ACS Catalysis

SUNY DOWNSTATE Medical Center

Article

Nitrogen-doped Metal-free Activated Carbon Catalysts for Aerobic Oxidation of Alcohols

Hiroyuki Watanabe, Sayaka Asano, Shin-ichiro Fujita, Hiroshi Yoshida, and Masahiko Arai

ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.5b00375 • Publication Date (Web): 23 Mar 2015

Downloaded from http://pubs.acs.org on March 28, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications
High quality. High impact.

ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036
Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Nitrogen-doped Metal-free Activated Carbon Catalysts for Aerobic Oxidation of Alcohols

Hiroyuki Watanabe, Sayaka Asano, Shin-ichiro Fujita, Hiroshi Yoshida, Masahiko Arai*

Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

* E-mail marai@eng.hokudai.ac.jp

ABSTRACT: Various nitrogen-doped carbon materials were prepared via treatments of an activated carbon (AC) with ammonia and hydrogen peroxide and their catalytic performance was tested for aerobic oxidation of several alcohols in ethanol. The amount and nature of doped nitrogen-species were examined by X-ray photoelectron spectroscopy to discuss the genesis of active species by nitrogen doping. The nitrogen-doped AC catalysts are active for the oxidation of such alcohols as benzyl alcohol, cinnamyl alcohol, and 5-(hydroxymethyl)-2-furaldehyde and, in some cases, they are even more selective to the oxidation of hydroxyl group compared to conventional Pt/C and Ru/C catalysts, for which coupling products with the ethanol solvent are formed at low conversion levels. Graphite-type doped nitrogen species are significant for the formation of active sites on the surface of AC. The present results demonstrate the potential of nitrogen-doped AC materials as metal-free carbon-based catalysts useable for organic synthetic reactions.

KEYWORDS: *activated carbon, nitrogen doping, metal-free carbon catalyst, oxidation, alcohol*

1. INTRODUCTION

Nitrogen-doped carbon and carbon nitride are interesting functional materials that may be useful as electrochemical- and chemical-catalysts and supports for transition metal catalysts.[1-4] Those carbon-based materials can be prepared in different methods, for example, chemical vapor deposition, well-designed organic synthesis, and doping of nitrogen to parent bulk carbon materials. In addition to their effectiveness in electrochemical applications, those carbon-based materials will serve as metal-free catalysts in synthetic organic reactions. For example, Thomas et al. indicate that their well-designed synthetic carbon nitride materials can catalyze Friedel-Craft and cyclization reactions.[1, 5, 6] Jin et al.[7] and Xu et al.[8] show porous carbon nitride materials, prepared using porous silica materials as templates, to be active for Knonevenagel and transesterification reactions, which are usually catalyzed by base catalysts. Bitter et al.[9] and Wang et al.[10] used chemical vapor deposition using nitrogen-containing compounds (nitriles, pyridine, amines) to prepare nitrogen-doped carbon nanotubes. These were observed to be active catalysts for Knoevenagel condensation. Bitter et al. suggest the importance of pyridine type of doped nitrogen species for the genesis of catalytic activity.[9] A theoretical study indicate that carbon atoms at edge sites of graphite sheets may interact with oxygen molecules with the aid of adjacent doped nitrogen atoms and the nitrogen-doped carbon can then work similar to Pt metal,[11] resulting in a good performance as a Pt-free electrode in proton exchange membrane fuel cells.[12, 13]

The present authors doped nitrogen to an activated carbon (AC) by treating in a mixture of ammonia and air at temperatures of 400 – 800 ºC. The nitrogen-doped AC materials are active catalysts for liquid-phase reactions including Knoevenagel condensation,[14] transesterification,[14] chemoselective reduction of nitrobenzene, styrene, and 3-nitrostyrene with hydrazine,[15, 16] and aerobic oxidation of xanthene,[17] which are catalyzed by bases, metals, and metal oxides.[18] Fujita et al. suggest that, for the oxidation of xanthene, pyridine-type N species in a large graphitic sheet is important for the activity of nitrogen-doped AC catalysts on the basis of X-ray photoelectron spectroscopy (XPS) measurements and reaction runs with melamine, pyridine, and 2-pyridone.[17] Recently, Liao et al. have reported that the liquid phase aerobic oxidation of cumene to cumene hydroperoxide can effectively be catalyzed by metal-free carbon nanotube materials synthesized by chemical vapor deposition using mixtures of xylene and aniline[19] and heat treatment of commercial carbon nanotubes with nitric acid.[20] They suggest the significance of interactions between hydroperoxide cumene and the surface of nitrogen-doped carbon nanotubes for their high catalytic activity.[19] Those results indicate the importance of nitrogen and oxygen species doped on the surface of carbon materials for the catalytic

performance observed [14-20] but their chemical structure and role in the catalysis are still not clear in depth. Their catalytic activity depends on the conditions of nitrogen doping to AC, in our cases, such as ammonia concentration and treatment temperature, which change the amount and nature of nitrogen species doped on its surface. [14-17] Long et al. investigated the catalysis of nitrogen-doped graphene nano-sheets for aerobic oxidation of benzyl alcohol and a few other benzylic alcohols. [21] They reported that the graphite-type nitrogen species contributed to the formation of active sites and discussed reaction mechanisms. Recently, nitrogen-containing graphene-based catalysts were applied for oxidation reactions using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidants.[22-24]

Thus, one can say that the nitrogen-doped metal-free carbon materials would be promising catalysts for organic synthetic reactions, which could replace conventional base, metal, and metal oxide catalysts. After considering the previous results obtained so far, it is still desirable to test their catalytic activity for other synthetic reactions and to make an effort at clarifying the active sites in more detail. Using a porous bulk material of AC, the present work has been undertaken to investigate the potential of nitrogen-doped AC materials for aerobic oxidation of several alcohols, one of industrially important reactions, and the nature of doped nitrogen species involved in active sites through surface characterization by XPS. The catalyst recyclability has also been examined because it is one of merits of using heterogeneous catalysts in organic synthetic reactions. Furthermore, conventional carbon-supported Pt and Ru catalysts have also been used for the oxidation reactions and the features of the metal-free nitrogen-doped AC catalysts have been compared to those of the supported noble metal catalysts.

2. EXPERIMENTAL SECTION

2.1. Preparation of Nitrogen-doped Carbon

A commercial AC powder (GL Science Co.) was used as a starting carbon source and treated in the following procedures. [14, 15] About 500 mg of AC sample was set in a quartz tube reactor and an NH_3 stream of pure NH_3 or a mixture of NH_3 (90 %) in air was passed over the sample at 100 cm^3 min^{-1} for 30 min. The reactor was heated at 10 ºC min^{-1} up to a certain temperature lower by 100 ºC than the desired temperature and then at 5 ºC min^{-1} up to the desired temperature, at which the sample was treated in the NH_3 stream for 1 h. The AC sample was cooled in the same NH_3 stream to 300 ºC and, after switching the NH_3 stream to pure N_2, the sample was further cooled to room temperature. The AC powder was also treated by 30% hydrogen peroxide: 300 mg AC powder was dispersed in 15 cm^3 of

30% hydrogen peroxide and the mixture was treated in a Teflon tubular reactor in a stainless steel autoclave at 100 or 130 ºC for 5 h while stirring by a magnetic stirrer. After the treatment, the AC powder was cooled to room temperature, separated by filtration, washed with anhydrate ethanol (Wako), and dried under ambient conditions and then at 100 ºC overnight. In some cases, AC powder was treated by the hydrogen peroxide followed by the NH_3 treatment.

For comparison, commercially available carbon-supported noble metal catalysts, 5 wt.-% Pt/C and 5 wt.-% Ru/C (Wako) were also used. The degree of metal dispersion measured by CO chemisorption (BEL-METAL-1) was 0.25 for the former and 0.56 for the latter. The CO pulse chemisorption was measured after pretreatment with H_2 at 100 ºC for 30 min and then with He at 110 ºC for 30 min. A stoichiometry of metal/CO = 1/1 was assumed.

2.2 Characterization of Carbon-based Catalysts

The textural properties of AC materials prepared were measured by N_2 adsorption/ desorption on Quantachrome NOVA 100. [14,15] The specific surface area was determined by the Brunauer-Emmet-Teller equation. The surface of nitrogen-doped AC samples was examined by XPS (JOEL JPS-9200) using monochromatic Al Kα radiation.[14,15] A pelletized AC sample on an iridium foil was subjected to the XPS measurement without any pretreatment and the charge-up shift corrections of binding energies were made by reference to C_{1s} of 284.0 eV.

2.3. Aerobic Oxidation of Alcohols

The catalytic performance of those nitrogen-doped AC samples was tested for liquid phase aerobic oxidation of alcohols according to similar procedures as described previously.[16] The reaction runs were conducted in a Teflon tube in a stainless steel reactor (100 cm^3), which was loaded with 1 mmol substrate, 100 mg AC-based catalyst, and 5 cm^3 ethanol (solvent) and closed. Air in the reactor, its pressure being 0.1 MPa at room temperature, was used as an oxidant. The other reaction conditions used (temperature and time) will be indicated later. The reaction mixture was analyzed by a gas chromatograph (GL Science GC-390B) with a high resolution capillary column (30 m, 0.25 mm OD, 0.25 μm ID) packed with TC-WAX and a flame ionization detector. The substrates used were benzyl alcohol, cinnamyl alcohol, 3-phenyl-1-propanol, 1-heptanol, cyclohexylmethanol, and 5-(hydroxymethyl)-2-furaldehyde, the former four compounds being purchased from Wako and the latter two from Aldrich. These substrates were used as received.

3. RESULTS AND DISCUSSION

Various nitrogen-doped AC catalyst samples were prepared under different conditions given in Table 1, which includes the results of their BET surface area measurements. The treatment with 90% NH_3 and 10% air burned off AC to some extent. The weight loss was found to be 27% by the treatment at 800 ºC and smaller at lower temperatures. Note that the surface area is not a significant factor determining the catalytic performance.[14,17] These samples were applied for aerobic oxidation of benzyl alcohol, cinnamyl alcohol, and others. In addition, the results with the nitrogen-doped AC catalysts were compared to those with conventional carbon-supported noble metal catalysts of 5 wt.-% Ru/C and 5 wt.-% Pt/C, for which the degree of metal dispersion was 0.56 and 0.25, respectively, measured by CO chemisorption.

Table 1

3.1. Oxidation of Benzyl Alcohol

The results of benzyl alcohol oxidation (Scheme 1) with various nitrogen-doped AC catalysts are also given in Table 1. Under the conditions used, benzaldehyde was observed to form without any other byproducts and no reaction occurred in the absence of catalyst (blank test). The parent and H_2O_2 – treated AC samples were less active (#1 – #3). A sample treated with NH_3 at 800 ºC was a little active (#4). When AC was treated by H_2O_2 followed by NH_3, the oxidation activity was enhanced significantly (#6 – #8) and a maximum conversion of 23% was obtained with the AC catalyst prepared through the H_2O_2 treatment at 130 ºC and the subsequent one with NH_3 at 800 ºC (#8). The other AC catalysts prepared with 90% NH_3 were less active (#9, #10) and those prepared through the treatments with H_2O_2 and 90% NH_3 were moderately active (#11- #13). Thus, the catalyst preparation conditions were crucial for determining the oxidation activity of AC-based catalysts. The large difference in the catalytic performance observed cannot be explained by that in the BET surface area (Table 1).

Scheme 1

The surface of those AC samples was examined by XPS and three different nitrogen species were detected to exist, which were pyridine-, pyrrole-, and graphite-type nitrogen species (Figure 1). [21, 25-28] The XPS results measured with the samples #4 - #13 are

presented in Supporting Information (Figure S1). Figure 2 shows the surface concentration of these three different nitrogen species doped on the surface of various AC-based catalysts (#4 - #13 of Table 1). No XPS analysis was made for the AC samples #1 - #3 that were not treated by NH_3. The conversion of benzyl alcohol measured is plotted against the amounts of those different nitrogen species in Figure 3. The amount of a certain nitrogen species in a carbon sample was estimated by the product of the surface concentration (mole fraction) of the nitrogen species measured by XPS and the BET surface area of the sample (m^2 g^{-1}). The conversion cannot be correlated with the amount of either pyridine-type or pyrrole-type nitrogen species but there is a good relationship with the amount of graphite-type nitrogen species, which should contribute to the genesis of active sites on the surface of AC for the oxidation of benzyl alcohol. This is in accordance with the result of Long et al. using nitrogen-doped graphene nano-sheet catalysts for the same oxidation reaction. [21] There were oxygen species on the surface of those carbon materials but the conversion of benzyl alcohol was not related to the amount of oxygen species measured by XPS (Figure S2 in SI). XRD was used to examine their structural features but no significant difference was observed among those carbon samples (Figure S3 in SI). It was previously observed for base-catalyzed Knoevenagel and transesterification reactions that the catalytic activity was correlated with the ratio of surface nitrogen species against surface oxygen ones for the nitrogen-doped AC catalysts.[14] This is different from the correlation of Figure 3(c), due to the difference in the nature of the reactions studied.

Figure 1, Figure 2, Figure 3

There is a scatter at small amounts of graphite-type nitrogen species (< 0.15 %) for the relationship of Figure 3(c). This suggests the presence of other active sites on the surface AC samples. Hayashi and coworkers examined various aerobic oxidation reactions over untreated AC catalysts.[29, 30] They reported that surface oxygen-containing groups, which were evolved as CO at high temperatures, were active sites for oxidative cyclization.[30] In addition, the present authors recently indicated that pyridine-type nitrogen species were active for the aerobic oxidation of xanthene.[17] Those other surface species should catalyze the aerobic oxidation of alcohols but less active compared to the graphite-type nitrogen species. This would cause a scatter in the range of small amount of graphite-nitrogen species as observed in Figure 3(c).

3.2. Oxidation of Cinnamyl Alcohol

A few selected AC-based catalysts (#1, #4, #7, and #8 in Table 1) were applied for the oxidation of a different substrate of cinnamyl alcohol at 80 ºC (Scheme 2). Cinnamaldehyde

was observed to form in 100% selectivity under the conditions used. These AC catalysts were active and the conversion was also correlated with the amount of graphite-type nitrogen species, as seen in Figure 4. This suggests again that these nitrogen species are involved in the formation of active sites.

Scheme 2, Figure 4

3.3. Oxidation of Other Alcohols

The catalytic performance of a selected nitrogen-doped AC catalyst #8, most active among those listed in Table 1, was examined in the aerobic oxidation of other alcohols. Table 2 summarizes the results obtained with several alcohols including benzyl and cinnamyl alcohols. As already described, the nitrogen-doped AC catalyst can oxidize benzyl alcohol and cinnamyl alcohol to corresponding aldehydes with 100% selectivity (entries 1, 2). For 3-phenyl-1-propanol, cyclohexylmethanol, and 1-heptanol, the nitrogen-doped AC was inactive (entries 3, 4, 5). For the oxidation of 5-(hydroxymethyl)-2-furaldehyde, a conversion of 24% was achieved with the nitrogen-doped AC catalyst in 15 h with a selectivity of 93% (entry 6). The byproduct was the acetal from the substrate and the solvent of ethanol. For benzyl alcohol, cinnamyl alcohol, and 5-(hydroxymethyl)-2-furaldehyde (entries 1, 2, 6), the carbon bonding to hydroxyl group may be activated by its adjacent conjugated system and so they can be easily oxidized. In contrast, the other alcohols (entries 3, 4, 5) do not have such a conjugated system so that they cannot be activated and oxidized.

Table 2

3.4. Catalyst Recyclability

The catalyst reusability was examined using a nitrogen-doped AC catalyst #8 and a model substrate of benzyl alcohol. The sample was separated by filtration after the first oxidation run and used for the second one under the same conditions. Figure 5 gives the results of repeated oxidation runs, indicating a decrease in the conversion obtained, in particular after the first run. The surface of fresh and recycled (three times) catalyst samples was examined by XPS. Figure 6 displays the XPS N 1s spectra and Table 3 gives the surface concentration of nitrogen species as measured by XPS. The results show a significant decrease in the amount of graphite-type species on the recycling, which should be involved in the active sites as above-mentioned (Figures 3 and 4). These nitrogen species was found to change to oxide-type ones, as indicated from the XPS results (Figure 6). The amounts of oxygen

species measured by XPS were 5.3% and 7.0% for the fresh and recycled samples. As mentioned later, the presence of gaseous oxygen was needed to improve the rate of benzyl alcohol oxidation. It was assumed, therefore, that the surface oxygen species were insignificant for the catalyst deactivation observed (Figure 5). The catalyst deactivation due to the disappearance of graphite-type nitrogen species should occur during the oxidation reaction. Attempts were made to regenerate the nitrogen-doped AC catalyst #8 after the first reaction run, which was treated in ethanol at 1 MPa H_2 and 120 ºC for 8 h or by hydrazine (8 cm^3) at 120 ºC for 2 h and then used for the second run. The conversion values observed were 13% and 7.5% after the former treatment and the latter one, respectively, which were 50% and 30% of the initial performance of the fresh catalyst. These two treatments failed to activate the catalyst that lost its activity after the first reaction run.

Figure 5, Figure 6, Table 3

The occurrence and extent of catalyst deactivation of nitrogen-doped AC catalysts depends on the type of reaction and the type of active sites involved. The catalysts lose their activity for oxidation reactions of xanthene [17] and alcohols (this work) and Knoevenagel condensation [14] in which water is produced and could have an effect in the deactivation. In contrast, no catalyst deactivation occurs for transesterification reaction, [14] which is a base-catalyzed reaction similar to Knoevenagel condensation. The catalyst recyclability was not mentioned by Long et al. for their nitrogen-doped graphene nano-sheet catalysts. [21] The group of Peng et al. prepared nitrogen-doped carbon nanotubes by chemical vapor deposition using aniline and xylene as nitrogen and carbon sources.[31, 32] They showed that these carbon materials were metal-free active catalysts for liquid-phase oxidation of an aromatic alkene of cyclohexene using molecular oxygen and, in addition, these catalysts were recyclable for five runs, in contrast to the present case (Figure 5). Nitrogen species should exist in the structure of graphene sheets for Peng's carbon nanotubes while they are likely to be doped to such structure irregular sites as edge ones for our AC-derived materials. This difference in the structural features might explain the absence and presence of catalyst deactivation in the oxidation reactions.

3.5. Oxidation Processes over Nitrogen-doped AC Catalysts

For nitrogen-doped graphene nano-sheet catalysts, Long et al. pointed out the significance of graphite-type nitrogen species for their catalysis in the oxidation of alcohols. [21] These authors propose a Langmuir – Hinshelwood process, in which a sp^2 N – O_2 adduct is formed on the graphite-type nitrogen active sites and this is a key step for the oxidation. A model calculation of Ikeda et al. indicates that an oxygen molecule may be activated on a

carbon atom bonded to a doped nitrogen atom.[11] The present results also indicate that the oxidation of alcohols proceeds over the surface of nitrogen-doped AC catalysts and the graphite-type nitrogen species contribute to the formation of active sites. Additional reaction runs were conducted to consider reaction mechanisms. A reaction with benzyl alcohol was conducted with the nitrogen-doped AC catalyst #8 in the presence of a radical scavenger of *p*-benzoquinone (0.1 mmol) in the reaction mixture under the standard conditions (benzyl alcohol 1.0 mmol, for others see caption of Table 1). The conversion was observed to be only 3%, which was even smaller than 23% obtained in the absence of *p*-benzoquinone. This suggests that radical species may be included in the oxidation processes. Another additional run was conducted in an atmosphere of pure N_2 instead of air. The oxidation was found to occur but with an even smaller conversion of 9% as compared to 23%, suggesting that a source of oxidant is the gaseous O_2 in the air but not the doped O species. After considering those additional results and the above-mentioned previous works[11, 21] possible reaction pathways may be envisaged as follows (Scheme 3). An oxygen molecule dissolved in the liquid phase is adsorbed on a carbon site adjacent to the graphite-type nitrogen and/or on the carbon atom and the nitrogen atom. Then, some oxygen radical is formed and reacts with an alcohol molecule, which might be activated by interactions between graphite-type nitrogen and C1 atom of benzyl alcohol, producing benzaldehyde and regenerating the active sites. In some cases, undesired process should occur, in which the graphite-type nitrogen is changed to the oxidized-type nitrogen during the oxidation reaction, causing the unavoidable catalyst deactivation. The formation of a byproduct of water might play a role in the catalyst deactivation, similar to the case of Knoevenagel condensation.[14]

The group of Peng et al. report that the nitrogen-doped carbon nanotube materials are active for the liquid-phase oxidation of cyclohexene, in which the nitrogen doping enhances the rate of oxidation and the selectivity to 2-cyclohexene-1-one.[31, 32] It is noted that these catalytic features are explained by their capability of promoting the radical chain propagation via stabilizing peroxyl and cycloxyl radicals and, as a result, 2-cyclohexene-1-ol is further converted to 2-cyclohexene-1-one as well. As above-mentioned, the well-organized carbon nanostructure (graphene wall) of their catalysts could be different in the catalytic performance with our commercial AC-based nitrogen-doped carbon catalysts.

Scheme 3

In a previous work,[17] the aerobic oxidation of xanthene was investigated with nitrogen-doped AC catalysts, which were prepared in similar manners but without the

ACS Paragon Plus Environment

pretreatment with hydrogen peroxide and so they contained a trace amount of graphite-type nitrogen species on their surface. It was assumed that the presence of pyridine-type nitrogen species gave Lewis base nature to the neighboring carbon atoms and these carbon sites were more effective for the activation of methylene group of the substrate. As a result, the catalytic activity tended to increase with an increase in the amount of surface pyridine-type nitrogen species. Although the graphite-type species were little doped, the activation of oxygen should occur on those AC-based catalysts but less effectively as compared with the present AC-based catalysts containing the graphite-type nitrogen species. This is a reason for that a higher reaction temperature of 100 ºC is required for the oxidation of xanthene [17] and the activation oxygen should be less significant than that of xanthene under the reaction conditions used.

3.6. Comparison with Conventional Noble Metal Catalysts

The catalytic performance of a selected nitrogen-doped AC catalyst #8, most active among those listed in Table 1, was examined in the aerobic oxidation of other alcohols and compared with that of conventional carbon-supported noble metal catalysts, 5 wt.-% Ru/C and 5 wt.-% Pt/C. Table 4 summarizes the results obtained with several alcohols including benzyl and cinnamyl alcohols. Benzyl alcohol was oxidized to benzaldehyde in 23% conversion in 5 h with 100 mg nitrogen-doped AC catalyst (entry 1) while a similar conversion was achieved with a smaller amount (10 mg) of Ru/C in a shorter time (3 h) (entry 5). It is interesting to note that benzaldehyde was formed in 100% selectivity with the former but in a lower selectivity of 60% for the latter at similar conversion levels, with which an acetal was produced in a large quantity from the oxidized product (benzaldehyde) and the solvent (ethanol). The Pt/C was less active for the oxidation of benzyl alcohol (entries 2, 4). The nitrogen-doped AC catalyst was inactive for the oxidation of cyclohexylmethanol (entry 6); the supported noble metal catalysts were active but the desired product of cyclohexyl aldehyde was not detected (entries 7, 8). For the oxidation of an aliphatic alcohol of 1-heptanol, the nitrogen-doped AC was inactive (entry 9). A small conversion of 9% was obtained with 100% selectivity with Ru/C under the conditions used (entry 11). For cinnamyl alcohol, the meta-free AC catalyst (100 mg) gave a conversion of 21% and a selectivity of 100% in 15 h (entry 12). A similar conversion of 17% was obtained in a shorter time of 7 h with a smaller amount of Ru/C (entry 14). Similar to the case of benzyl alcohol, the selectivity to the desired product (cinnamaldehyde) was even low (38%), which gave an acetal from cinnamaldehyde and ethanol. Again Pt/C was less active (entry 13). For the oxidation of 5-(hydroxymethyl)-2-furaldehyde, a conversion of 24% was achieved with the nitrogen-doped AC catalyst (100 mg) in 15 h with a selectivity of 93% (entry 16). Both Pt/C and Ru/C were active but their selectivity values to the

desired oxidation product were low (entries 17-19), which gave an acetal from the substrate and the solvent, in contrast to the cases of benzyl and cinnamyl alcohols.

Table 4

The comparison was further made among the nitrogen-doped AC and carbon-supported noble metal catalysts in the oxidation of benzyl alcohol. Table 4 shows that the performance of Pt/C (entry 3) was not good as compared to Ru/C (entry 2) under the same reaction conditions, as above-mentioned. The AC-based and Ru/C catalysts gave very similar conversion levels under the conditions used and so these two can be compared (entries 1, 2). For the Ru/C catalyst, TOF is 29 h^{-1} and the selectivity to the desired oxidation product of benzaldehyde is 60%, in which the acetal is formed from benzaldehyde and the solvent (ethanol) in a large amount. For the nitrogen-doped AC catalyst, the graphite-type nitrogen species can be assumed to contribute to the formation of active sites and so TOF was determined using the number of these species determined by XPS (see footnote b of Table 4). The metal-free AC catalyst produces benzaldehyde in 100% selectivity but has a TOF of 1.6 h^{-1}, which is even smaller by more than one order of magnitude compared to 29 h^{-1} for the Ru/C catalyst. In addition, apparent activation energy, E_a, was measured at temperatures of 100 – 130 ºC for the nitrogen-doped AC and 90 – 110 ºC for Ru/C using the data collected at conversion < 15%. Arrhenius-type plots of reaction rate against 1/temperature are presented in Figure 7. The E_a value was determined to be 22 kJ mol^{-1} and 32 kJ mol^{-1} for the metal-free AC and Ru/C catalysts, respectively. The E_a value is smaller by 10 kJ $mol^{-1}$for the former than the latter; however, TOF is even smaller. These results suggest that the reaction mechanisms are different between the two catalysts or the rate-determining step is the same but the required activation energy is different depending on the nature of active sites. A detailed kinetics analysis was made by Long et al. for the oxidation of benzyl alcohol over their nitrogen-doped graphene nano-sheet catalysts. [21] Their oxidation reactions were conducted in the presence of water in the reaction mixture at the start of reaction. An activation energy of 56 kJ mol^{-1} was reported for the oxidation of benzyl alcohol over the nitrogen-doped graphene nano-sheet catalysts, which was close to 51 kJ mol^{-1} for a Ru/Al_2O_3 catalyzed oxidation using $PhCF_3$ solvent reported in the literature. [33] The apparent activation energy determined for the nitrogen-doped AC catalyst in the present work is different from those previous values [21, 29] and from that of a reference of Ru/C catalyst (Table 5). Those results indicate again that the catalytic actions of nitrogen-doped carbon materials are different depending on the carbon structure, well-structured graphene and nanotubes or less-structured carbons like AC used in the present work, which determines the location and environment of nitrogen dopants. More detailed reaction kinetics analysis is in progress to shed light on the catalysis of the

metal-free nitrogen-doped bulk AC catalyst of our interest.

Table 5, Figure 7

4. CONCLUSIONS

The nitrogen-doped metal-free AC catalyst is active for the aerobic oxidation of alcohols such as benzyl alcohol, cinnamyl alcohol, and 5-(hydroxymethyl)-2-furaldehyde to the desired aldehydes but inactive for the oxidation of 3-phenyl-1-propanol, 1-heptanol and cyclohexylmethanol under the conditions used. In other words, the alcohols in which the carbon bonding to hydroxyl group may be activated by its adjacent conjugated system can be oxidized by the nitrogen-doped AC catalysts. On nitrogen-doping, different types of nitrogen species are formed on the surface of AC, which are pyridine-, pyrrole-, and graphite-type. The graphite-type nitrogen species are involved in the genesis of catalytically active sites, which should adsorb and activate an oxygen molecule. The nitrogen-doped metal-free AC catalyst has a smaller TOF value by more than one order of magnitude compared to those for carbon-supported Ru and Pt catalysts. But, the apparent activation energy is smaller for the former than the latter, suggesting different reaction mechanisms. The graphite-type nitrogen species are likely to change to the less active oxidized ones, causing the catalyst deactivation during the oxidation reaction, which could not be avoidable owing to the nature of reaction.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: ○○○○○○○○○○.

Catalyst characterization results (XPS, XRD) and relation between conversion in benzyl alcohol oxidation and amount of surface oxygen species (PDF)

REFERENCES

(1) Thomas, A.; Fischer, A.; Goettmann, F.; Antonietti, M.; Müller, J.-O.; Schlögl, R.; Carlsson, J. M. *J. Mater, Chem*. **2008**, *18*, 4893-4908.

(2) Su, D. S.; Zhang, J.; Frank, B.; Thomas, A.; Wang, X.; Paraknowitsch, J.; Schlögl, R. *ChemSusChem* **2010**, *3*, 169-180.

(3) Mabena, L. F.; Sinha Ray, S.; Mhlanga, S. D.; Coville, N. J. *Appl. Nanosci*. **2011**, *1*, 67-77.
(4) Yu, D.; Nagelli, E.; Du, F.; Dai, L. *J. Phys. Chem. Lett*. **2010**, *1*, 2165-2173.
(5) Goettmann, F.; Fischer, A.; Antonietti, M.; Thomas, A. *Angew. Chem. Int. Ed*. **2006**, *45*, 44657-4471.
(6) Goettmann, F.; Thomas, A.; Antonietti, M. *Angew. Chem. Int. Ed*. **2007**, *46*, 2717-2720.
(7) Jin, X.; Balasubramanian, V. V.; Selvan, S. T.; Sawant, D. P.; Chari, M. A.; Lu, G. Q.; Vinu, A. *Angew. Chem. Int. Ed*. **2008**, *48*, 7884-7887.
(8) Xu, J.; Shen, K.; Xue, B.; Li, Y. X.; Cao, Y. *Catal. Lett*. **2013**, *143*, 600-609.
(9) van Dommele, S.; de Jong, K. P.; Bitter, J. H. *Chem. Commun*. **2006**, *64*, 4858-4861.
(10) Wang, L.; Wang, L.; Jin, H.; Bing, N. *Catal. Commun*. **2011**, *15*, 78-81.
(11) Ikeda, T.; Boero, M.; Huang, S.; Terakura, K.; Oshima, M.; Ozaki, J. *J. Phys. Chem. C*, **2008**, *112*, 14706-14709.
(12) Ozaki, J.; Anahara, T.; Kimura, N.; Oya, A. *Carbon*, **2006**, *44*, 3348-3361.
(13) Ozaki, J.; Kimura, N.; Anahara, T.; Oya, A. *Carbon*, **2007**, *45*, 1847-1853.
(14) Kan-nari, N.; Okamura, S.; Fujita, S.; Ozaki, J.; Arai, M. *Adv. Synth. Catal*. **2010**, *352*, 1476-1484.
(15) Fujita, S.; Watanabe, H.; Katagiri, A.; Yoshida, H.; Arai, M. *J. Mol. Catal. A Chem*. **2014**, *393*, 257-262.
(16) Yoshida, H.; Watanabe, H.; Katagiri, A.; Fujita, S.; Arai, M. Abstract of 7th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT7), Kyoto, June 1-6, 2014, O-E23.
(17) Fujita, S.; Yamada, K.; Katagiri, A.; Watanabe, H.; Yoshida, H.; Arai, M. *Appl. Catal. A Gen*. **2014**, *488*, 171-175.
(18) Sheldon, R. A.; van Bekkum, H., "Fine Chemicals through Heterogeneous Catalysis", Eds.; Wiley-VCH: New York, 2001, pp. 309-326, pp. 491-551.
(19) Liao, S.; Chi, Y.; Yu, H.; Wang, H.; Peng, F. *ChemCatChem* **2014**, *6*, 555-560.
(20) Liao, S.; Peng, F.; Yu, H.; Wang, H. *Appl. Catal. A Gen*. **2014**, *478*, 1-8.
(21) Long, J.; Xie, X.; Xu, J.; Gu, Q.; Chen, L.; Wang, X. *ACS Catal*. **2012**, *2*, 622-631.
(22) Li, W.; Gao, Y.; Chen, W.; Tang, P.; Li, W.; Shi, Z.; Su, D.; Wang, J.; Ma, D. *ACS Catal*. **2014**, *4*, 1261-1266.
(23) Gao, Y.; Hu, G.; Zhong, J.; Shi, Z.; Zhu, Y.; Su, D.; Wang, J.; Bao, X.; Ma, D. *Angew. Chem. Int. Ed*. **2013**, *52*, 2109-2113.
(24) Yang, J.; Sun, G.; Gao, Y.; Zhao, H.; Tang, P.; Tan, J.; Lu, A.; Ma, D. *Energy Environ. Sci.* **2013**, *6*, 793-798.
(25) Woods, M.P.; Biddinger, E.J.; Matter, P.H.; Mirkelamoglu, B.; Ozkan, U.S. *Catal. Lett.* **2010**, *136*, 1–8.
(26) Raymundo-Piňero, E.; Cazorla-Amorós, D.; Linares-Solano, A.; Find, J.; Wild, U.;

Schlögl, R. *Carbon* **2002**, *40*, 597–608.

(27) Maldonals, S.; Morin, S.; Stevenson, K. J. *Carbon* **2006**, *44*, 1429–37.

(28) Kondo T.; Casolo, S.; Suzuki, T.; Shikano, T.; Sakurai, M.; Harada, Y.; Saito, M.; Oshima, M.; Trioni, M.I.; Tantardini, G.F.; Nakamura, J. *Phys. Rev. B* **2012**, *86*, 035436.

(29) Sano, Y.; Tanaka, T.; Hayashi, M. *Chem. Lett.* **2007**, *36*, 1414-1415.

(30) Kawashita, Y.; Yanagi, J.; Fujii, T.; Hayashi, M. *Bull. Chem. Soc. Jpn*. **2009**, *82*, 482-488.

(31) Cao, Y.; Yu, H.; Peng, F.; Wang, H. *ACS Catal*. **2014**, *4*, 1617-1625.

(32) Yu, H.; Peng, F.; Tan, J.; Hu, X.; Wang, H.; Yang, J.; Zheng, W. *Angew. Chem. Int. Ed.* **2011**, *50*, 3978-3982.

(33) Yamaguchi, K.; Mizuno, N. *Chem. Eur. J.* **2003**, *9*, 4353-4361.

Table 1. List of nitrogen-doped metal-free AC catalysts prepared and their catalytic performance for aerobic oxidation of benzyl alcohol

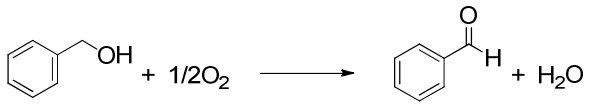
Catalyst number	Treatment		Surface area (m^2 g^{-1})	Conversion [a] (%)
	First (H_2O_2 temp.)	Second (NH_3 conc., temp.)		
1	—	—	1031	3.0
2	100 ºC	—	1188	7.0
3	130 ºC	—	—[b]	4.0
4	—	100%, 800 ºC	1205	8.1
5	100 ºC	100%, 600 ºC	1050	15
6	100 ºC	100%, 700 ºC	707	12
7	100 ºC	100%, 800 ºC	1276	19
8	130 ºC	100%, 800 ºC	1198	23
9	—	90%, 400 ºC	971	2.8
10	—	90%, 600 ºC	1075	3.2
11	—	90%, 800 ºC	1172	10
12	100 ºC	90%, 600 ºC	803	7.2
13	100 ºC	90%, 800 ºC	1063	10

First: AC was treated in H_2O_2 at temperatures given for 5 h.

Second: AC was then treated in a stream of NH_3 and/or air at temperatures given for 1 h.

a. Reaction conditions: substrate 1.1 mmol, catalyst 100 mg, solvent (ethanol) 5 cm^3, temperature 120ºC, time 5 h.

b. Not measured.



Scheme 1. Oxidation of benzyl alcohol to benzaldehyde

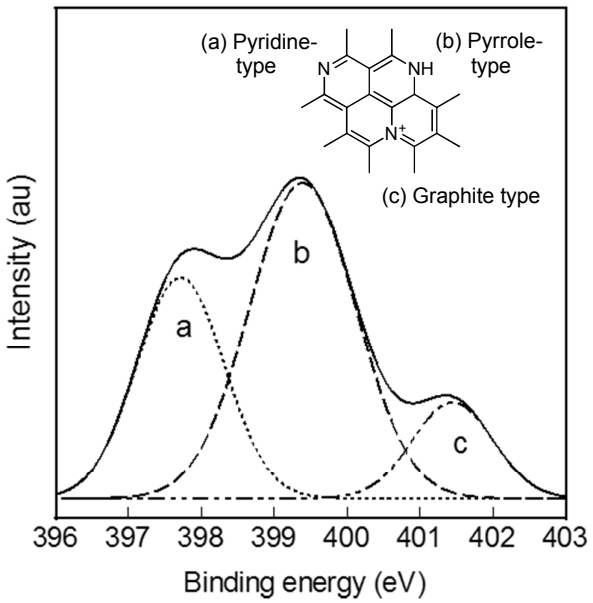


Figure 1. A typical N1s XPS spectrum showing the presence of pyridine-type (a), pyrrole-type (b), and graphite-type (c) nitrogen species doped on the surface of a nitrogen-doped AC catalyst #8

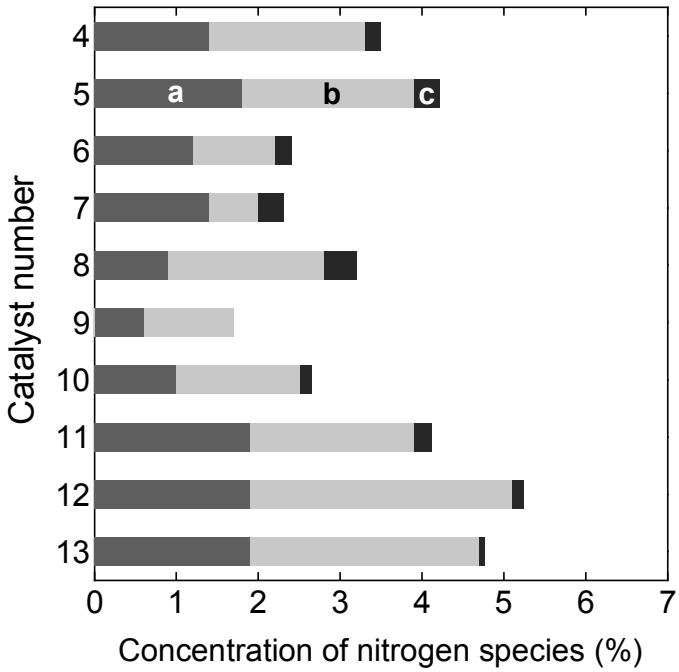


Figure 2. Composition of nitrogen species, pyridine-type (a), pyrrole-type (b), and graphite-type (c), on the surface of nitrogen-doped AC catalyst samples. No XPS analysis was made for the samples #1 - #3 given in Table 1, which were parent AC and AC samples treated with H_2O_2 but not with NH_3.

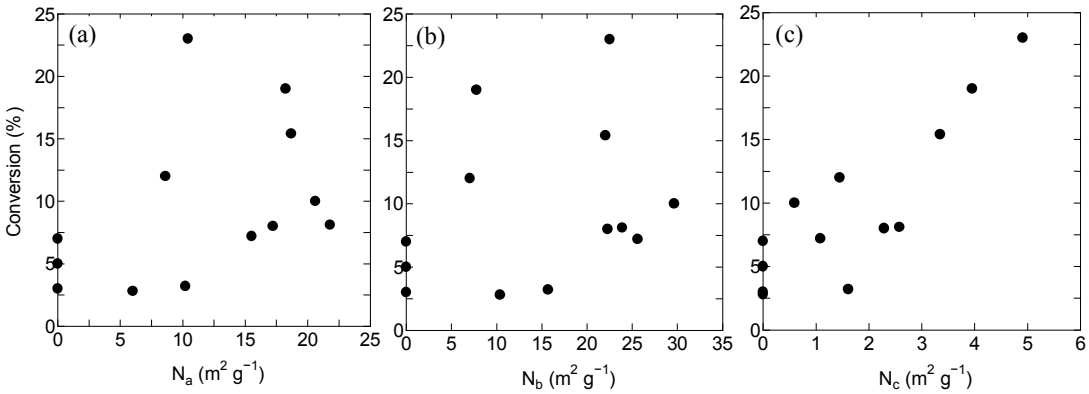
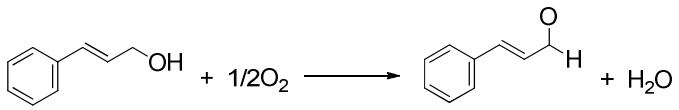


Figure 3. Plots of total conversion in oxidation of benzyl alcohol to benzaldehyde against the amount of pyridine-type (N_a), pyrrole-type (N_b), and graphite-type (N_c) nitrogen species on the surface of nitrogen-doped AC catalysts listed in Table 1.



Scheme 2. Oxidation of cinnamyl alcohol to cinnamaldehyde

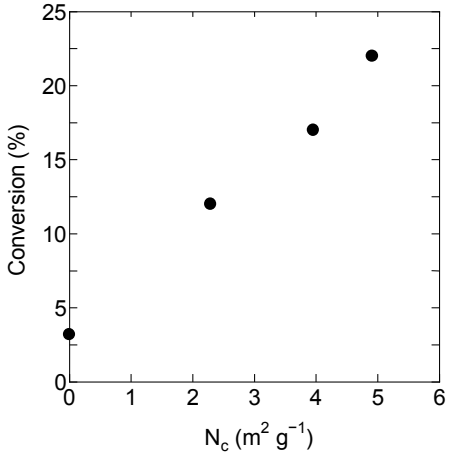
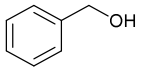
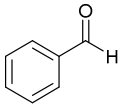
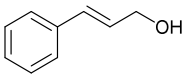
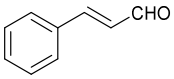
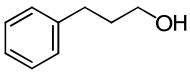
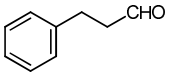
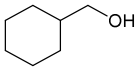
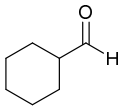
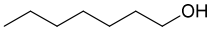
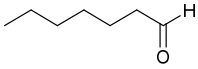
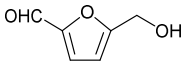
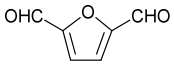


Figure 4. Plot of total conversion in oxidation of cinnamyl alcohol to cinnamaldehyde at 80 ºC for 15 h against the amount of graphite-type (N_c) nitrogen species on the surface of a few selected nitrogen-doped AC catalysts (#1, #4, #7, #8) listed in Table 1

Table 2. Results of aerobic oxidation of several alcohols with the nitrogen-doped metal-free AC #8 catalyst

Entry	Substrate	Product	T [a] (ºC)	t [a] (h)	X [a] (%)	S [a] (%)
1			120	5	23	100
2			80	15	21	100
3			80	15	0	–
4			120	5	0	–
5			80	15	0	–
6			80	15	24	93

Reaction conditions: solvent ethanol 5 cm^3, substrate 1.1 mmol, catalyst 100 mg.

[a] T: reaction temperature, t: reaction time, X: total conversion, S: selectivity to the desired oxidation product

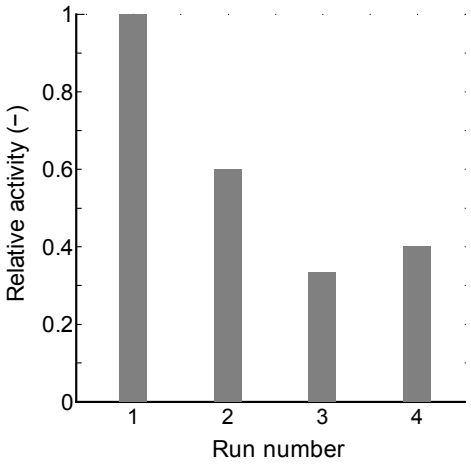


Figure 5. Results of recycling test of a nitrogen-doped AC catalyst #8 in the aerobic oxidation of benzyl alcohol. Reaction conditions: Initial weight of catalyst 100 mg, benzyl alcohol 1.1 mmol, ethanol 5 cm^3, 120 ºC, 5 h.

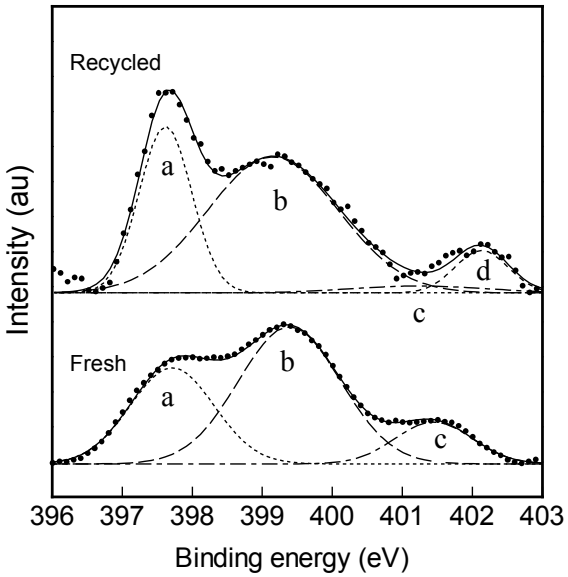
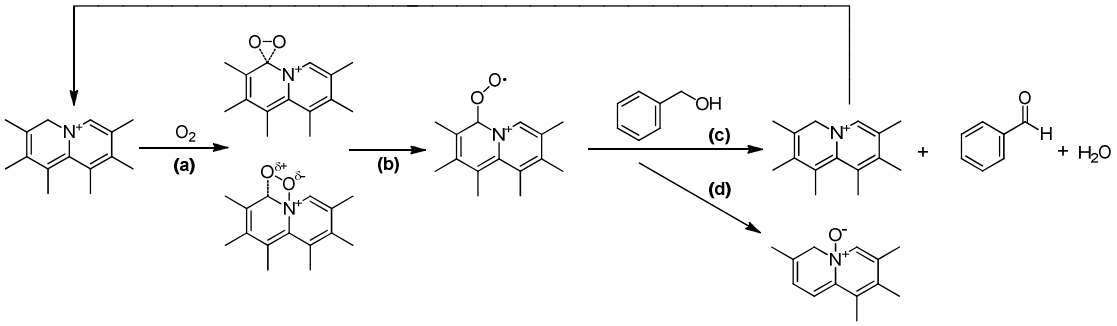


Figure 6. N1s XPS spectra of fresh and recycled (three times) nitrogen-doped AC based catalyst #8. (a) pyridine-type, (b) pyrrole-type, (c) graphite-type, (d) oxide-type nitrogen species.

Table 3. Concentration of surface nitrogen species in a nitrogen-doped AC catalyst #8 before and after the repeated oxidation runs (three times)

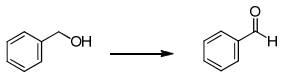
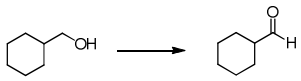
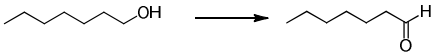
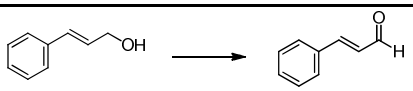
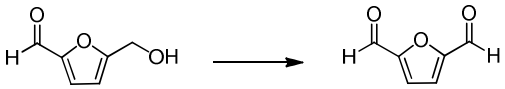
Catalyst	Surface concentration (atom %)				
	Total N	Pyridine-type N	Pyrrole-type N	Graphite-type N	Total O
Fresh	3.2	0.87	1.9	0.41	5.3
Recycled	1.8	0.57	1.2	0.06	7.0

Reaction conditions: Initial weight of catalyst 100 mg, benzyl alcohol 1.1 mmol, ethanol 5 cm^3, 120 ºC, 5 h.



Scheme 3. Possible reaction pathways for aerobic oxidation of benzyl alcohol over nitrogen-doped AC catalyst: (a) adsorption of oxygen molecule, (b) formation of oxygen radical, (c) oxidation of alcohol producing aldehyde and regenerating active sites, (d) change of active sites (graphite-type nitrogen) into inactive sites (oxide-type nitrogen) causing catalyst deactivation

Table 4. Results of aerobic oxidation of alcohols with the nitrogen-doped metal-free AC #8 and conventional carbon-supported noble metal catalysts

Entry	Catalyst	w [a] (mg)	T [a] (ºC)	t [a] (h)	X [a] (%)	S [a] (%)
(a)						
1	N-Carbon	100		5	23	100
2	Pt/C	10		0.5	7	100
3		100	120	3	9	87
4	Ru/C	20		1	9	100
5		10		3	22	60
(b)						
6	N-Carbon	100		5	0	–
7	Pt/C	10	120	5	20	0
8	Ru/C	10		5	21	0
(c)						
9	N-Carbon	100		15	0	–
10	Pt/C	10	80	5	< 1	–
11	Ru/C	10		5	9	100
(d)						
12	N-Carbon	100		15	21	100
13	Pt/C	10	80	15	7	100
14	Ru/C	10		7	17	38
15		10		15	43	21
(e)						

16	N-Carbon	100		15	24	93
17	Pt/C	10	80	5	29	0
18	Ru/C	10		2	28	14
19		10		5	44	12

Reaction conditions: solvent ethanol 5 cm^3, substrate 1.1 mmol.

[a] w: weight of catalyst used, T: reaction temperature, t: reaction time, X: total conversion, S: selectivity to the desired oxidation product

Table 5. Comparison of a nitrogen-doped AC catalyst sample #8 with conventional supported noble metal catalysts for aerobic oxidation of benzyl alcohol at 120 ºC

Entry	Catalyst	Weight (mg)	Time (h)	Conversion (%)	Selectivity [a] (%)	TOF [b] (h^{-1})	E_a [c] (kJ mol^{-1})
1	N-doped AC #8	100	5	23	100	1.6	22
2	5% Ru/C	10	3	22	60	29	32
3	5% Pt/C	10	3	8.6	87	49	–

Reaction conditions: see caption for Figure 1.

a. Selectivity to benzaldehyde

b. TOF to the consumption of benzyl alcohol. The number of exposed active sites was determined as follows: the number of exposed Ru and Pt atoms was measured by CO pulse chemisorption assuming a stoichiometry of CO/metal = 1. The degree of metal dispersion determined was 56% and 25% for the Ru/C and Pt/C samples, respectively. The number of graphite-type nitrogen species was estimated from the surface composition (0.41%) measured by XPS and a BET surface area of 1198 m^2 g^{-1} assuming a density of a carbon atom per 0.02625 nm^2 for graphitic surface.

c. Apparent activation energy determined at 100 ºC – 130 ºC and at 90 ºC – 110 ºC for the N-doped AC and 5% Ru/C catalysts, respectively, using the data of conversion < 15% (Figure 7)

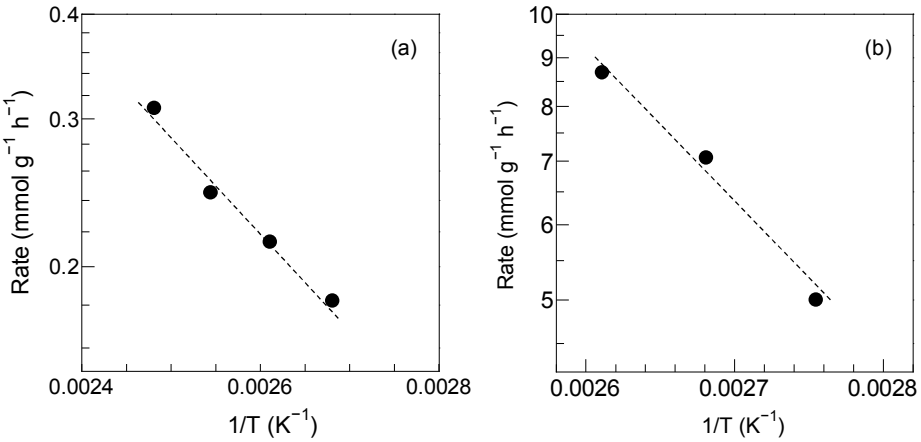
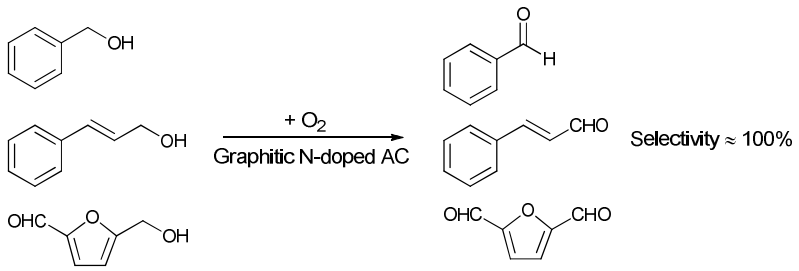


Figure 7. Arrhenius type plots of the rate of reaction against 1/reaction temperature for the oxidation of benzyl alcohol over the nitrogen-doped metal-free AC catalyst #8 (a) and a carbon-supported Ru one (b)

Graphical Abstract

Nitrogen-doped Metal-free Activated Carbon Catalysts for Aerobic Oxidation of Alcohols