aminobenzenethiol to aldehyde was 1:1, 1.1:1, and 1:1, respectively. As for activated carbon, one gram of Darco® KB (Aldrich Inc.) was used per 8 mmol of aldehyde for Entries 1–15 and 0.63 g of Shirasagi KL (Japan EnviroChemicals, Ltd.) was used per 5 mmol of aldehyde for Entries 16–21. b) *o*-, *m*-, *p*-xylene mixture. c) Isolated yields by recrystallization unless otherwise noted. d) Isolated yields by silica gel column chromatography. e) ^{1}H NMR analysis.

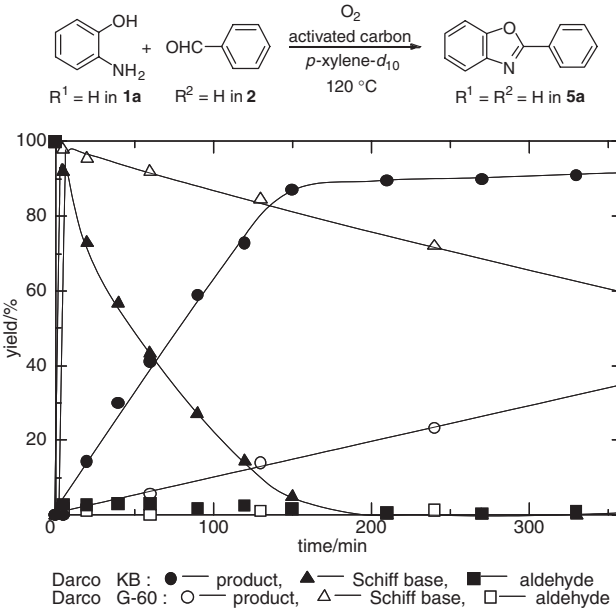


Figure 1. Time course of 2-phenylbenzoxazole, Schiff base, and aldehyde using activated carbon as catalyst. Darco® KB and G-60, which have different properties as shown in Table 2, were employed. Reactions were performed using 2-aminophenol (0.5 mmol), benzaldehyde (0.5 mmol), and activated carbon (50 mg) in *p*-xylene-d_{10} (2 mL) at 120 °C under O_2. Yields were determined by ^{1}H NMR analyses. Anthracene (0.1 mmol) was used as internal standard.

^{1}H NMR analyses. We found that Schiff base ($R^1 = R^2 = H$ in **3a**) was generated at an early stage in both reactions employing high- and low-reactivity activated carbons (Darco® KB and G-60, respectively). In addition, we found that the peak assignable to prospective cyclization product ($R^1 = R^2 = H$ in **4a**) of Schiff base ($R^1 = R^2 = H$ in **3a**) did not appear in the ^{1}H NMR spectra measured at room temperature when the reaction was incomplete. To confirm that cyclization product ($R^1 = R^2 = H$

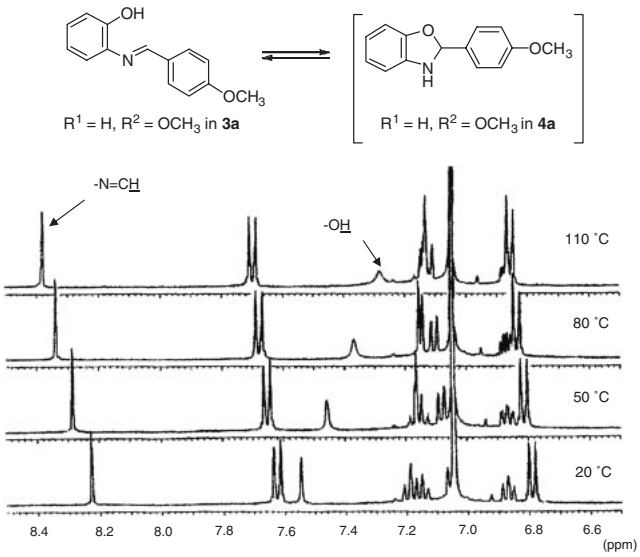


Figure 2. Temperature effect on ^{1}H NMR spectrum of intermediate 2-[(4-methoxybenzylidene)amino]phenol ($R^1 = H$ and $R^2 = OCH_3$ in **3a** in Scheme 1).

in **4a**) was produced, a >C–H peak should appear at around 6 ppm instead of the 8.23 ppm peak that was assignable to –N=C–H.

Next, to investigate the effect of temperature we measured ^{1}H NMR spectra of the intermediate 2-[(4-methoxybenzylidene)amino]phenol ($R^1 = H$ and $R^2 = OCH_3$ in **3a** in Scheme 1) in *p*-xylene-d_{10} at 20, 50, 80, and 110 °C, respectively. As shown in Figure 2, cyclization product ($R^1 = H$ and $R^2 = OCH_3$ in **4a**) was not detected in all cases. On the other hand, cyclization products **4c** was detected in the ^{1}H NMR spectra even at room temperature (see Supporting Information). Thus, we concluded that in the reaction of **1a** with **2**, the equilibrium preferred Schiff base **3a** to cyclization product **4a** even at 110 °C without activated carbon because the nucleophilicity of O is less than that of S. Based on these results, activated carbon would promote not only the dehydrogenation step (**4a** → **5a**) but also the cyclization step (**3a** → **4a**).

Role of Activated Carbon: Investigation of the Effect of Metal Contaminants. We investigated the role of activated carbon in the reaction of 2-aminophenol ($R^1 = H$ in **1a** in Scheme 1) with 4-methoxybenzaldehyde ($R^2 = OCH_3$ in **2**) via oxidative cyclization of intermediate 2-[(4-methoxybenzylidene)amino]phenol ($R^1 = H$ and $R^2 = OCH_3$ in **3a**). First, we examined the effect of metal contaminants in activated carbon on reactivity in the oxidative aromatization, employing six tailor-made activated carbons (samples A to F). These activated carbons were made from wood (sample A), coal (sample B), and coconut shell (samples C, D, E, and F). As for the activation method, we used two methods: one was chemical activation using $ZnCl_2$ (samples A, E, and F) and the other was steam activation (samples B, C, and D).

Samples A–F were treated with 3% HCl aq for 10 min and then with water ten times with boiling. The reaction yields using unwashed activated carbons (samples A to F) were compared with those using washed activated carbons (samples A′ to F′), respectively. Metal contaminants in activated carbon, such as Zn, Co, Mn, Fe, Cr, Mg, V, Cu, Pd, Ca, Na, and K, were measured by ICP-AES in washed and unwashed samples. We confirmed that the amounts of those metal contaminants decreased after washing (concerning the contents and amounts of metal contaminants, see Supporting Information). The yields of 2-(4-methoxyphenyl)benzoxazole ($R^1 = H$ and $R^2 = OCH_3$ in **5a**) using washed activated carbons were higher than those using unwashed activated carbons (Figure 3). Therefore, we concluded that the driving factor of this oxidation system was not the metal contaminants in activated carbon but other factors. The reason why washed activated carbons exhibited higher yields than unwashed activated carbons will be discussed in the next section.

Role of Activated Carbon: Investigation of the Effects of Specific Surface Area, Pore Volume, Mean Pore Diameter, and Surface Functionality. Then, we investigated the role of activated carbons in the reaction of 2-aminophenol ($R^1 = H$ in **1a** in Scheme 1) with 4-methoxybenzaldehyde ($R^2 = OCH_3$ in **2**) via oxidative cyclization of intermediate 2-[(4-methoxybenzylidene)amino]phenol ($R^1 = H$ and $R^2 = OCH_3$ in **3a**). To examine the effects of specific surface area, pore volume, mean pore diameter, and surface functionality, we employed nineteen activated carbons, including sixteen tailor-made activated carbons (Entries 1–16 in Table 2) and three commercially available activated carbons (Entries 17–19). These activated carbons were obtained by using different raw materials and activation methods, and therefore, they have different specific surface areas, pore volumes, mean pore diameters, and surface oxygen group contents and amounts, as summarized in Table 2. Specific surface area was measured using the Brunauer–Emmett–Teller (BET) method[20,21a,21c] with nitrogen gas as adsorbate. Pore volume and mean pore diameter were calculated according to the Cranston–Inkley (CI) method[20,21a,21b] from the volume of adsorbed N_2. Oxygen content was determined by GC measurement of evolved gases, such as CO and CO_2, at 900 °C, which originated in decomposed surface oxygen groups of 1 g of activated carbon.

Figure 4 shows the relationship between the properties of activated carbons and the yields in oxidative aromatization. It is clear that chemically activated carbons (filled symbols ● and ■ in Figure 4) had higher reactivity than steam-activated carbons (unfilled symbols ○, □, and △ in Figure 4). Then, we turned our attention to surface oxygen groups because the chemical activation method was usually conducted at a lower temperature than the steam activation method and thus more surface oxygen groups remained on the surface of activated carbons obtained by the former method. As shown in Figure 4f, surface oxygen groups that evolved as CO have the best tendency to increase reaction yields among all the properties examined. The total oxygen amounts evolved as CO and CO_2 and the oxygen amounts evolved as CO_2 did not have a strong relationship with the reaction yields (Figures 4d and 4e). Here, CO would be derived from phenol, carbonyl, and quinone groups, and CO_2 would be derived from carboxyl and lactone groups that existed on original activated carbon surfaces.[20,21a] Specific surface area, pore volume, and mean pore diameter appeared to be little related to the reaction yield (Figures 4a, 4b, and 4c).

Furthermore, to confirm the effect of oxygen groups evolved as CO, the reaction was performed using activated carbon

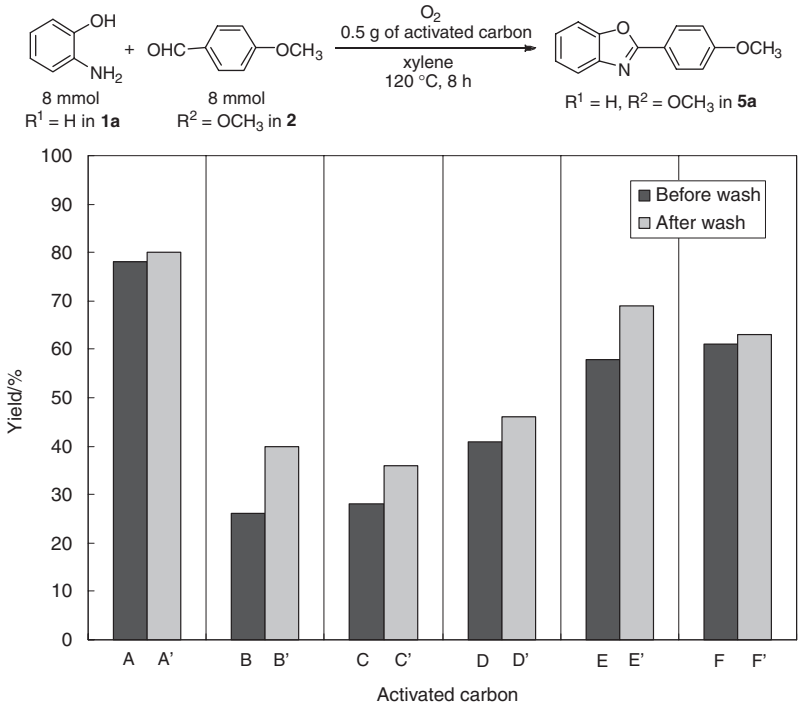


Figure 3. Reaction yields using washed and unwashed activated carbons.

Table 2. Properties of Activated Carbons

Entry	Sample[a)]	Activation method	Material	$S^{b)}$ /$m^2\,g^{-1}$	$V^{c)}$ /mL g^{-1}	$D^{d)}$ /nm	O-CO[e)] /mg g^{-1}	O-CO_2[e)] /mg g^{-1}	O-Total[e)] /mg g^{-1}
1	A	$ZnCl_2$	Wood	1455	1.310	3.60	31.3	17.0	48.3
2	A′	$ZnCl_2$	Wood	1446	1.294	3.58	32.4	14.0	46.4
3	B	Steam	Coal	1042	0.541	2.08	15.0	7.4	22.4
4	B′	Steam	Coal	1038	0.536	2.06	17.7	6.6	24.3
5	C	Steam	Coconut shell	1230	0.553	1.80	12.2	5.7	17.9
6	C′	Steam	Coconut shell	1251	0.567	1.81	16.6	6.1	22.8
7	D	Steam	Coconut shell	1640	0.776	1.89	15.0	6.5	21.5
8	D′	Steam	Coconut shell	1640	0.777	1.90	20.0	6.0	26.0
9	E	$ZnCl_2$	Coconut shell	1413	0.742	2.10	29.3	15.7	45.0
10	E′	$ZnCl_2$	Coconut shell	1400	0.730	2.09	39.6	18.7	58.3
11	F	$ZnCl_2$	Coconut shell	1279	0.569	1.78	31.1	11.8	42.9
12	F′	$ZnCl_2$	Coconut shell	1300	0.589	1.81	34.7	12.4	47.1
13	G	Steam	Wood	1033	0.603	2.34	22.6	26.2	48.8
14	H	Steam	Wood	995	0.575	2.31	19.9	27.7	47.6
15	I	$ZnCl_2$	Wood	1111	1.007	3.63	37.1	35.3	72.5
16	J	$ZnCl_2$	Wood	991	0.803	3.24	43.4	42.6	86.1
17	Darco KB	H_3PO_4	Wood	1474	1.260	3.42	29.9	11.9	41.8
18	Darco KB-B	H_3PO_4	Wood	1505	1.313	3.49	30.8	14.3	45.2
19	Darco G60	Steam	Coal	964	0.625	2.60	13.5	7.3	20.8

a) X′ indicates sample X that was treated with 3% HCl aq for 10 min and then with water ten times with boiling. b) Specific surface area. c) Pore volume. d) Mean pore diameter. e) Amount of oxygen calculated from the amount of CO and/or CO_2 gas that evolved from 1 g of corresponding activated carbon at 900 °C.

whose surface oxygen groups were removed at 850 °C under nitrogen atmosphere. As shown in Table 3, the yield was low compared with that of the original activated carbon. This result is evidence that surface oxygen groups evolved as CO during the heating to 850 °C play an important role in the present oxidative aromatization. One of the reasons why the reaction gradually proceeded would be that molecular oxygen regenerated active surface oxygen groups and/or some effective surface oxygen groups remained in spite of the heat treatment at 850 °C. Similarly, washed activated carbons (in the previous section) might promote this reaction more efficiently than unwashed activated carbons because of the increase in the number of surface oxygen groups evolved as CO at 900 °C (Table 2 and Figures 3 and 4).

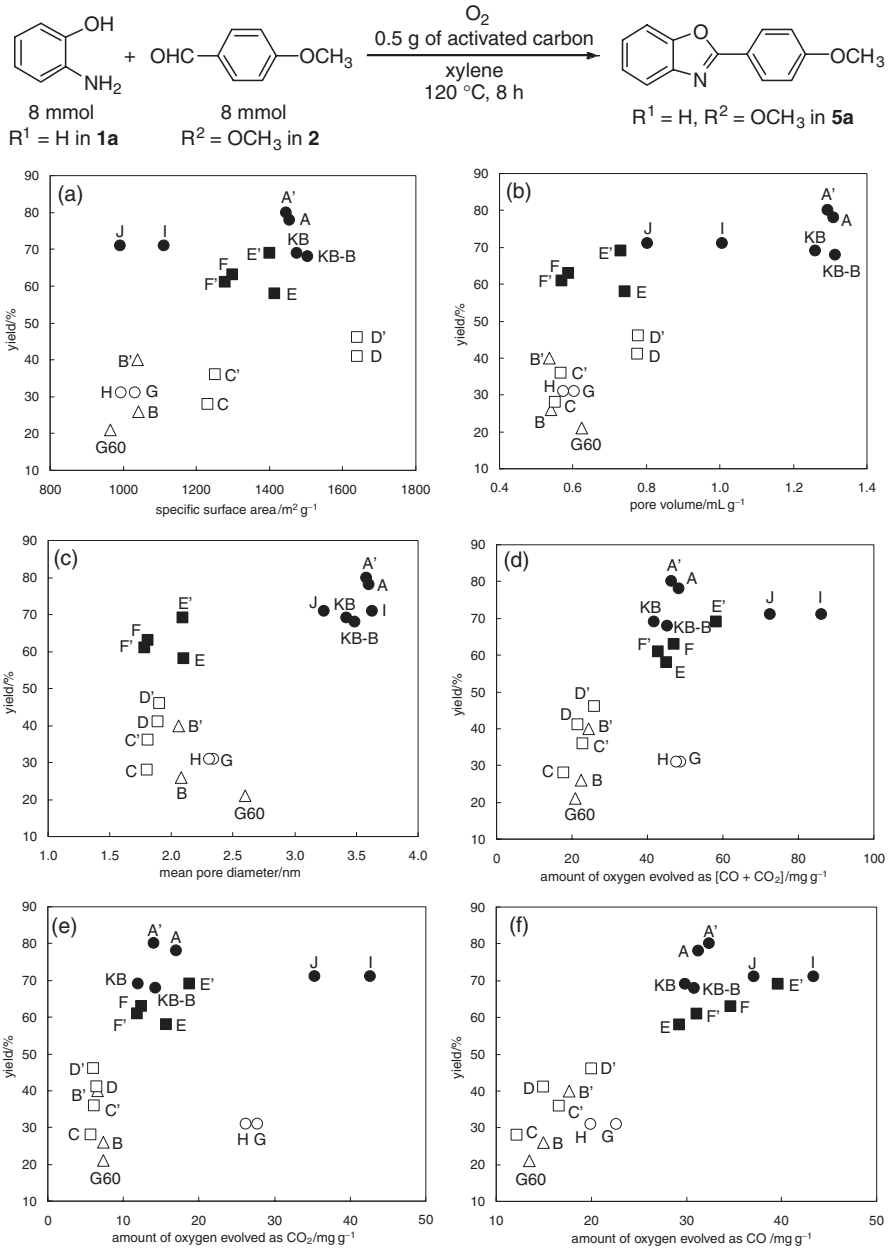


Figure 4. Effect of properties of activated carbons listed in Table 2 on reaction yields. (a) Specific surface area, (b) pore volume, (c) mean pore diameter, (d) amount of oxygen evolved as [CO + CO_2], (e) amount of oxygen evolved as CO_2, and (f) amount of oxygen evolved as CO. ●: Chemical activation (wood), ■: chemical activation (coconut shell), ○: steam activation (wood), □: steam activation (coconut shell), and △: steam activation (coal).

Conclusion

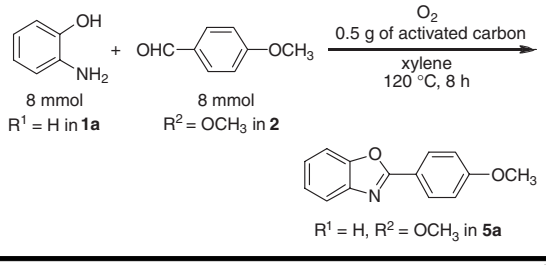
Functionalized 2-arylbenzoxazoles, 2-arylbenzimidazoles, and 2-arylbenzothiazoles were synthesized via oxidative aromatization of their dihydro compounds using the activated carbon–molecular oxygen system. Detailed mechanistic studies revealed that surface oxygen groups evolving as CO, such as carbonyl groups on the surface of activated carbon, promoted the dehydrogenation step in this activated carbon–molecular oxygen system. Additionally, in the synthesis of 2-arylbenzoxazoles, activated carbon would also promote the cyclization of intermediate Schiff base. It should be mentioned that recovery and reuse of activated carbon were available.

Experimental

Syntheses of 2-Arylbenzoxazoles (Table 1, Entry 1). A mixture of 2-aminophenol (873 mg, 8 mmol), benzaldehyde (849 mg, 8 mmol), and Darco® KB (1 g) in xylene (15 mL) was placed in a 100-mL three-necked flask under oxygen atmosphere and stirred at 120 °C for 4 h. Then, the reaction mixture was filtered using Celite. After concentration of the filtrate, the product was isolated by silica gel column chromatography to give a pale yellow crystalline solid (1.2 g, 78%).

Syntheses of 2-Arylbenzimidazoles (Table 1, Entry 11). A mixture of 1,2-diaminobenzene (952 mg, 8.8 mmol) and Darco® KB (1 g) in xylene (10 mL) was placed in a 100-mL three-necked flask under oxygen atmosphere and stirred at 120 °C. After 0.5 h,

Table 3. Effect of Surface Oxygen Groups



Entry	Activated carbon	Yield/%[a)]
1	Sample K[b)]	91
2	Pre-treated sample K[c)]	41

a) ^{1}H NMR analyses after silica gel column chromatography. b) Oxygen amount evolved as CO and CO_2 is 32.1 mg g^{-1} and 15.6 mg g^{-1}, respectively. c) Surface oxygen group was removed at 850 °C under nitrogen atmosphere. Oxygen amount evolved as CO and CO_2 is 15.3 mg g^{-1} and 13.0 mg g^{-1}, respectively.

benzaldehyde (849 mg, 8 mmol) in xylene (5 mL) was added slowly at the rate of 0.1 mL s^{-1} with stirring for 2 h. Then, the reaction mixture was filtered using Celite. After concentration of the filtrate, the desired product was isolated by recrystallization to give a yellow crystalline solid (1.2 g, 79%).

Syntheses of 2-Arylbenzothiazoles (Table 1, Entry 16). A mixture of 2-aminobenzenethiol (505 mg, 5 mmol), benzaldehyde (531 mg, 5 mmol), and Shirasagi KL (625 mg) in xylene (8 mL) was placed in a 100-mL three-necked flask under oxygen atmosphere and stirred at 50 °C for 3 h. Then, the reaction mixture was filtered using Celite. After concentration of the filtrate, the product was isolated by silica gel column chromatography to give a pale yellow crystalline solid (0.84 g, 79%).

Preparation of Sample A (Table 2, Entry 1). To 50 g of dry wood flour, 140 g of 60% $ZnCl_2$ aq was added, mixed well, and placed in a crucible, which was then covered with a lid. This was placed in an electric furnace and was heated from 100 to 250 °C over 2 h and from 250 to 550 °C over 1 h, held at that temperature for 30 min, and then cooled. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample A was obtained.

Preparation of Sample B (Table 2, Entry 3). Daxi coal produced in Shanxi Province, China was used as a raw material. This charcoal was pulverized and regulated to a particle diameter within the range of from 2.36 to 1.18 mm. It was heated to 350–550 °C over 1 h and then was subjected to stream activation at 850 °C for 5 h. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample B was obtained.

Preparation of Sample C (Table 2, Entry 5). Coconut shell was pulverized and regulated to a particle diameter within the range of from 2.36 to 1.18 mm. It was heated to 350–550 °C over 1 h and then was subjected to stream activation at 850 °C for 3 h. This was placed in a washing vessel with filter cloth and 2% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample C was obtained.

Preparation of Sample D (Table 2, Entry 7). Coconut shell was pulverized and regulated to a particle diameter within the range of from 2.36 to 1.18 mm. It was heated to 350–550 °C over 1 h and then was subjected to stream activation at 850 °C for 4 h. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample D was obtained.

Preparation of Sample E (Table 2, Entry 9). To 50 g of dry wood flour, 83 g of 60% $ZnCl_2$ aq was added, mixed well, and placed in a crucible, which was then covered with a lid. This was placed in an electric furnace and was heated from 100 to 250 °C over 2 h and from 250 to 550 °C over 1 h, held at that temperature for 30 min, and then cooled. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample E was obtained.

Preparation of Sample F (Table 2, Entry 11). To 50 g of dry wood flour, 50 g of 60% $ZnCl_2$ aq was added, mixed well, and placed in a crucible, which was then covered with a lid. This was placed in an electric furnace and was heated from 100 to 250 °C over 2 h and from 250 to 550 °C over 1 h, held at that temperature for 30 min, and then cooled. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 0.25 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample F was obtained.

Preparation of Samples A′, B′, C′, D′, E′, and F′ (Table 2, Entries 2, 4, 6, 8, and 12). Samples A, B, C, D, E, and F were boiled with 3% HCl aq for 10 min, respectively. Each sample was cooled, filtrated, and then the residue was boiled with water ten times. Subsequently they were filtrated and dried in an electric dryer held at 115 ± 5 °C. Then samples A′, B′, C′, D′, E′, and F′ were obtained, respectively.

Preparation of Sample G (Table 2, Entry 13). Commercially available steam-activated carbon flour (made in Japan), steam-activated carbon flour (made in Southeast Asia), and $ZnCl_2$ activated carbon flour were mixed in the ratio of 4:5:1. 600 g of the mixture was stirred with 6 L of 2% HNO_3 aq for 2 h at 50 °C. This was placed in a washing vessel with filter cloth. Subsequently, the residue was washed with water at 50 °C at a rate of 2.5 L h^{-1} for 24 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. Thus, sample G was obtained.

Preparation of Sample H (Table 2, Entry 14). Commercially available steam-activated carbon flour (made in Southeast Asia) and $ZnCl_2$-activated carbon flour were mixed in the ratio of 9:1. 600 g of the mixture was stirred with 6 L of 2% HNO_3 aq for

2 h at 50 °C. This was placed in a washing vessel with filter cloth. Subsequently, the residue was washed with water at 50 °C at a rate of 2.5 L h^{-1} for 24 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. Thus, sample H was obtained.

Preparation of Sample I (Table 2, Entry 15). Commercially available steam activated carbon derived from wood (made in Southeast Asia) 600 g was stirred with 6 L of 2% HNO_3 aq for 4 h at 75 °C. This was placed in a washing vessel with filter cloth. Subsequently, the residue was washed with water at 50 °C at a rate of 2.5 L h^{-1} for 24 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample I was obtained.

Preparation of Sample J (Table 2, Entry 16). Commercially available steam activated carbon derived from wood (made in Southeast Asia) 600 g was stirred with 6 L of 2.5% HNO_3 aq for 4 h at 75 °C. This was placed in a washing vessel with filter cloth. Subsequently, the residue was washed with water at 50 °C at a rate of 2.5 L h^{-1} for 24 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample I was obtained.

Preparation of Sample K (Table 3, Entry 1). To 500 g of dry wood flour, 2.3 kg of 60% $ZnCl_2$ aq was added, mixed well, and placed in a crucible. This was placed in an electric furnace and was heated from 100 to 250 °C over 2 h and from 250 to 550 °C over 1 h, held at that temperature for 1 h, and then cooled. This was placed in a washing vessel with filter cloth and 8% HCl aq was added thereto. Stirring and washing were continued for 2 h and then the water was drained off. Subsequently, the residue was washed with water at 50 °C at a rate of 2.5 L h^{-1} for 4 h. The washed activated carbon was dried in an electric dryer held at 115 ± 5 °C. The dried activated carbon was pulverized with a ball mill. Thus, sample K was obtained.

Preparation of Pre-Treated Sample K (Table 3, Entry 2). 200 g of sample K (before ball milling) was placed in 6-L rotary type electronic funnel held at 850 °C.

The cooled activated carbon was pulverized with a ball mill. Thus, sample K′ was obtained.

Experiments to Investigate the Role of Activated Carbon. The yields of the synthesis of 2-(4-methoxyphenyl)benzoxazole were used to compare the properties of activated carbons. The reaction was carried out as follows. A mixture of 2-aminophenol (8 mmol), 4-methoxybenzaldehyde (8 mmol), and the corresponding activated carbon (500 mg) in xylene (15 mL) was placed in a 100-mL three-necked flask under oxygen atmosphere and stirred at 120 °C for 8 h. Then, the reaction mixture was filtered using Celite. After concentration of the filtrate, the mixture of the desired product, the intermediate Schiff base, and the aldehyde was obtained by silica gel column chromatography and the yield was determined by ^{1}H NMR analysis.

The amounts of metal contaminants, such as Zn, Co, Mn, Fe, Cr, Mg, V, Cu, Pd, Ca, Na, and K were measured by ICP-AES (Varian Liberty Series II). Specific surface area was measured using the Brunauer–Emmett–Teller (BET) method[20,21a,21c] with nitrogen gas as adsorbate by using ASAP2400 (Micromeritics). Pore volume and mean pore diameter were calculated according to the Cranston–Inkley (CI) method[20,21a,21b] from the volume of adsorbed N_2. Measurement of the amount of surface oxygen groups was carried out by GC after wet gas meter analysis of 25 L desorbed gas at 900 °C (See Supporting Information).

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Supporting Information

Experimental procedure and compound characterization data. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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