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Acid-Catalyzed Reactions on Flexible Polycyclic Aromatic Carbon in Amorphous Carbon

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Carbonization of D-glucose at 573−723 K followed by sulfonation produces a functionalized amorphous carbon material with acid catalytic activity as a solid-acid replacement for sulfuric acid. The carbon material contains phenolic hydroxyl, carboxylic acid, and sulfonic acid groups and exhibits high catalytic performance for liquid-phase acid-catalyzed reactions. Carbonization at higher temperature followed by sulfonation also results in amorphous carbon, but the resultant does not exhibit catalytic activity although the amorphous carbon has sufficient amount of sulfonic acid groups. Structural and active site analyses suggest that the marked difference in catalytic activity is due to the accessibility of reactants to sulfonic acid groups in the carbon structure.

Introduction

Sulfuric acid is an essential catalyst for the production of industrially important chemicals. However, such liquid-acid catalysts require special processing in the form of neutralization, which involves costly and inefficient catalyst separation from products and results in an unrecyclable sulfate waste. According to the principles of "green chemistry" and "green technology", production methods should be refined so as to minimize adverse effects on the environment or human health.[1] The migration to strong solid acids, which are recyclable and nontoxic, from liquid acids such as sulfuric acid is therefore a desirable goal.[2−4]

For a solid material to provide catalytic activity comparable to sulfuric acid, it should be highly stable and host many strong Brønsted acid sites. Water participates in many acid-catalyzed reactions involving esterification, hydration, and hydrolysis, and as such it is essential for the material to maintain strong acidity even in water. Inorganic-oxide solid acids such as zeolite and niobic acid (providing acidic OH groups) have low densities of effective acid sites and thus cannot achieve adequate performance in acid-catalyzed reactions in the presence of water as a replacement for homogeneous Brønsted acids. Although strong acidic cation-exchangeable resins such as perfluorosulfonated ionomers have sufficient sulfonic acid groups (SO_3H) that function as strong acid sites even in water, these resins are expensive and the acid activities are still much lower than achievable by homogeneous Brønsted acids.[3,5] These limitations have restricted the practical utility of acidic cation-exchangeable resins.

An amorphous carbon material consisting of small polycyclic aromatic carbon sheets with a high density of sulfonic acid sites is a promising solid replacement for sulfuric acid catalyst.[6,7] Such a material can be readily prepared by incomplete carbonization of sulfopolycyclic aromatic hydrocarbons[6] or sulfonation of incompletely carbonized organic compounds[7] and exhibits high catalytic performance as a stable catalyst for various liquid-phase acid-catalyzed reactions. In many reactions, this solid catalyst rivals sulfuric acid at the same weight, and the reactivity of the Brønsted acid sites is at least 10 times greater than that of sulfuric acid. Despite the relatively simple preparation procedure, it is possible to produce insoluble and stable carbon materials with high densities of active sites. The material also functions as a good proton conductor comparable to Nafion. However, the details of the properties of the material are not clear. The SO_3H densities of the material are 0.7−4.9 mmol g^{-1} despite the small surface areas (2−20 m^2 g^{-1}). These densities are much too high to be attributed to SO_3H groups

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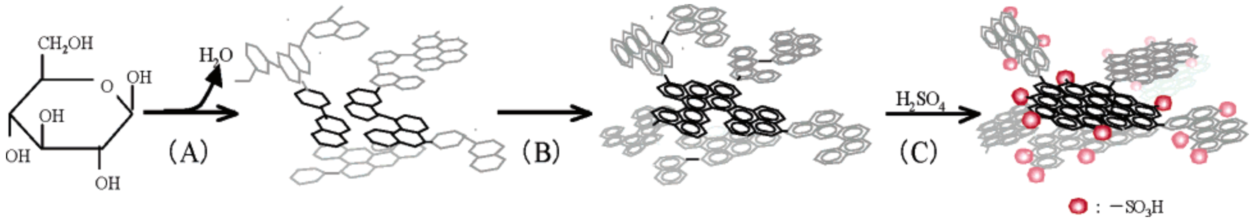

Figure 1. Preparation of sulfonated carbon material. (A) Pyrolysis, (B) carbonization, and (C) sulfonation.

attached to the carbon surface. This suggests that SO_3H groups in the amorphous carbon bulk takes part in the acid-catalyzed reactions, whereas the incorporation of large organic molecules into the bulk of amorphous carbon has not been reported. These solid-catalyst carbon materials cannot be synthesized by sulfonation of familiar carbon materials such as graphite, carbon black, graphitized carbon fiber, activated carbon, or glassy carbon. Samples prepared from such starting materials do not exhibit activity for the catalysis of esterification, hydration, or hydrolysis.[6] These suggest that the acid catalysis in sulfonated carbon materials is closely related to the carbon structure. In this study, a sulfonated carbon material prepared from D-glucose is prepared, and the properties of active sites, the structure, and the catalytic activity are examined.

The carbon material was prepared by carbonization of D-glucose followed by sulfonation, as shown schematically in Figure 1. In the first stage of carbonization (A), D-glucose is pyrolyzed, accompanied by dehydration and dissociation of −C−O−C−, leading to the formation of polycyclic aromatic carbon rings at higher temperature and the amorphous carbon structure, as shown in (B). SO_3H is then introduced into the aromatic carbon rings by sulfonation (C).

Experimental Section

Preparation of Carbon Material. A 20 g sample of D-glucose powder was heated for 15 h at 573, 673, 723, or 823 K under N_2 flow to produce a brown-black solid. The solid was then ground to a powder and heated in 200 cm^3 of concentrated H_2SO_4 (>96%) or 150 cm^3 of fuming sulfuric acid (15 wt % SO_3) at 423 K under N_2 to introduce SO_3H into the aromatic carbon rings. After heating for 15 h and then cooling to room temperature, 1000 cm^3 of distilled water was added to the mixture to form a black precipitate, which was then washed repeatedly in hot distilled water (>353 K) until impurities such as sulfate ions were no longer detected in the wash water.

Characterization. Structural information was obtained for the prepared samples by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR). ^{13}C cross-polarization (CP)/magic-angle-spinning (MAS) NMR spectra were measured at room temperature using a Bruker ASX200 spectrometer at a Larmor frequency of 50.3 MHz. A Bruker MAS probe head was used with a 7 mm zirconia rotor. The spinning rate of the sample was 4.0 or 4.5 kHz. The frequency of the spectra is expressed with respect to neat tetramethylsilane. Experimentally, glycine was used as a second reference material, whose carbonyl signal was set at 176.48 ppm.

Acid densities were estimated for the prepared samples by neutralization titration. As COOH and SO_3H groups were present in samples prepared from D-glucose (see below), the acid densities estimated by neutralization titration are total amounts of both functional groups. According to XPS analysis, it is expected that all S atoms in the carbon materials are contained in SO_3H groups (see below). The densities of SO_3H groups were thus estimated based on the S content in sample compositions determined by elemental analysis. The acid strength of each sample was examined using color-producing reagents and ^{31}P MAS NMR.[8,9]

Acid Catalytic Reactions. The acid catalytic performance of the material was demonstrated through the hydration of 2,3-dimethyl-2-butene (343 K) and esterification of acetic acid (343 K). Hydration of 2,3-dimethyl-2-butene and esterification of acetic acid were carried out in an aqueous solution containing 2,3-dimethyl-2-butene (H_2O, 0.42 mol; 2,3-dimethyl-2-butene, 0.013 mol) and an ethanol−acetic acid mixture (ethanol, 1.0 mol; acetic acid, 0.1 mol), respectively, in an Ar atmosphere. All tested catalysts except sulfuric acid were evacuated at 373−453 K for 1 h prior to reaction, and 0.2 g of each catalyst was used in the reactions. The liquid phase during reaction was analyzed by gas chromatography with capillary columns.

Results and Discussion

Morphology and Properties of Sulfonated Carbon Material. Figure 2A shows SEM images of the resulting sample powder after sulfonation. No difference in morphology was observed among the prepared samples. The grain sizes of the irregular particles are greater than 1 μm, and the layered or lamellar structures seen in well-carbonized materials are not present. The powders can readily be

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(8) As the coloration of the reagents cannot be observed by inspection on these black carbon materials, the acidity was examined by ultraviolet−visible diffuse reflectance spectroscopy (UV−vis DRS; V560, Jasco). A mixture of the carbon material (0.2 g) and $BaSO_4$ (a reference material for DRS measurement, 1.0 g) powder was evacuated at 423 K for 1 h to remove adsorbed water. In an Ar-filled glovebox, the mixture was packed into a sealable quartz cell, and benzene (with or without color-producing reagent) was then added to the cell. The DRS of the mixture in each benzene solution was measured without exposure to air. The DRS of the color-producing reagent in the presence of the carbon material was obtained by subtracting the spectrum for the mixture in pure benzene from that of the mixture in the benzene solution solving the color-producing reagent. The DRS for each color-producing reagent was also observed using $BaSO_4$ in benzene with and without the color-producing reagent in a similar manner.

(9) The acid strength was also examined by ^{31}P MAS NMR using trimethylphosphine oxide (TMPO) as a probe molecule.[10,11] ^{31}P MAS NMR spectra for TMPO-adsorbed samples were measured at room temperature using a Bruker ASX400 spectrometer at Larmor frequency of 162.0 MHz. The pulse sequence was a single-pulse sequence with high-power proton decoupling. A Bruker MAS probe head was used with a 4 mm zirconia rotor. The spinning rate of the sample was 10 kHz. The ^{31}P chemical shift was referenced to 85% H_3PO_4 at 0.0 ppm. Experimentally, $(NH_4)_2HPO_4$ was used as a second reference material, the signal of which was set at 1.33 ppm. TMPO-adsorbed samples were prepared as follows. Samples dehydrated by evacuation at 423 K for 1 h were soaked in a THF solution containing an adequate amount of TMPO at room temperature for 2 days in a glovebox under an argon atmosphere, followed by evacuation to remove the THF solvent. The TMPO-adsorbed samples were then packed into a rotor in a glovebox under an N_2 atmosphere.

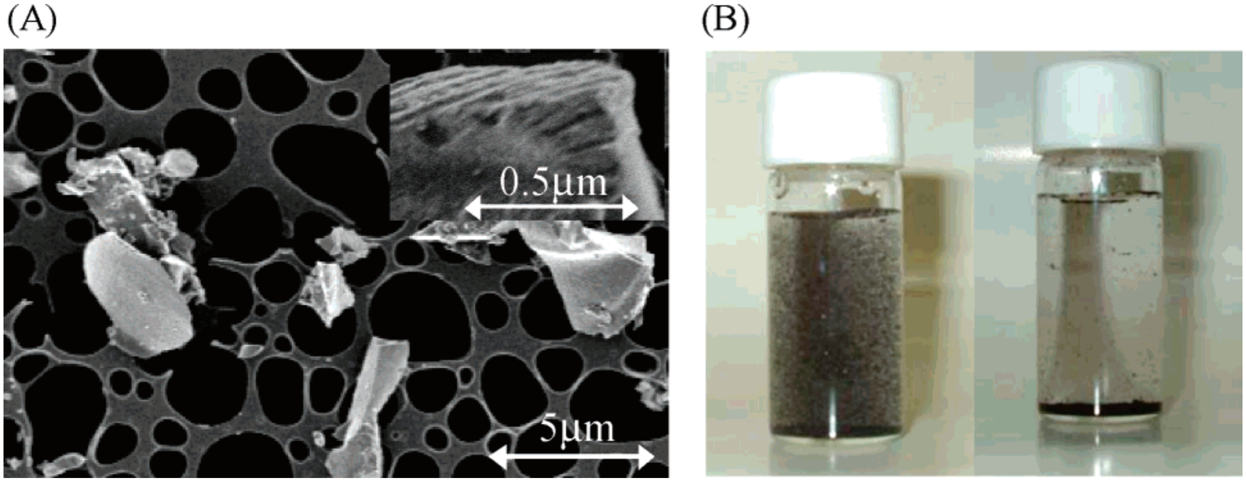

Figure 2. (A) SEM image of carbon material prepared by sulfonation of D-glucose carbonized at 673 K. (B) Carbon material in distilled water with and without stirring.

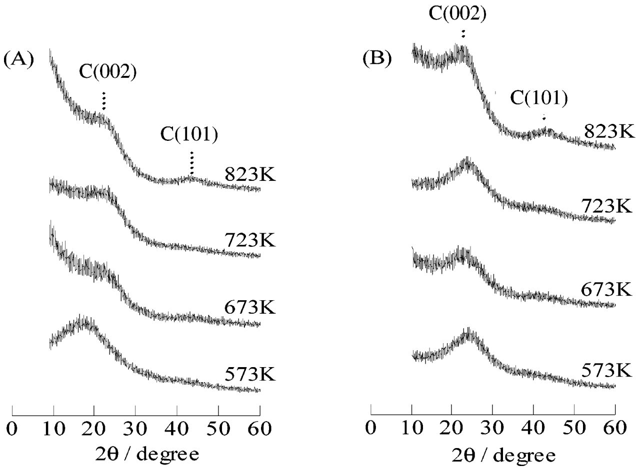

Figure 3. XRD patterns for carbonized D-glucose (A) before and (B) after sulfonation.

dispersed in solvents by stirring, and precipitates form rapidly when stirring is ceased (Figure 2B). The prepared samples were insoluble in the solvents tested (water, methanol, ethanol, benzene, hexane, *N*,*N*-dimethylformamide, and acetonitrile) even at boiling temperatures.

Structures of Carbon Material before and after Sulfonation. Figure 3 shows the XRD patterns for carbonized D-glucose before and after sulfonation. All XRD patterns exhibit a weak and broad C(002) diffraction peak ($2\theta = 10-30°$) attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion. In the case of d-glucose carbonized at 823 K, a definitive C(101) diffraction peak ($2\theta = 35-50°$) due to the a axis of the graphite structure can be seen. This indicates that this sample is composed of larger carbon sheets and is more carbonized than the D-glucose prepared at 723 K or below. Such differences in the structure are preserved upon sulfonation.

Figure 4 shows the ^{13}C MAS NMR spectra for carbonized D-glucose before and after sulfonation. The S 2p XPS spectrum for the 673 K carbon sample after sulfonation is also shown. The sample compositions before and after sulfonation and the acid densities and surface areas of sulfonated samples are summarized in Table 1. Prior to sulfonation, the NMR spectrum for the 573 K carbon sample consists of many peaks due to C−OH and C−O−C (72 ppm), $CH_2=$ and $=CH-$ (102 ppm), polycyclic aromatic carbon (130 ppm), phenolic OH (150 ppm), and COOH (172 ppm),[10,11] indicating that carbonization of D-glucose and the subsequent formation of polycyclic aromatic carbons proceed slowly at 573 K. This sample consists of D-glucose degradation products containing polycyclic aromatic carbon rather than amorphous carbon. Peaks due to polycyclic aromatic carbon appear in all samples carbonized at higher temperatures, and the peaks due to phenolic OH are observed for the 673 and 723 K carbon samples. The H and O contents in the 823 K sample are lower than those in the other samples (see below, Table 1), indicating that this carbon material is more dehydrated and carbonized, consistent with the XRD results.

The ^{13}C MAS NMR spectrum for the 573 K carbon sample after sulfonation in concentrated H_2SO_4 exhibits peaks at 130, 150, 172, and 180 ppm attributable to polycyclic aromatic carbon atoms, phenolic OH, COOH, and carboxyl groups (−CO− in COOH groups), respectively.[7] As the sp^3-bonding-based −C−C− and C−O−C in this sample dissociate under severe sulfonation conditions at 423 K, the peaks due to those bonds are not observed in the spectrum. The ^{13}C MAS NMR spectra for the 673 and 723 K samples are similar to that for the 573 K sample. The peak due to polycyclic aromatic carbon also appears for the 823 K sample after sulfonation, while a slight phenolic OH peak is observed in the spectrum. Figure 4 also shows the NMR spectrum for 673 K carbon after sulfonation with fuming H_2SO_4. No appreciable differences can be seen between this spectrum and that for the carbon materials sulfonated with concentrated H_2SO_4. The peak due to aromatic carbon with SO_3H groups (ca. 140 ppm)[12] is not distinguished in the spectra for samples after sulfonation because broad peaks due to aromatic carbon atoms (130 ppm) and OH groups (150 ppm) obscure the peak due to $Ar-SO_3H$. The XPS spectra for all carbon materials after sulfonation exhibit a single S 2p peak attributable to

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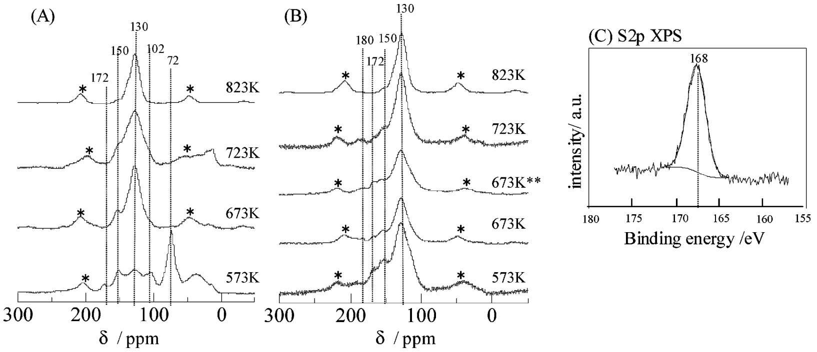

Figure 4. ^{13}C CP/MAS NMR spectra for carbonized d-glucose (A) before and (B) after sulfonation and (C) S 2p XPS spectrum for carbonized d-glucose (673 K) after sulfonation. 673 K**: the NMR spectrum for 673 K carbon after sulfonation with fuming H_2SO_4. Asterisks denote spinning sidebands.

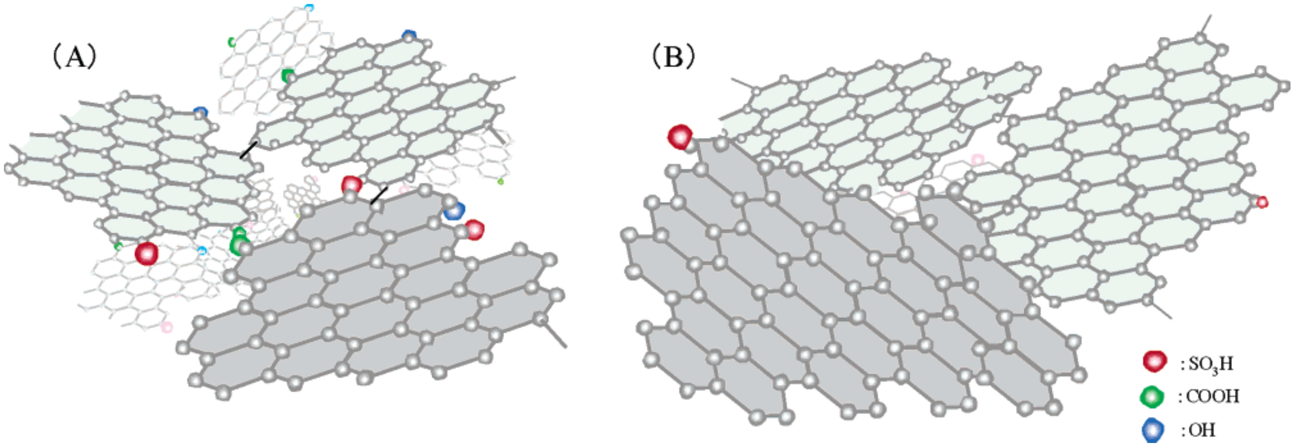

Figure 5. Proposed structures of carbonized D-glucose after sulfonation: (A) carbon prepared at 573−723 K; (B) carbon prepared at 873 K.

Table 1. Sample Compositions before and after Sulfonation, and Acid Densities and Surface Areas of Sulfonated Samples

temperature of carbonization (K)	composition before sulfonation	composition after sulfonation	acid amount (SO_3H) (mmol g^{-1})	surface area (m^2 g^{-1})
		Sulfonated Carbon		
573	$CH_{1.08}O_{0.57}$	$CH_{0.71}O_{0.58}S_{0.011}$	0.48	2
673	$CH_{0.51}O_{0.13}$	$CH_{0.45}O_{0.39}S_{0.014}$	0.74	2
673[a]	$CH_{0.51}O_{0.13}$	$CH_{0.37}O_{0.48}S_{0.028}$	1.34	2
723	$CH_{0.74}O_{0.07}$	$CH_{0.50}O_{0.30}S_{0.014}$	0.71	2
873	$CH_{0.35}O_{0.05}$	$CH_{0.37}O_{0.05}S_{0.005}$	0.37	2

[a] The 673 K sample sulfonated with fuming H_2SO_4.

SO_3H groups at 168 eV (see Figure 4). After sulfonation, the carbon materials therefore contain SO_3H, and all S atoms in the carbon materials are contained in SO_3H groups.

To summarize, carbon sulfonated after carbonization at 573, 673, and 723 K is expected to have an amorphous carbon structure composed of polycyclic aromatic carbon sheets with SO_3H, COOH, and phenolic OH groups, as illustrated in Figure 5A. The carbon (101) diffraction peak ($2\theta = 35-50°$) is not observed clearly in these samples, suggesting that these samples consist of small polycyclic aromatic carbon sheets (ca. 1−2 nm) containing 10−20 hexagonal carbon rings. Sulfonation of the 823 K carbon also results in amorphous carbon, although the SO_3H-containing carbon is more carbonized and is composed of larger carbon sheets (Figure 5B). Judging from the slight peak due to phenolic OH, the density of phenolic OH carbon is expected to be considerably small. The carbon materials become harder with increasing carbonization temperature due to plane growth and stacking of the carbon sheets. The 823 K sample is a “hard” carbon material compared to the other samples. The samples carbonized at lower temperatures have smaller carbon sheets and therefore have higher SO_3H densities because the SO_3H groups are attached only to the edges of the carbon sheets. It should be noted that the 673 K sample sulfonated with fuming H_2SO_4 exhibits twice the SO_3H density than the equivalent sample sulfonated in concentrated H_2SO_4. This can be attributed to the strong sulfonation and consumption of H_2O in fuming H_2SO_4, where the generated H_2O is converted to H_2SO_4 by SO_3, forcing the equilibrium of sulfonation ($Ar-H + H_2SO_4 \leftrightarrow Ar-SO_3H + H_2O$) toward the formation of SO_3H groups.

Stability. The thermal stabilities of the materials were examined by thermogravimetric analysis (TGA) and temperature-programmed desorption (TPD) under air flow. In TGA, the sample weights decreased with increasing temperature, reaching a plateau at 400 K. Heating above 500 K resulted in a further decrease in weight. TPD also revealed that H_2O (mass number: 18), SO_2 (mass number: 64), and CO_2 (mass number: 44) evolved due to decomposition of SO_3H and COOH groups at above 500 K, indicating that the material is not inferior to perfluorosulfonated ionomers in terms of chemical and thermal stability. The carbon materials also have high hydrothermal stability: it was confirmed that the SO_3H groups were completely preserved even after boiling the material in water for 1 day followed by exposure to steam at 400−440 K for 1 day.

Catalytic Performance. The acid catalytic activities of the prepared samples were demonstrated through the hydration of 2,3-dimethyl-2-butene (343 K) and esterification of

Table 2. Catalytic Activities of Various Catalysts for Hydration of 2,3-Dimethyl-2-butene and Esterification of Acetic Acid

catalyst	temperature of carbonization (K)	surface area (m^2 g^{-1})	acid amount (SO_3H) (mmol g^{-1})	yield of 2,3-dimethyl-2-butanol[a] (%)	rate of ethyl acetate (mmol g^{-1} min^{-1})
sulfonated carbon	573	2	0.48	2.5	1.02
	673	2	0.75	3.0	1.36
	673[b]	2	1.34	4.5	2.20
	723	2	0.71	3.3	1.16
	823	2	0.37	0.7	0.05
H_2SO_4			20.4	4.4	9.38
Nafion		<0.1	0.8	2.2	1.19
$Nb_2O_5 \cdot nH_2O$		128	0.3	0.4	0.32
blank				0.4	0.04

[a] The yield of 2,3-dimethyl-2-butanol after 5 h. [b] The 673 K sample sulfonated with fuming H_2SO_4.

acetic acid (343 K). The results for 0.2 g of the tested samples are shown in Table 2. For comparison, the results for 0.2 g of concentrated sulfuric acid (>96%), protonated Nafion (NR50) and niobic acid ($Nb_2O_5 \cdot nH_2O$) are also shown. Niobic acid is a typical inorganic oxide strong solid acid that is widely used in industrial acid-catalyzed reactions. However, niobic acid showed moderate catalytic activity for both reactions. The catalytic activities of typical oxide solid acids—$SiO_2-Al_2O_3$ (JRC-SAH-1, Si/Al = 2.1), H-MOR (JRC-Z-HM20, Si/Al = 18.3), activated clay, and sulfated ZrO_2—for the reactions were also examined, and it was confirmed that these acid catalysts with large surface areas (>200 m^2 g^{-1}) have lower catalytic activity than niobic acid. Sulfonated carbon prepared at 723 K or below displayed good catalytic performance for both reactions, with activities for hydration rivaling that of H_2SO_4 and for esterification comparable to that of Nafion,[6] a high SO_3H density-cation-exchange resin exhibiting very high activity for reactions involving thermostable solid acids.[3,5] The sample sulfonated with fuming H_2SO_4 exhibits higher catalytic activity for both reactions than the carbon materials sulfonated with concentrated H_2SO_4.[7] This can be attributed to the higher density of SO_3H sites in the fumed sample (twice that in samples sulfonated with concentrated H_2SO_4). No decrease in activity or leaching of SO_3H from the carbon materials were observed, even for samples subject to repeated reaction after recovery by simple decantation.[6,7] At 423 K, the sample sulfonated with fuming H_2SO_4 had much higher catalytic activity for the hydration reaction than H_2SO_4. The same hydration as above (0.42 mol:0.013 mol, H_2O:2,3-dimethyl-2-butene) was repeated in an autoclave at 423 K. In the case of the sample sulfonated with fuming H_2SO_4, the yield of 2,3-dimethyl-2-butanol after 5 h reached 32%, that is, 2 times that of H_2SO_4 (15%). The activity of the sample remained unchanged even after the sample was recycled for a fifth time. This suggests that the carbon material can be used as a replacement for sulfuric acid in secondary or tertiary alcohol production from olefins, industrially important chemical processes. On the other hand, the yield of 2,3-dimethyl-2-butanol after 5 h at 423 K on conventional polymer-based solid acids such as protonated Nafion (NR50) and Amberlyst-15 (sulfonated polystyrene-based cation-exchangeable resin, SO_3H density: 4.2 mmol g^{-1}) was at most 6−7% even at the first reaction. In addition, these resins recovered after the reaction showed no catalysis for further reaction. Reaction temperature beyond ca. 373 K is favorable for many acid-catalyzed reactions, and the thermostable carbon material with stable SO_3H groups functions as an efficient acid catalyst at such reaction temperature. However, these conventional resins are not available for reactions at relatively high temperature because of leaching of SO_3H groups or denaturation of polymer substrates.

The sample carbonized at 823 K, on the other hand, exhibited little or no activity for either catalysis. Figure 6 correlates the catalytic activities (hydration of 2,3-dimethyl-2-butene and esterification of acetic acid) of the tested solid acid catalysts and the acid amounts. The tested solid acids, except niobic acid in the hydration and the sample carbonized at 823 K in both reactions, show catalytic activity proportional to the acid amount. In the case of the hydration of 2,3-dimethyl-2-butene by niobic acid, the yield corresponding to the acid amount of niobic acid is not observed because of hydration of acidic OH groups on $Nb_2O_5 \cdot nH_2O$ in the presence of excess water: hydration of acidic OH groups on oxide solid acids remarkably decreases the acid catalysis. While the sample carbonized at 823 K has sufficient SO_3H groups that function as active acid sites even in water, the catalytic activities are much lower than those expected from the SO_3H density. This cannot be explained only by a decrease in SO_3H density with the growth of polycyclic aromatic carbon sheets at higher carbonization temperature.

Active Sites and Carbon Structure. As shown above, the sulfonation of D-glucose carbonized below 723 K results in a stable and highly active solid acid catalyst, whereas sulfonation of the carbon material prepared at 823 K does not produce any appreciable catalytic activity, despite the material hosting a sufficient density of SO_3H. One possible explanation for this difference is the acidity (i.e., acid strength) of the samples. The acidities of these carbon materials were therefore examined using color-producing reagents and ^{31}P MAS NMR. Figure 7 shows the DRS (diffuse reflectance spectroscopy) spectra for the sulfonated 673 K carbon after adsorption of the color-producing reagents. The spectra are those obtained after subtraction of the reflection due to the carbon material, and the spectra for the color-producing reagents are shown for comparison. A broad absorption band appears at 450−600 nm in the spectrum for the sulfonated 673 K carbon dyed with anthraquinone, attributable to the yellow coloration of anthraquinone in strong acid ($pK_a \leq -8.2$), whereas yellow coloration of *p*-nitrotoluene ($pK_a \leq -11.4$) is not observed. This indicates that SO_3H in the sulfonated 673 K carbon has a pK_a of −11 to −8, corresponding to acidity comparable to that of concentrated H_2SO_4. The carbon material therefore has much stronger acidity than sulfoaromatic compounds such as benzene sulfonic acid and *p*-toluene sulfonic acid (pK_a = ca. −2). No coloration was observed for the sulfonated 823 K carbon sample dyed with *p*-nitrotoluene, anthraquinone, chalcone ($pK_a = -5.6$), or benzenazodiphenylamine ($pK_a = +1.2$).

^{31}P MAS NMR spectra for the sulfonated 673 and 823 K carbon samples are shown in Figure 8. ^{1}H MAS NMR is often used for acid strength measurement of Brønsted acids. As these carbon materials contain a substantial amount of

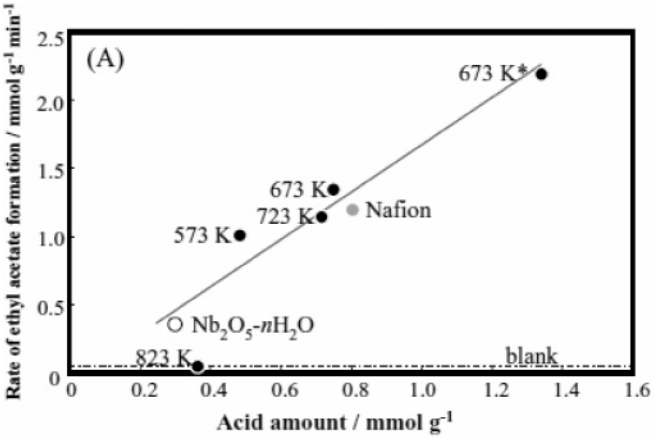

Figure 6. Catalytic activities and acid amount on ethyl acetate formation (A) and 2,3-dimethyl-2-butanol formation (B). Closed circles: prepared carbon samples 673 K*: Sample obtained by carbonization at 673 K, followed by fuming-H_2SO_4 sulfonation. The acid amounts for the carbon samples and Nafion are the SO_3H densities. That of $Nb_2O_5 \cdot nH_2O$ is the acidic OH density.

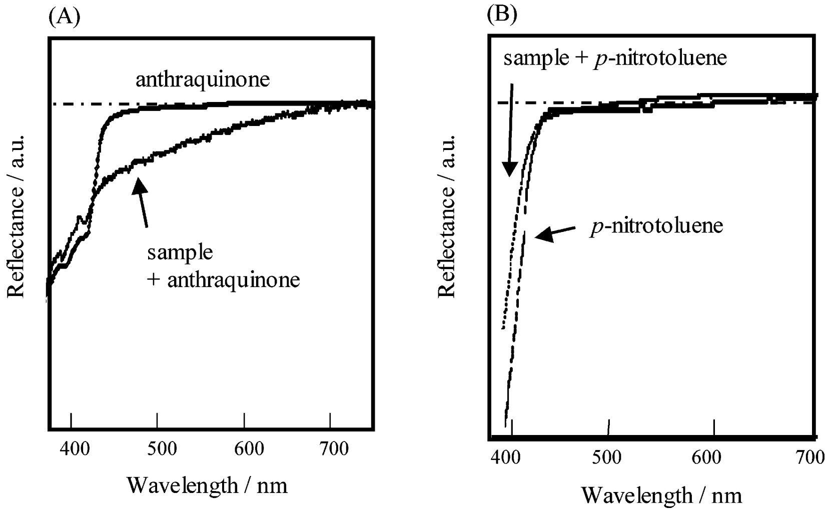

Figure 7. DRS spectra for sulfonated 673 K carbon after adsorption of (A) anthraquinon and (B) *p*-nitrotoluene.

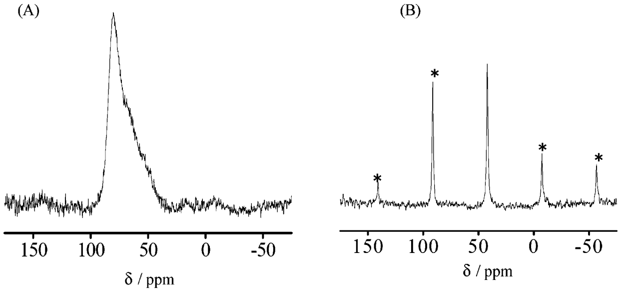

Figure 8. ^{31}P MAS NMR spectra for the sulfonated (A) 673 K and (B) 823 K carbon samples after exposure to TMPO (0.75 and 0.19 mmol of TMPO, respectively, per 1 g of the carbon sample). Asterisks denote spinning sidebands (SSB).

H, as shown in Table 1, it is difficult to separate only the resonance peaks due to Brønsted acids. The acidities of Brønsted acid sites in such materials can be estimated by ^{31}P-MAS NMR measurement of acid sites that adsorb probe molecules such as trimethylphosphine oxide (TMPO).[13,14] TMPO-adsorbed samples were prepared by soaking the sample in a THF solution containing TMPO at less than the acid amount ($-SO_3H$) in the sample.[15] The large excess of TMPO that does not adsorb to active sites aggregates on the solid surface, producing a sharp resonance peak at ca. 40 ppm. In the ^{31}P MAS NMR spectrum for the sulfonated 673 K carbon after TMPO adsorption, a broad asymmetric peak appears at 80 ppm. The sharp resonance peaks at 41 ppm due to TMPO crystal are not observed, indicating that all of the introduced TMPO had adsorbed to the material without surface aggregation. TMPO adsorbed to strong acid sites in HZSM-5—which have strong acidity comparable to that of concentrated H_2SO_4—produces a resonance peak at ca. 80 ppm.[14] The acid strength of the sulfonated 673 K carbon is therefore estimated to be equivalent to that of concentrated H_2SO_4. This is consistent with the colorimetry results above. In contrast, the spectrum for the sulfonated 823 K carbon exhibits only the peak due to TMPO crystal, even though the amount of TMPO introduced was much smaller than the amount of SO_3H in the sample. This indicates that most of the introduced TMPO molecules do not adsorb to the SO_3H

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(13) Karra, M. D.; Sutovich, K. J.; Mueller, K. T. *J. Am. Chem. Soc.* **2002**, *124*, 902.

(14) Zhao, Q.; Chen, W.-H.; Huang, S.-J.; Wu, Y.-C.; Lee, H.-K.; Liu, S.-B. *J. Phys. Chem. B* **2002**, *106*, 17, 4462.

(15) One gram of the sulfonated 673 K carbon material contains 0.75 mmol of SO_3H and 0.70 mmol of COOH. One gram of sample was soaked in THF solution, solving 0.75 mmol of TMPO corresponding to the amount of SO_3H in the sample. In the case of the sulfonated 823 K carbon, with only SO_3H (acid density: 0.37 mmol g^{-1}), 1 g of sample was exposed to 0.19 mmol of TMPO, much less than the amount of SO_3H in the sample.

groups and instead form surface aggregates of crystal TMPO. SO_3H groups in sulfoaromatic hydrocarbons are strong acid sites below $pK_a = -2$ and usually react with basic probe molecules such as TMPO and benzenazodiphenylamine ($pK_a = +1.2$). The fact that the SO_3H groups in the 873 K sample did not react with TMPO or benzenazodiphenylamine indicates that the reactants cannot reach most of the SO_3H groups in the material.

It was confirmed by TGA that the sulfonated samples prepared using D-glucose carbonized at temperatures of 723 K and below absorb a large amount of water, similar to ion-exchangeable resins. The samples were exposed to saturated water vapor at room temperature for several weeks and then heated at 313 K under N_2 flow in a thermogravimetric analyzer. TGA profiles were measured after no further weight loss was observed at that temperature. These sample weights decreased with increasing temperature, reaching a plateau at 400 K. The weight loss is due to the desorption of water, and the results indicate that ca. 10% of the original sample weight is attributable to water. As the surface area is small ($2\ m^2\ g^{-1}$ after dehydration at 423 K, see Table 1), this result suggests that the samples retain a considerable amount of water in the bulk, again similar to ion-exchangeable resins. The apparent volumes of the samples increased by up to 1.3−1.5 times when immersed in water, methanol, ethanol, and THF. This type of swelling in solvents would provide good access of the reactants in solution to the SO_3H groups in the carbon material, giving rise to the high catalytic performance, despite the small surface areas. The sulfonated carbon materials prepared at 723 K or below are therefore “soft” carbon materials composed of flexible polycyclic aromatic carbon with functional groups, and are thus distinct from conventional amorphous carbon materials. In contrast, a similar TGA experiment for the sulfonated 873 K carbon, which has the same surface area as the other samples, revealed that this sample contains only 1.5% water by weight. The material did not swell in water, methanol, ethanol, or THF. These results suggest that the sulfonated 873 K carbon is unable to incorporate large amounts of reactants, and therefore does not exhibit activity for acid catalysis. This is considered to be due to the lesser flexibility of the constituent polycyclic aromatic carbon. With increasing carbonization temperature, carbon materials become harder and the flexibility of the polycyclic aromatic carbon decreases through plane growth and carbon sheet stacking. The sulfonated 823 K carbon material is more carbonized than the other carbon materials examined here, as indicated by the composition (Table 1) and the strength of the C(101) diffraction peak (Figure 3). The polycyclic aromatic carbon in this sample is thus expected to be less flexible. It is also well-known that a large amount of sulfuric acid can be intercalated into interlayers even between large carbon (graphene) sheets in well-crystallized graphite through the formation of cationic graphene sheet$-HSO_4^{-}-H_2SO_4$ complexes.[16] Thus, although large inflexible polycyclic aromatic carbon in “rigid” carbon materials can be sulfonated with H_2SO_4, it is difficult for large neutral molecules to reach the SO_3H groups in the bulk of such materials, resulting in very limited acid catalysis. As mentioned above, sulfonated graphite, carbon black, graphitized carbon fiber, activated carbon, and glassy carbon cannot function as active acid catalysts for esterification, hydration, or hydrolysis.[6] These familiar carbon materials are obtained by heating at temperatures above 1023 K. The present results suggest that the lack of acid catalytic activity for such well-carbonized materials is not due solely to lower SO_3H densities, but rather may be primarily attributable to the inflexibility in the large polycyclic aromatic carbon produced at higher temperatures. Further detailed study will be necessary to determine how the carbonization and carbon sheet size in highly active carbon materials differ from those in nonactive carbon prepared by high-temperature carbonization.

Conclusions

The sulfonation of carbon materials prepared by low-temperature carbonization (≤723 K) of D-glucose resulted in a highly active, stable solid acid catalyst as a replacement for sulfuric acid. The catalysts are composed of polycyclic aromatic carbon with SO_3H, COOH, and OH. Sulfonation of the carbon material carbonization at higher temperature did not produce a catalytically active material. The marked difference in activity between these high- and low-temperature samples was attributed to strong differences in the incorporation of reactants related to the degree of carbonization and the size of polycyclic aromatic carbon.

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