

Surface-sulfonated Diamond Powder for Solid Acid

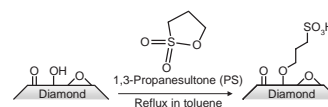
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The surface of diamond powder (DP) was sulfonated via a covalent modification method using 1,3-propanesultone, for the fabrication of a new class of solid acid material. X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy studies confirmed successful introduction of sulfo groups on the DP surface. The optimal condition for the preparation of sulfonated DP (S-DP) was investigated in terms of acid amount on the surface. The S-DP exhibited solid Brønsted acid properties in pure water and catalytic activity toward the formation of ethyl acetate.

The development of surface-sulfonated solid materials is important, because these materials can be utilized as solid acid catalysts and proton-conducting materials for fuel cells, which are closely related to environmentally conscious processes. As substrates for such materials, relatively chemically inert silica^{1,2} and carbon materials³⁻⁵ have been investigated as sulfonated solid acid substrates, as well as perfluoro polymer constituting Nafion[®]. As a catalyst, the solid acid material itself is required to be insoluble in the reaction media, which guarantees reusability of the catalyst and a pollution-free production process.^{6,7} As a proton-conducting material in a fuel cell, dimensional stability, in addition to thermal and chemical stability, is desirable for long-term durability with respect to the performance of the fuel cell.¹ Diamond should be one of the best materials to meet the above requirements, owing to its extremely high mechanical, thermal, and chemical stability. However, to the best of our knowledge, there have been no attempts to employ diamond as a substrate material for a solid acid. In contrast to the chemical inertness of the bulk, a diamond surface can be chemically modified by various methods including wet⁸⁻¹⁰ and dry¹¹⁻¹³ processes. Thus, the surface of diamond powder (DP) was sulfonated via a covalent modification method using 1,3-propanesultone (PS) (Scheme 1). The sulfonated DP obtained was found to exhibit solid Brønsted acid properties and catalytic activity toward the formation of ethyl acetate.

DP (Micron+ SND, Element Six, nominal particle size <500 nm) was successively washed with aqua regia and 30% H₂O₂ for 30 min at 60 °C to remove any contaminants and to oxidize the surface, and then with pure water, 2-propanol, and acetone. 0.25 g of the oxidized DP (O-DP) was then added to 20 mL of a PS/toluene solution at a given concentration, and the suspension was refluxed at 100 °C for a given time. After washing with toluene and drying, sulfonated DP (S-DP) was obtained. The amount of acid on the DP surface was estimated by neutralization titration of the DP suspension in pure water. 0.2 mM NaOH was titrated into 30 mL of pure water containing 0.1 g of DP sample, and the pH was monitored under the stirred condition. The solid acid catalytic properties of DP were estimated using ethyl acetate formation as a model reaction. A



Scheme 1. Surface sulfonation of the diamond powder.

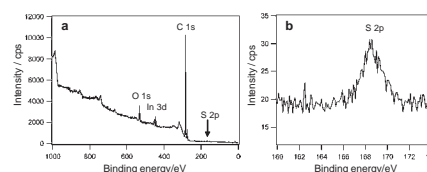


Figure 1. XPS spectra of (a) the S-DP sample, and the (b) S 2p peak of S-DP. The sample was fixed on indium foil.

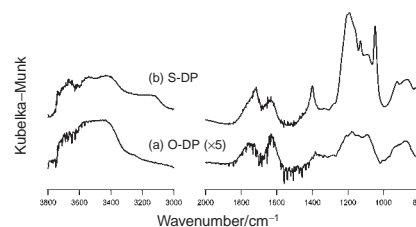


Figure 2. DRIFT spectra of the (a) O-DP and (b) S-DP samples.

given amount of DP sample was added to a mixed solution of 0.25 mol ethanol and 0.25 mol acetic acid, and the suspension was stirred in a screw-cap bottle sealed with Teflon tape at 70 °C. The amount of ethyl acetate produced was analyzed by gas chromatography.

Surface sulfonation of DP was characterized using X-ray photoelectron spectroscopy (XPS) and diffusion reflectance infrared Fourier transform (DRIFT) spectroscopy. In an XPS spectrum of an O-DP sample, only C 1s (284 eV) and O 1s (532 eV) peaks were observed. After reaction with PS, a new peak assigned to S 2p appeared at 168.5 eV, which can be clearly observed in the narrow scan (Figure 1). This indicates the surface immobilization of sulfur-containing species on DP.

Figure 2 shows DRIFT spectra of O- and S-DP. In addition to adsorption bands for C=O (1720–60 cm⁻¹) and C–O–C (1030–1280 cm⁻¹),^{11,14} which are also shown for O-DP, new bands appeared for S-DP. Absorption bands at 1046 and 1129 cm⁻¹ were assigned to the SO₂ asymmetric and symmetric stretching modes of the sulfonic acid groups combined with trace water, respectively.⁵ On the other hand, the bands at 924 and 1400 cm⁻¹ can be assigned to S–OH and S=O stretching modes of the undissociated sulfonic acid groups, respectively.¹⁵ These results indicate that sulfo groups were successfully introduced onto the DP surface by reaction with PS. This reagent is considered to react with OH groups^{1,2} on the DP surface, while

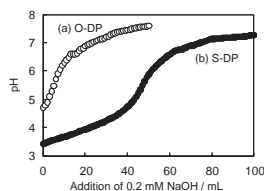


Figure 3. Neutralization titration curves for (a) O-DP and (b) S-DP suspensions. 30 mL of pure water containing 0.1 g of DP sample was neutralized by the addition of 0.2 mM NaOH.

various other types of oxygen-containing functionalities such as C=O and C–O–C should also be present on the O-DP surface.⁹ Thus, absorption bands assigned to these groups were also observed for the DP sample after reaction with PS.

The amount of sulfo groups on S-DP was estimated using neutralization titration. When 0.1 g of O-DP was added to 30 mL of pure water, the pH of the suspension was 4.7. Suspensions containing S-DPs prepared under various conditions always had lower pH values (3.4–4.3) than that of O-DP. In addition, the titration curve showed sigmoidal behavior, which indicates that S-DP can act as a solid Brønsted acid based on the sulfo groups on the surface (Figure 3). Although the reason why the equivalence point of the titration curve was around 5–6 is still unclear, however, such behaviors were exhibited for other samples. Perhaps dispersion condition of the sample during titration could be related to the behavior. In order to determine the optimal conditions for the preparation of S-DP, the PS concentration and reaction time for the sulfonation reaction were investigated. The amount of Brønsted acid was tentatively defined from the inflection point of the titration curve as the equivalence point. When 0.1 M PS was used, the acid amount was increased as the reaction time increased, and the behavior corresponds well to a pseudo-first-order reaction with $\tau = 13$ h and was almost saturated at 48 h.¹⁶ The relatively slow reaction rate for sulfonation may indicate that the immobilization of sulfo-containing groups is due to covalent bond formation rather than physisorption. The PS concentration used for the preparation of S-DP was also investigated. After a 48-h treatment, the acid amount increased as the PS concentration increased from 0.1 to 1.0 M and became almost constant up to 2.0 M.¹⁶ The acid amount of the S-DP sample prepared with 1.0 M PS was estimated to be 0.072 mmol g⁻¹, which corresponds to the surface coverage of 1.6×10^{14} cm⁻² from the specific surface area of DP measured by BET method (27 m² g⁻¹). This coverage is roughly 10% of the surface carbon atoms on diamond.

Finally, the solid acid catalytic properties of S-DP were estimated using the esterification of ethanol and acetic acid as a model reaction. Figure 4a shows the amount of ethyl acetate produced as a function of reaction time in the presence of 0.5 g of DP. By comparison, it was found that the reaction rate was greater for a solution containing S-DP than that for O-DP. Figure 4b shows the amount of ethyl acetate produced after 6 h of reaction as a function of the DP amount in the reaction solution. For the reaction solution containing O-DP, the amount of ethyl acetate produced was substantially constant and was similar to that obtained without any catalyst. This result indicates that the O-DP does not exhibit catalytic activity for esterification. On the other hand, the amount of ethyl acetate produced was linearly increased with the amount of S-DP added to the solution. Thus,

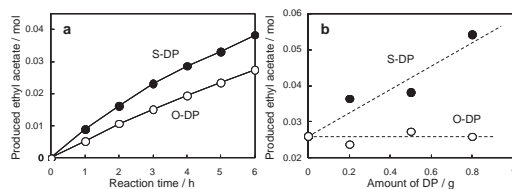


Figure 4. (a) Amount of ethyl acetate produced as a function of reaction time in the presence of 0.5 g of (○) O-DP and (●) S-DP. The reaction solution was a mixture of 0.25 mol ethanol and 0.25 mol acetic acid. (b) Amount of ethyl acetate produced as a function of the amount of DP in the reaction solution. The reaction time was fixed at 6 h.

it can be concluded that S-DP can act as solid Brønsted acid catalyst for esterification. The catalytic activity was, however, still rather weak comparing to Nafion[®].¹⁶ Thus, improvements in the acid amount and strength by other types of surface modification method are now under study. Stability of the surface sulfo group in water is also needed to be improved because the surface S/C ratio estimated by XPS was reduced from 0.013 to 0.004 after ultrasonication in pure water for 30 min. However, the S-DP sample used for esterification (6 h) still exhibited catalytic activity in the repeated experiment under an identical condition without significant reduction in the amount of produced ethyl acetate ($\approx 90\%$).¹⁶ Combined with confirmation by DRIFT spectra, the sulfo groups on S-DP exhibited sufficient stability during esterification reaction.

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