

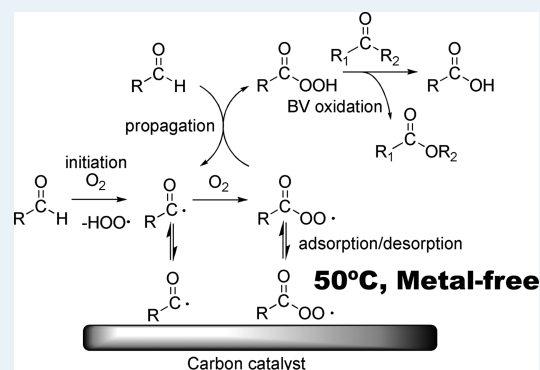
# Catalysis by Carbon Materials for the Aerobic Baeyer–Villiger Oxidation in the Presence of Aldehydes

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**ABSTRACT:** Aerobic Baeyer–Villiger oxidation of ketones to corresponding esters was performed using metal-free carbon as a solid catalyst and benzaldehyde as the sacrificing agent. Several carbon materials were tested for the oxidation of cyclohexanone to  $\epsilon$ -caprolactone, and it was found that Ketjen Black showed the highest catalytic activity, over 90% of  $\epsilon$ -caprolactone yield at 50 °C. A catalyst recycling test suggests that the catalyst has high durability under the reaction condition of oxygen atmosphere at 50 °C. Mechanistic study suggests that peracid species produced by a series of chain propagation reactions is the key intermediate, and the carbon catalyst contributes to high aldehyde efficiency by buffering the radical species, which are essential for the chain propagation reactions.

**KEYWORDS:** partial oxidation, oxygen reduction, peracid, cyclohexanone,  $\epsilon$ -caprolactone



## INTRODUCTION

Aerobic oxidations of hydrocarbons with heterogeneous catalysts are quite attractive and challenging chemical reactions from an industrial viewpoint. Although numerous efforts have been made to use oxygen in air as the oxidant, reducing agents such as hydrogen have been sometimes utilized as a sacrificing agent because the real aerobic oxidation with oxygen generally suffers from an extremely low reaction rate. When this type of reducing reagent is used, one oxygen atom from  $O_2$  oxidizes the reactant, whereas the other is reduced by the sacrificing agent.<sup>1–6</sup> This type of reaction is similar to enzymatic reactions such as cytochrome P-450. As to the Baeyer–Villiger type oxidation, which is a valuable reaction to oxidize a ketone to an ester directly,<sup>7–12</sup> several examples have been demonstrated in homogeneous<sup>2,3</sup> and heterogeneous<sup>4–8</sup> catalytic systems in the presence of aldehydes as a sacrificing agent. This  $O_2$ /aldehyde oxidation system will be quite attractive, since this can avoid using explosive peracetic acid as the oxidizing agent, which has been common in current industrial processes and requires expensive protection. However, these reported  $O_2$ /aldehyde systems require metal-containing catalysts with large amounts of sacrificing agents over the stoichiometric ratio (e.g., 3 equiv). If the catalysts become metal-free, and if the efficiency of the sacrificing agent becomes higher, the system will become more attractive and environmentally friendly.

Recently, our research group has been interested in the catalysis of carbon materials. Carbon materials such as activated carbon have been largely used as catalytic support for metal species in numerous industrial catalytic processes. However, quite recently, the catalytic activity of carbon materials

themselves has received a great deal of attention. For instance, Hayashi reported the aerobic oxidation of benzylic alcohols to ketones over activated carbon.<sup>13</sup> We have developed new catalytic systems with carbon-based catalysts for the aerobic oxidation of alcohols.<sup>14–16</sup>

Although the majority of the reported carbon-catalyzed systems so far have focused on alcohol oxidation, our present interest is to apply these simple and attractive catalytic systems to a wider range of reactants. In this context, we hereby report aerobic Baeyer–Villiger oxidation of ketones to the corresponding esters using metal-free carbon as a solid catalyst. This system can avoid the use of transition metals and explosive peracids; therefore, it could establish quite environmentally friendly and safe oxidation systems. The mechanism of the catalysis in this system is discussed on the basis of the results of controlled experiments utilizing NMR and FT-IR. We believe that the present finding is quite unique since such catalysis by carbon materials has not been reported so far.

## RESULTS AND DISCUSSION

**Catalytic Performance of Carbon Materials.** The catalysis of the carbon materials for the Baeyer–Villiger type oxidation was examined by performing the oxidation of cyclohexanone to  $\epsilon$ -caprolactone in the presence of benzaldehyde. A silica catalyst (JRC-SIO-9, the Catalysis Society of Japan) was also tested for comparison. Table 1 summarizes the

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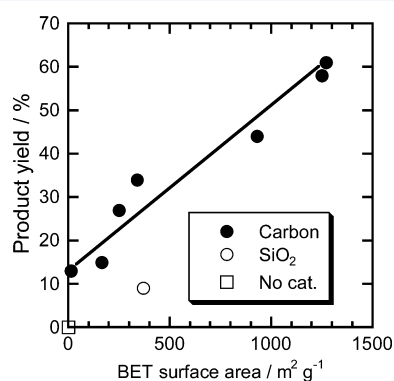
**Table 1. Cyclohexanone Oxidation over Various Carbon Materials in the Presence of Benzaldehyde<sup>a</sup>**

carbon	BET surface area(m <sup>2</sup> /g)	conv (%) <sup>b</sup>	caprolactone yield (%) <sup>b</sup>	sel (%) <sup>b</sup>	benzaldehyde conv (%) <sup>b</sup>	benzaldehyde efficiency <sup>c</sup>
Norit SX Plus	930	44	44	>99	55	0.79
XC72	250	27	27	>99	38	0.70
Ketjen Black	1270	61	61	>99	84	0.73
Ketjen Black_aw	1250	58	57	98	83	0.68
VGCF	13	13	13	>99	31	0.42
N-doped carbon	340	34	34	>99	46	0.73
B-doped carbon	165	15	15	>99	18	0.83
SiO <sub>2</sub>	370	11	9	82	13	0.69
No Cat.		<1	<1		<1	

<sup>a</sup>General conditions: cyclohexanone, 4.0 mmol; benzaldehyde, 4.0 mmol; carbon catalyst, 5 mg; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C; 4 h.

<sup>b</sup>Conversion, selectivity, and yield were calculated by GC/MS measurement based on the internal standard method (dodecane). <sup>c</sup>Calculated using (yield of  $\epsilon$ -caprolactone)/(conversion of benzaldehyde).

results of the cyclohexanone oxidation under oxygen atmosphere at 50 °C. All carbon materials tested in this study showed clear catalytic activity for the cyclohexanone oxidation. Ketjen Black showed the highest conversion, 61%, under this experimental condition, whereas the blank run without catalyst resulted in quite poor conversion, less than 1%. It should be noted that over 98%, quite high selectivity, to  $\epsilon$ -caprolactone was achieved with all tested carbon materials. The benzaldehyde efficiencies were in the range of 0.7–0.8, except for the case with VGCF. The conversion values from these experiments are plotted in Figure 1 against the BET surface



**Figure 1.** The effect of the BET surface area on the catalytic performance for cyclohexanone oxidation.

area. This plot suggests that the catalytic activity for the cyclohexanone oxidation shows a good correlation with the BET surface area. One might wonder if any high surface area

materials catalyze this type of reaction; however, the poor catalytic activity by the silica catalyst suggests that the observed catalytic activity relies on the carbon surface. Nitrogen- and boron-doped carbon materials were also tested because this type of alloying has been reported to catalyze oxygen reduction;<sup>17,18</sup> however, under the present reaction conditions for the cyclohexanone oxidation, these doped carbon materials do not seem to have a particular advantage compared with the other undoped carbon materials. Transition metal impurities might affect the catalytic performance because carbon blacks are known to contain metal impurities, such as Fe. Ketjen Black was washed with HCl repeatedly until the yellowish filtrate turn into clear, and the washed carbon (Ketjen Black aw) was used for the catalytic reaction. Such washed carbon also shows a similar catalytic performance; therefore, it is unlikely that transition metal impurities are responsible for the present catalytic performance.

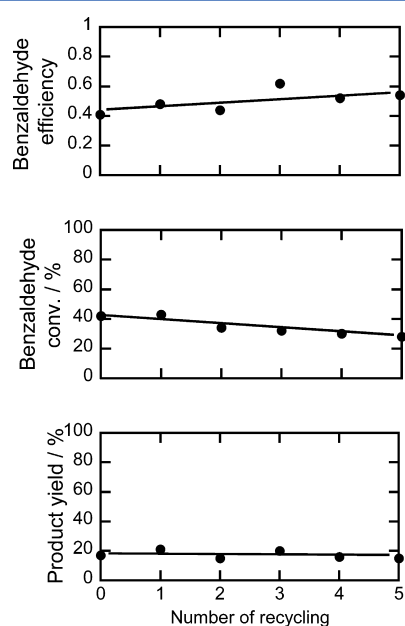
Table 2 summarizes the cyclohexanone oxidation over Ketjen Black in the presence of several different aldehydes. Benzaldehyde showed the best performance in the tested aldehyde so far. It should be noted that the product yield reaches over 90% when 1.5 equiv of benzaldehyde is used. This aldehyde efficiency is higher than those in previously reported studies because typical reported work used over 3 equiv of aldehyde.<sup>2–8</sup> *m*-Chlorobenzaldehyde, whose peracid from (*m*-chloroperoxybenzoic acid) is a typical oxidizing agent for the Baeyer–Villiger oxidation, also works as the sacrificing agent with the carbon catalyst. Considering the commercial availability of aldehyde, it is meaningful that acetaldehyde indeed works as the sacrificing agent in this oxidation system, although the reaction performance is not as good as that with benzaldehyde.

**Table 2. Cyclohexanone Oxidation over Ketjen Black in the Presence of Various Aldehydes<sup>a</sup>**

catalyst	aldehyde	equiv amt	conv (%) <sup>b</sup>	product yield (%) <sup>b</sup>	sel (%) <sup>b</sup>	aldehyde conv (%) <sup>b</sup>	aldehyde efficiency <sup>c</sup>
Ketjen Black	benzaldehyde	1	65	65	>99	83	0.77
		1.5	91	91	>99	87	0.69
		1	2	2	81	3	0.66
		3	28	19	68	32	0.20
Ketjen Black	<i>m</i> -chloro- benzaldehyde	1	49	44	90	86	0.51
		2	1	1	69	18	0.08
Ketjen Black	acetaldehyde	2	58	47	81	88	0.27
			trace			trace	

<sup>a</sup>General conditions: cyclohexanone, 4.0 mmol; Ketjen Black, 5 mg (if used); 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C; 6 h. <sup>b</sup>Conversion, selectivity, and yield were calculated by GC/MS measurement based on the internal standard method (dodecane). <sup>c</sup>Calculated on the basis of (yield of  $\epsilon$ -caprolactone)/(conversion of benzaldehyde).

Durability is a quite important property to consider for this series of materials as solid catalysts. Recycling tests were carried out by repeating the catalytic reaction after separating the catalyst powder from the reactants and products. Figure 2















**Figure 2.** The results of the recycling test of the carbon catalyst (Ketjen Black) for the cyclohexanone oxidation.

shows the catalytic activities of the carbon catalyst after each recycling test. The product yield did not show any obvious

degradation, even after five runs of catalytic reaction. This suggests that stability of this catalyst is good enough to work continuously in the present reaction condition. Interestingly, the benzaldehyde efficiency increased as the reaction was repeated. This might be due to an aging effect by this oxidation reaction. The fresh carbon surface would contain a considerable amount of ketone groups and could be oxidized to lactones under the present reaction conditions, and some of the benzaldehyde might have been consumed to oxidize the carbon surface.

The present oxidation system could be attractive if it can be applied to various ketones. Table 3 shows the Baeyer–Villiger type aerobic oxidation of various ketones in the presence of Ketjen Black and benzaldehyde. Cyclohexanone, 2-methylcyclohexanone, and 2-adamantanone were successfully oxidized with high selectivity and high benzaldehyde efficiency (entries 1, 2, 5). Other ketones—2,6-dimethylcyclohexanone, pentanone, and pinacol—were also oxidized under the same conditions, although the product yield and benzaldehyde efficiency were lower than those of cyclohexanone (entries 3, 4, 6). The stereochemistry and reactivity seem to follow the tendency reported in other literature for the Baeyer–Villiger type oxidation.<sup>4,5</sup> From asymmetrical ketone, the product arising from preferential migration of the more substituted carbon atom was selectively obtained. Note that an acyclic aliphatic ketone, such as pinacol, was certainly oxidized, whereas no oxidation product was observed in a previously reported catalytic system.<sup>5</sup> Although the reaction rate depends on the chemical structure of ketones, it can be concluded that the carbon catalysts can oxidize various ketones to corresponding lactones or esters under such mild reaction conditions.

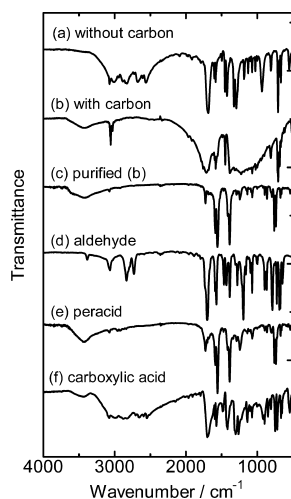
**Table 3.** Oxidation of Various Ketones over Ketjen Black in the Presence of Benzaldehyde

Entry	Substrate	Product	Conv. [%] <sup>[b]</sup>	Product Yield [%] <sup>[b]</sup>	Sel. [%] <sup>[b]</sup>	Benzaldehyde Conv. [%] <sup>[b]</sup>	Benzaldehyde Efficiency <sup>[c]</sup>
1			65	65	>99	83	0.77
2			75	71	95	99	0.71
3			38	29	76	95	0.30
4			80	42	53	98	0.43
5			67	65	97	92	0.71
6			31	31	>99	99	0.31

<sup>a</sup>General conditions: substrate, 4.0 mmol; benzaldehyde, 4.0 mmol; Ketjen Black, 5 mg; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C; 6 h. <sup>b</sup>Conversion, selectivity, and yield were calculated by GC/MS measurement based on the internal standard method (dodecane). <sup>c</sup>Efficiency was calculated using (yield of product)/(conversion of benzaldehyde).

**Catalytic Mechanism.** It is quite important to understand the reaction mechanism of the Baeyer–Villiger type oxidation catalyzed by carbon materials. The generally accepted reaction scheme for the O<sub>2</sub>/aldehyde oxidation system consists of two reaction steps: (a) peracid formation from aldehyde and O<sub>2</sub> and (b) the oxidation of the reactant by the peracid.<sup>2,3</sup> From the viewpoint of the catalytic mechanism, it is meaningful to know which reaction step is enhanced by the catalysts. For instance, Murahashi et al. reported Baeyer–Villiger oxidation catalyzed by Fe<sub>2</sub>O<sub>3</sub> in the presence of benzaldehyde<sup>2</sup> and proposed that Fe<sub>2</sub>O<sub>3</sub> enhances the formation of acylperoxy radical, which is the key intermediate. In contrast, Ueno et al. reported the same oxidation catalyzed by alumina-containing hydrotalcite<sup>4</sup> and proposed that the hydrotalcite enhances the ketone oxidation by peracid. We hereby discuss which reaction step is catalyzed by the carbon catalysts.

To clarify whether the peracid is the reaction intermediate, we tried confirming peracid formation from aldehyde and O<sub>2</sub> under the present reaction conditions. *m*-Chlorobenzaldehyde was treated under the same reaction conditions as the catalytic performance tests, whereas ketone was absent, and the residue was analyzed by FTIR after removing the solvent. Figure 3



**Figure 3.** FTIR spectra of (a) *m*-chlorobenzaldehyde treated without carbon, (b) *m*-chlorobenzaldehyde treated with Ketjen Black, (c) purified sample from sample b, (d) *m*-chlorobenzaldehyde, (e) *m*-chloroperoxybenzoic acid, and (f) *m*-chlorobenzoic acid. Treatment conditions: *m*-chlorobenzaldehyde, 4.0 mmol; Ketjen Black, 5 mg; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C; 4 h.

shows the FTIR spectra of the treated samples with and without Ketjen Black. Reference compounds (*m*-chlorobenzaldehyde, *m*-chloroperoxybenzoic acid, and *m*-chlorobenzoic acid) were also measured for comparison. Sample a, treated without carbon, seems to be *m*-chlorobenzoic acid showing several characteristic peaks: 2100–3300 cm<sup>-1</sup> (broadband, O–H stretch, H-bonded) and 1687 cm<sup>-1</sup> (C=O stretch). On the other hand, sample b, treated with the carbon catalyst, seems a kind of mixture. Sample b was then washed with NaHCO<sub>3</sub> aq and recrystallized in a CH<sub>2</sub>Cl<sub>2</sub> and hexane solution. The spectrum of this purified sample c corresponds to that of *m*-chloroperoxybenzoic acid, showing several characteristic peaks: 3420 (O–H stretch) and 1726 cm<sup>-1</sup> (C=O stretch). Therefore it is clearly evidenced that *m*-chloroperoxybenzoic acid is formed during the ketone oxidation by the O<sub>2</sub>/aldehyde oxidation system in the presence of the carbon catalyst. The

same purification procedure was applied to sample a, but no crystallization was observed. Thus, it could be concluded that carbon materials catalyze the formation of peracid from O<sub>2</sub> and aldehyde.

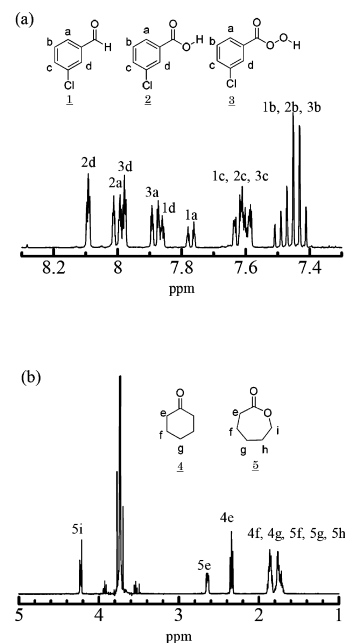
The next point of interest is whether the carbon catalysts enhance the ketone oxidation by the peracid. To clarify this, the oxidation of cyclohexanone by *m*-chloroperoxybenzoic acid was performed with and without a carbon catalyst; the results are summarized in Table 4. The experimental results clearly suggest that the carbon catalyst did not contribute to the ketone oxidation once peracid existed in the system.

**Table 4.** Cyclohexanone Oxidation by *m*-Chloroperoxybenzoic Acid

catalyst	conv (%)	yield (%)	sel (%)
Ketjen Black	56	56	>99
no catalyst	54	54	>99

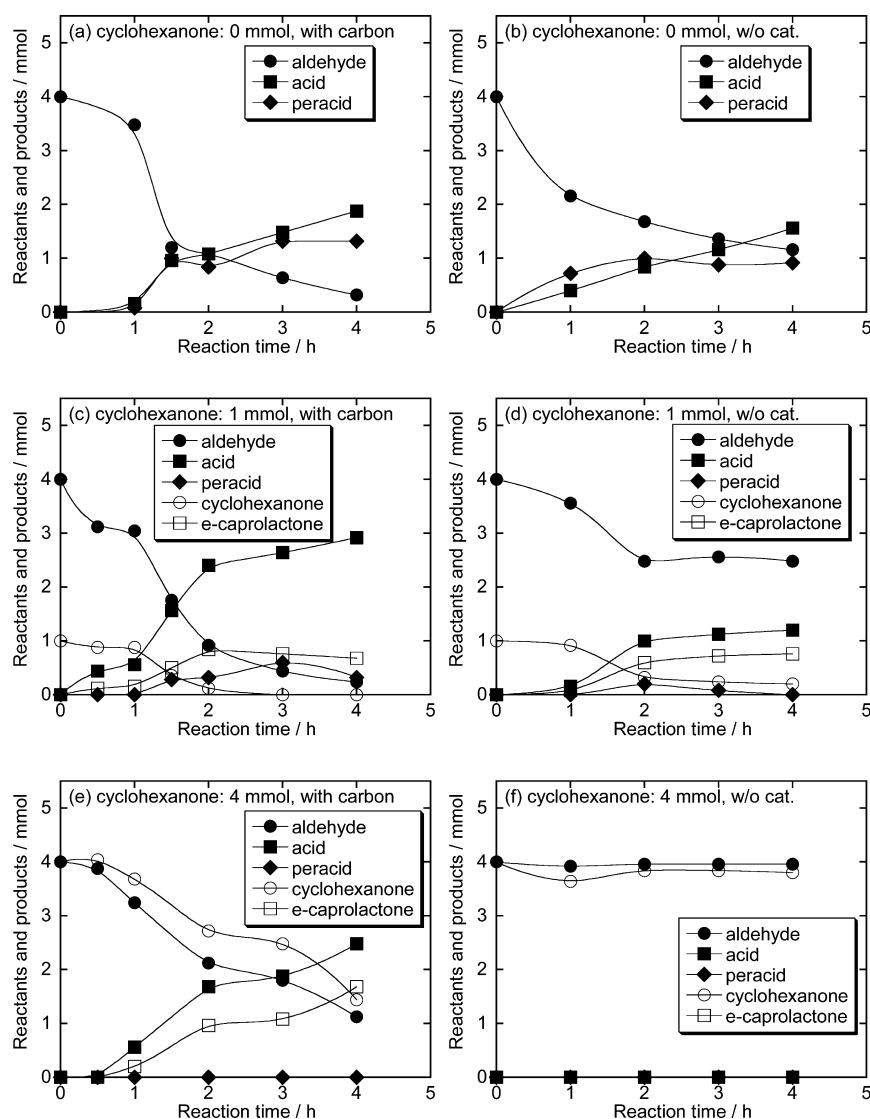
<sup>a</sup>General conditions: cyclohexanone, 1.0 mmol; *m*-CPBA, 1.0 mmol; carbon catalyst, 5 mg; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C.

To obtain more detailed information about the reaction kinetics, NMR study was carried out for the reaction mixtures. Ketjen black, cyclohexanone, and *m*-chlorobenzaldehyde were used for the catalyst, reactant, and sacrificing agent, respectively. Figure 4 shows typical <sup>1</sup>H NMR spectra of the reaction mixture



**Figure 4.** <sup>1</sup>H NMR spectra of the reaction mixture after filtration and replacing the reaction solvent with CDCl<sub>3</sub>: (a) aromatic protons after 3 h without cyclohexanone and (b) aliphatic protons after 4 h with 4 mmol of cyclohexanone. General conditions: *m*-chlorobenzaldehyde, 4.0 mmol; Ketjen Black, 5 mg; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C.

after filtering the catalyst and replacing the reaction solvent with CDCl<sub>3</sub>. The amounts of the reactants and products evaluated from the NMR spectra after different reaction time are summarized in Figure 5. Figure 5a, b shows the results in the presence and absence of carbon catalyst, respectively, and without cyclohexanone. These suggest that the oxidation of aldehyde proceeds even without catalyst. In the meantime, there seems to be an induction period in the oxidation of



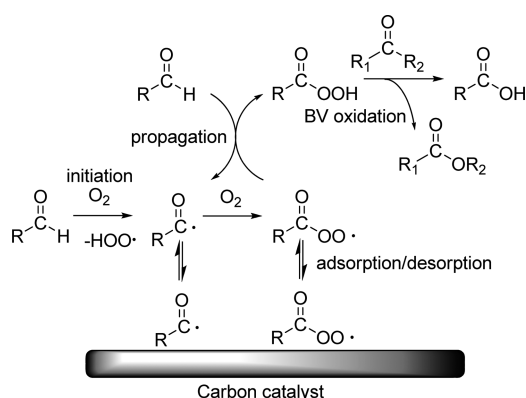
**Figure 5.** Time courses of the reactants and products with different amounts of cyclohexanone: (a, b) 0, (c, d) 1, and (e, f) 4 mmol. General conditions: *m*-chlorobenzaldehyde, 4.0 mmol; Ketjen Black, 5 mg only for a, c, and e; 1,2-dichloroethane, 10 mL; O<sub>2</sub>; 50 °C.

aldehyde when the carbon catalyst is used. Figure 5c, d shows the results in the presence and absence of carbon catalyst, respectively, and with 1 mmol of cyclohexanone (1/4 equivalent to aldehyde). In the cases of both c and d, the amounts of peracid species are lower than those in Figure 5a, b, suggesting that cyclohexanone was oxidized to  $\epsilon$ -caprolactone by *m*-chloroperoxybenzoic acid. One clear difference between c and d is that the aldehyde consumption stopped after 2 h in the case without catalyst, whereas it was readily converted into peracid and carboxyl acid in the presence of the carbon catalyst. Figure 5e, f shows the results in the presence and absence of carbon catalyst, respectively, and with 4 mmol of cyclohexanone (1 equivalent to aldehyde). In the presence of the carbon catalyst (panel e), the aldehyde was converted into the carboxyl acid form while cyclohexanone was oxidized to  $\epsilon$ -caprolactone. The fact that none of the peracid was detected suggests that the reaction rate of cyclohexanone oxidation by peracid is faster than the formation rate of peracid in the present reaction condition. It should be noted that very little aldehyde reacted under the conditions without the carbon catalyst. The observation in Figure 5d, e suggests that the

addition of cyclohexanone inhibits the oxidation of aldehyde to peracid if no carbon catalyst exists in the system. It seems to be characteristic of the carbon catalyst system that an induction period is observed in the aldehyde conversion, and the aldehyde conversion is not inhibited, even if a lower ratio of aldehyde is utilized relative to cyclohexanone.

On the basis of the experimental results shown above, we hereby propose a reaction mechanism in Figure 6 for the oxidation of ketones by the O<sub>2</sub>/aldehyde system catalyzed by carbon materials. The oxidation process starts from the autoxidation of aldehyde to form the peroxy acid, and the produced peroxy acid can readily enable the Baeyer–Villiger oxidation of ketone. The initiation reaction of this autoxidation could be the formation of carbonyl radical from aldehyde and O<sub>2</sub>.<sup>19</sup> This initiation probably occurs without any catalyst considering the conversion rates of aldehyde shown in Figure 5a, b. The chain propagation reactions, the insertion of O<sub>2</sub> into the carbonyl radical to form the peroxy radical species, and the formation of the peracid species by the reaction between the peroxy radical and aldehyde increase the concentration of peracid, which is the real oxidizing agent of the Baeyer–Villiger





**Figure 6.** Reaction mechanism of the ketone oxidation by the  $O_2$ /aldehyde system catalyzed by carbon materials.

oxidation. As long as a sufficient amount of radicals exists in the system, this chain propagation reaction would be much faster than the initiation reaction; therefore, the majority of the aldehyde is consumed by the propagation rather than initiation under the reaction conditions for Figure 5a–e. However, if a large amount of ketone was supplied into the system (Figure 5f), this chain reaction was inhibited by ketone. Probably the alpha hydrogen atom of the ketone was abstracted by the radical species, and the chain reactions were inhibited.<sup>20</sup> Note that cyclohexanone would not be a strong inhibitor, considering the fact that the inhibition failed if its amount was 1/4 equivalent to aldehyde (Figure 5d).

We assume that the main role of the carbon materials in this oxidation system is to adsorb and protect the radical species from the inhibition. Even if the majority of radical species were killed by the inhibitor, the carbon surface can supply active radical species. In other words, the carbon surface can act as a buffer for the radical species, which are necessary for the chain propagation reactions. This adsorption effect can explain the induction period observed in parts a, c, and e. The radical species formed by the initiation reaction would be readily adsorbed on the carbon surface, and the concentration of the radical species becomes quite low at the early stage of the reaction. Once the amount of adsorbed species is sufficiently high, the concentration of the radical species starts increasing in the homogeneous phase. This buffer effect would contribute to high aldehyde efficiency over 0.7 with the carbon catalyst, whereas such efficiency cannot be expected in an uncatalyzed system.

## CONCLUSION

It has been revealed that metal-free carbon materials catalyze the Baeyer–Villiger type oxidation from ketones to corresponding esters in the presence of aldehyde. The catalyst recycling tests suggest that the durability of the carbon catalyst is quite good in the tested reaction conditions. The mechanistic study has revealed that the peroxy-carboxylic acid is the important intermediate, and the carbon catalyst contributes to high aldehyde efficiency by buffering the radical species, which are essential for the chain propagation reactions. To our knowledge, such catalysis by carbon materials has not been reported so far. It should be noted that the present finding can eliminate transition metals from the reaction step to form peroxy-carboxylic acid from aldehyde and  $O_2$ , whereas this sort of reaction has been largely believed to require transition metals such as Co.<sup>3,8</sup> The present finding would contribute to the establish-

ment of environmentally friendly oxidation systems. Further studies are required to maximize the aldehyde efficiency and to clarify the detailed reaction mechanism.

## EXPERIMENTAL SECTION

Norit SX Plus, Vulcan XC-72R, Ketjen Black EC600JD, and VGCF were obtained from commercial sources and used without any treatment. JRC-SIO-9 was obtained from the Catalysis Society of Japan and used after calcining at 400 °C for 4 h. N-doped carbon was prepared by pyrolyzing a mixture of a polyimide and a phenolic resin at 900 °C<sup>17</sup> (N/C atomic ratio: 0.06). B-doped carbon was prepared by pyrolyzing a mixture of a borazine compound and a phenolic resin at 1000 °C<sup>18</sup> (B/C atomic ratio: 0.06).

Catalytic performance of the materials was tested using a Shibata Chemist Plaza CP100 multireactor equipped with 100 mL reactors. The products were quantified with a Shimadzu GCMS-QP2010 Plus equipped with a Restek Rxi-1 ms column. The conversion was calculated on the basis of the peak area ratio of ketones against the internal standard, dodecane. The product yields were calculated on the basis of the peak area ratio of lactones or esters against the internal standard.

FTIR spectra were obtained with a Jasco 4100 spectrometer by the KBr pellet method.

<sup>1</sup>H NMR (400 MHz) spectra of the reaction mixture were obtained using a JEOL JNM-ECS 400 NMR spectrometer after filtering the catalyst and replacing the reaction solvent with  $CDCl_3$ . The amounts of the reactants and products after the reaction shown in Figure 4 were estimated from the peak areas of the NMR spectra, as in

$$X_1 = X_{1,0} \times A_{1a} / (A_{1b} + A_{2b} + A_{3b}) \quad (1)$$

$$X_2 = X_{2,0} \times A_{2d} / (A_{1b} + A_{2b} + A_{3b}) \quad (2)$$

$$X_3 = X_{3,0} \times A_{3d} / (A_{1b} + A_{2b} + A_{3b}) \quad (3)$$

$$X_4 = X_{4,0} \times A_{4e} / 4(A_{1b} + A_{2b} + A_{3b}) \quad (4)$$

$$X_5 = X_{5,0} \times A_{5e} / 2(A_{1b} + A_{2b} + A_{3b}) \quad (5)$$

Here,  $X_n$  is the amount of the compound after the reaction,  $X_{n,0}$  is the initial amount of the compound, and  $A_{nx}$  is the peak area of corresponding proton.

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### Notes

The authors declare no competing financial interest.

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