Heterogeneous Catalysis

A Carbon Material as a Strong Protonic Acid**

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Solid acids are conventional materials that have wide applications in chemical production, separation/purification, and polymer–electrolyte fuel-cell (PEFC) technologies, and the chemical industry is currently searching for a highly active and stable solid acid to improve the environmental safety of the production of chemicals and energy. Over 15 million tons of sulfuric acid is annually consumed as "an unrecyclable catalyst"—which requires costly and inefficient separation of the catalyst from homogeneous reaction mixtures—for the production of industrially important chemicals, thus resulting in a huge waste of energy and large amounts of waste products. The "green" approach to chemical processes has stimulated the use of recyclable strong solid acids as replacements for such unrecyclable "liquid acid" catalysts.[1–4] Thermostable strong solid acids would have genuine applications in PEFCs as proton conductors, for improving fuel efficiency, and for reducing the use of noble-metal catalysts by increasing the working temperature.[5] However, a major obstacle to such progress is the lack of a solid acid that is as active, stable, and inexpensive as sulfuric acid.

An ideal solid material for the applications considered here should have high stability and numerous strong protonic acid sites. It is essential for the solid acid to maintain strong acidity even in water since water participates in fuel-cell reactions and many industrially important acid-catalyzed reactions. While organic acid/inorganic solid oxide hybrids and strong acidic cation-exchangeable resins, including perfluorosulfonated ionomers (for example, nafion), have been studied extensively as promising approaches for the construction of desired solid acids or proton conductors,[6] such materials are expensive and the acid activities are still much lower than that of sulfuric acid.[3] These drawbacks have limited their practical utility. Herein, we report the synthesis of a carbon-based solid acid with a high density of sulfonic acid groups (SO_3H) and discuss its performance as a novel strong and stable solid acid. Here, a new strategy is adopted for the development of new types of solid acid: a carbon material is obtained by incomplete carbonization of sulfoaromatic hydrocarbons and consists of small polycyclic aromatic carbon sheets with attached SO_3H groups. This approach is simple and allows for the use of sulfoaromatic hydrocarbons—strong, stable solvent-soluble acids (for example, benzene sulfonic acid and naphthalene sulfonic acid)—as insoluble solid acids.

Such carbon-based solid acids can be readily prepared by heating aromatic compounds such as naphthalene in sulfuric acid at 473–573 K.[7] In this synthesis, the sulfonation of the aromatic compounds is the first stage of the reaction. The resulting sulfonated aromatic compounds are incompletely carbonized, which results in the formation of a solid with a nominal sample composition of $CH_{0.35}O_{0.35}S_{0.14}$. The total yield of the product based on carbon is about 55 % by this method. The resulting black powder is insoluble in the tested solvents (water, methanol, ethanol, benzene, and hexane), even at boiling temperatures. A pellet formed from the powder has a high resistance of over 30 MΩ.

The powder X-ray diffraction (XRD) pattern and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum of the sample are shown in Figure 1 a and b. The XRD pattern exhibits two broad, weak diffraction peaks ($2\theta = 10–30°$, $35–50°$) attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.[8] The two peaks ($\delta = 141$ and 130 ppm) in the ^{13}C MAS NMR spectrum are assigned to aromatic carbon atoms with and without SO_3H groups.[9] A neutralization titration gave 4.9 mmol g^{-1} SO_3H attached to 11 % of the aromatic carbon atoms (Table 1). This finding means that the effective density of the acid sites in the sample is about five times that of nafion, which is a highly active and stable perfluorosulfonated ionomer. These results indicate that this material is amorphous carbon consisting of polycyclic aromatic carbon sheets with attached SO_3H groups that functions as a strong solid acid with a high density of acid sites.

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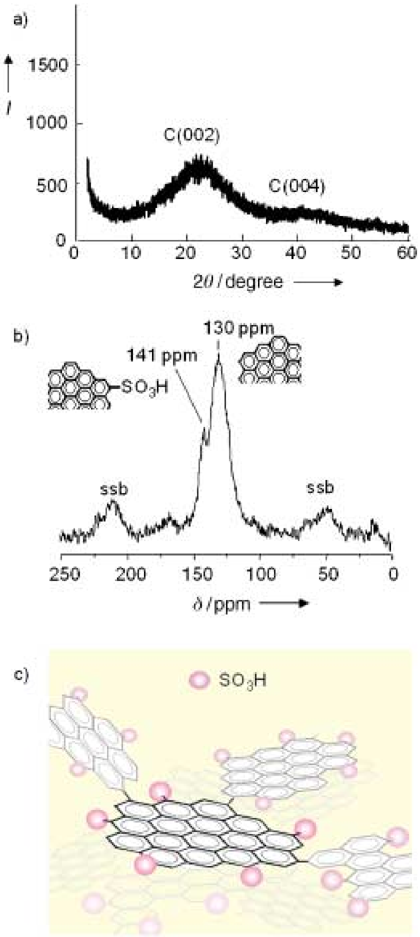

Figure 1. a) Powder XRD pattern, b) ^{13}C MAS NMR spectrum measured at 50.3 MHz, and c) proposed schematic structure of the carbon-based solid acid ($CH_{0.30}O_{0.33}S_{0.16}$). The carbon-based solid acid was evacuated at 180 °C for 1 h prior to ^{13}C-MAS NMR measurement. Spinning sidebands (ssb) appear at $\delta = 50$ and 210 ppm. The material is amorphous carbon composed of small sulfopolycyclic aromatic carbon rings oriented in a random fashion. SO_3H groups are attached to 11 % of the aromatic carbon atoms.

Table 1: Effective densities of the acid sites and catalytic activities of the tested samples in the formation of ethyl acetate.

Acid	Acid density [mmol g^{-1}]	Surface area [m^2 g^{-1}]	Catalytic activity [mmol min^{-1}]
carbon-based solid acid ($CH_{0.35}O_{0.35}S_{0.14}$)	4.90	24	1.3
protonated nafion (NR50)	0.93	<0.1	0.2
H_2SO_4-treated carbon materials			
carbonized resin	0.08	19	–
glassy carbon	0.05	26	–
activated carbon	0.15	1250	–
natural graphite	0.05	25	–
H_2SO_4	20.4	–	1.9

This carbon-based solid acid is not an electron conductor and contains relatively high densities of H and SO_3H groups, which suggests that the material is composed of sulfopolycyclic aromatic hydrocarbons as illustrated in Figure 1 c, rather than aromatic carbon sheets as seen in conducting amorphous carbon materials.

The thermal stability of the material was examined by thermogravimetric analysis (TGA) and temperature-programmed desorption (TPD) under a flow of air (Figure 2).[10] The sample weight decreased in with increasing temperature in the TGA (Figure 2 a), and reached a plateau at 390–420 K. Heating the sample above 500–550 K resulted in a decrease in weight. TPD (Figure 2 b) revealed that H_2O evolution ($M_r = 18$ Da) from the sample increases rapidly with temperature above 520 K, at which both SO_2 ($M_r = 64$ Da) and CO_2 ($M_r = 44$ Da) begin to evolve. No SO_3 ($M_r = 80$ Da) evolution was detected from the sample. No significant differences in the ^{13}C MAS NMR spectra or sample composition were observed before and after heating at 473 K. Heating the sample at 523 K caused a gradual reduction in the resonance of the sulfonated aromatic carbon atoms ($\delta = 144$ ppm) in the ^{13}C MAS NMR spectrum and a decrease in the H, O, and S compositions with increasing heating time. These results clearly indicate that the solid acid functions as such at temperatures up to 500–520 K, thus the material is not at all inferior to perfluorosulfonated ionomers in chemical and thermal stability.

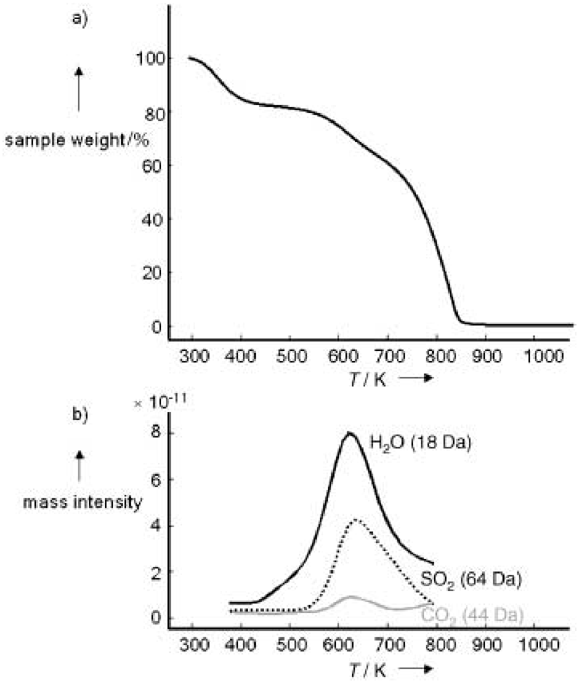

Figure 2. a) TGA of the carbon-based solid acid; b) TPD curves for the carbon-based solid acid. The sample was heated at 10 K min^{-1}.

The strength and density of the acid sites of the material were demonstrated through the esterification of acetic acid (343 K), hydrolysis of cyclohexyl acetate (353 K), and hydration of 2,3-dimethyl-2-butene (343 K).[11] Figure 3 shows the rates of formation of ethyl acetate (Figure 3 a), cyclohexanol (Figure 3 b), and 2,3-dimethyl-2-butanol (Figure 3 c) on the carbon-based solid acid (0.2 g). For comparison, the results

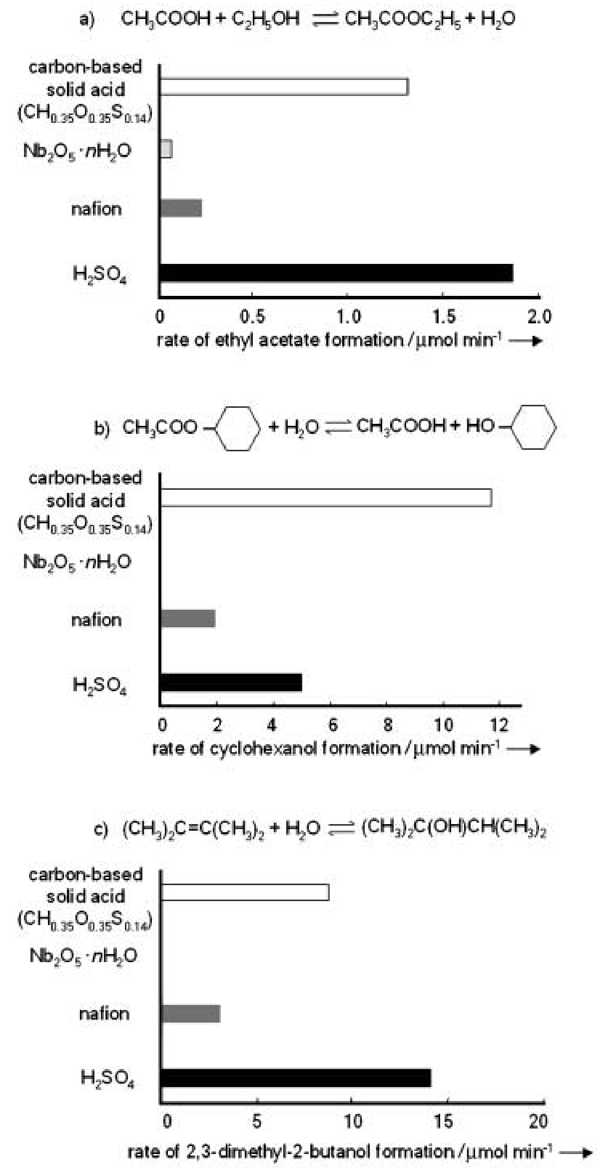

Figure 3. Acid-catalyzed liquid-phase reactions: a) Rate of formation of ethyl acetate during the esterification of acetic acid (343 K); b) rate of formation of cyclohexanol in the hydrolysis of cyclohexyl acetate (353 K); c) rate of formation of 2,3-dimethyl-2-butanol (343 K). Rates were measured in the early stage of the reaction (1 h).

for 0.2 g of concentrated sulfuric acid (>96%), protonated nafion (NR50), and niobic acid ($Nb_2O_5{\cdot}n\,H_2O$) are also shown. Niobic acid is a rare inorganic solid acid that exhibits only marginal acidity in the presence of water, whereas protonated nafion, which is used as a proton conductor in PEFC, exhibits very high activity for reactions involving thermostable solid acids.[3,6] The carbon-based solid acid exhibited a remarkably high activity for the formation of ethyl acetate: the activity is much higher than those of conventional solid acids and is comparable to that of sulfuric acid. After the reaction had reached equilibrium (7–10 h), the carbon-based solid acid was simply recovered by decantation and recycled for further reaction. It was confirmed that both the activity for the formation of ethyl acetate and the sample composition ($CH_{0.35}O_{0.35}S_{0.14}$) remained unchanged, even after the sample had been recycled for a fourth time. Figure 3b and c also show that the carbon-based solid acid rivals sulfuric acid in the hydrolysis of cyclohexyl acetate and the hydration of 2,3-dimethyl-2-butene, and also attacks hydrophobic reactants in excess water to the same extent as sulfuric acid. Since many industrial important chemicals such as alcohols, esters, ethers, and acetals are produced by such reactions in the presence of a sulfuric acid catalyst, the comparable performance of the carbon-based solid acid as indicated by the present results demonstrates that it has the potential to replace the sulfuric acid catalyst in such applications.

The carbon-based solid acid has clear potential for use as a replacement for the sulfuric acid catalyst. Furthermore, the SO_3H groups act as proton carriers, which means that the material with a high density of SO_3H groups is also useful as a proton conductor. A pellet formed from the sample powder ($CH_{0.35}O_{0.35}S_{0.14}$) exhibited a protonic conductivity of $0.11\,S\,m^{-1}$ at 323 K (humidity: 100%), which is comparable to that of nafion ($0.1\,S\,m^{-1}$, 353 K).[12] The conductivity in the current case is considered to be limited by the irregular shape of particles in the pellet, which prevents rapid protonic conduction. In addition, the high density of SO_3H groups in the material suggests that the carbon-based material itself displays much higher protonic conductivity than the measured value.

The same carbon-based solid acids can also be synthesized from various polycyclic aromatic hydrocarbons, such as anthracene ($C_{14}H_{10}$), perylene ($C_{20}H_{20}$), and coronene ($C_{24}H_{12}$), in coal tar. This suggests that coal tar, petroleum pitch, and asphalt, which are composed predominantly of polycyclic aromatic hydrocarbons, are also potential strong solid acids. However, stable and active solid acids could not be prepared by sulfonation of an incompletely carbonized resin, amorphous glassy carbon, activated carbon, or natural graphite. Heating these carbon materials in sulfuric acid resulted in carbon materials with only a low density of SO_3H groups,[13] and these H_2SO_4-treated carbon materials did not act as an acid catalyst in the esterification of acetic acid. Effective acid site densities, surface areas, and catalytic activities of the tested samples are summarized in Table 1. There was no difference in the surface areas of the carbon materials before and after treatment with H_2SO_4. The SO_3H groups on the carbon atoms were preserved in water at room temperature, but all were removed under the reaction conditions used or in warm water above 323 K. Apparently, there is a definitive distinction between the stability and SO_3H density of H_2SO_4-treated carbon materials and carbon-based solid acids, even though the SO_3H groups are bonded to aromatic carbon atoms in both materials. Thus, it is difficult to introduce large amounts of active functional groups into carbon materials,[14] but these results suggest that highly active and stable carbon materials with high densities of functional groups can be readily prepared by incomplete carbonization of aromatic compounds in sulfuric acid.

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[7] In a typical synthesis, naphthalene (20 g) was heated in concentrated sulfuric acid (>96%, 200 mL) at 523 K under a flow of N_2. After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 523 K for 5 h, which resulted in a black solid. The solid was then ground to a powder and was washed repeatedly in boiling water until impurities such as sulfate ions were no longer detected in the wash water. The nominal sample composition was determined by elemental analysis to be $CH_{0.35}O_{0.35}S_{0.14}$.

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[10] TPD analyses were carried out using a TPD-1-AT (BEL Japan) equipped with a quadrupole mass spectrometer. The sample (20 mg) was placed in a quartz cell and heated at 423 K for 1 h under a flow of He then cooled to 373 K. The sample was heated at 10 K min^{-1} under a flow of dry air. Desorbed species were detected by the mass spectrometer.

[11] Esterification of acetic acid (343 K), hydrolysis of cyclohexyl acetate (353 K), and hydration of 2,3-dimethyl-2-butene (343 K) were carried out in a mixture of ethanol (1.0 mol) and acetic acid (0.1 mol) and distilled water (3.3 mol) containing cyclohexyl acetate (4.4 mmol) or distilled water (0.22 mol) containing 2,3-dimethyl-2-butene (0.22 mol) in an Ar atmosphere. All catalysts tested 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 was analyzed during the reaction by gas chromatography using capillary columns.

[12] The proton conductivity of the carbon-based material was obtained by an alternating current impedance method. A pellet (5 mmϕ, 1 mm thickness) between carbon papers was set in a measurement cell in an atmosphere of H_2 and saturated H_2O vapor (total pressure: atmospheric pressure).

[13] In a typical preparation, carbon powder (20 g; carbonized resin, glassy carbon, activated carbon, and natural graphite) was heated in concentrated sulfuric acid (>96%, 200 mL) at 523 K for 15 h under a flow of N_2. The resulting carbon material was washed repeatedly with water at room temperature until sulfate ions were no longer detected in the wash water. Carbonized resin was obtained by incomplete carbonization of polymerized furfuryl alcohol. Furfuryl alcohol was polymerized in the presence of acid. The resulting polymer was heated at 543 K for 72 h in a flow of Ar. The carbonized resin was a considerably amorphous carbon material ($CH_{0.35}O_{0.35}S_{0.14}$)

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