Mechanism of the sulfonation by plasma-sulfuric acid interactions

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Abstract: Sulfonated carbon catalysts are essential in various reactions, making carbon sulfonation a popular research topic. Plasma sulfonation stands out as an eco-friendly method, requiring only diluted sulfuric acid and a short treatment time of 1 hour. However, its reaction mechanisms are not well understood. This study reveals that sulfate radicals (•SO4–) formed during plasma sulfonation react with carbon materials, creating -OSO3H and -SO3H groups, along with other oxygen-containing groups on the carbon surface. The process achieves efficient sulfonation without high temperatures or concentrated acids, offering valuable insights for optimizing this sustainable technique.

1. Introduction

Li et al. introduced a plasma-based carbon sulfonation method using dilute acids and gas-liquid interfacial plasma (GLIP)[1][2], but the improvements in sulfonation were limited. Active species like OH radicals, confirmed in our earlier research, react with sulfur-containing species and attach to defects on the carbon surface, forming sulfur-containing functional groups. Additionally, Jiang et al. demonstrated that sulfate radicals ($\bullet SO_4^-$) can form through reactions between HSO_4^- and OH radicals, highlighting their potential role in plasma sulfonation[3]. Sulfate radicals may be key species in the plasma sulfonation process. Common methods to activate persulfate include base activation, UV irradiation, heat, and metal oxides. However, due to their high reactivity, $\bullet SO_4^-$ is challenging to detect in sulfuric acid solutions, particularly during plasma discharge.

In this study, we activated 0.1–0.5 mol/L Na2S2O8 solutions in two ways to generate $\bullet SO_4^-$ and explore its role in carbon sulfonation. Using DC plasma, we compare sulfonation results and catalytic performance of carbon treated under different discharge polarities and treatment durations.

2. Methods

In this experiment, a DC plasma system was used to produce sulfonated carbon materials. The setup, shown in Figure S1, included a DC power supply (Matsusada HAR-5R60) and a reactor with a high-voltage electrode, a liquid electrode, and a quartz glass tube (50 mm inner diameter). The high-voltage stainless steel electrode was placed 2 mm above the solution surface, while the grounded electrode was immersed in the solution. The reactor was set on a magnetic stirrer (Yamato MD200) to continuously mix the solution and carbon material during plasma discharge. Argon gas was supplied at 100 sccm through the hollow high-voltage electrode.

3. Results and Discussion

The catalytic performance of the produced catalyst was tested through cellulose and cellobiose hydrolysis. The yield of reducing sugars during cellulose hydrolysis increased with longer plasma treatment of CNTs, matching the increase in functional group density observed earlier.
Negative plasma-treated CNTs showed lower glucose selectivity due to insufficient functional groups to fully hydrolyze cellobiose into glucose. Positive plasma-treated CNTs also had reduced glucose selectivity, likely due to a decrease in functional groups.

4. Conclusion

This study explores plasma sulfonation as an eco-friendly and efficient method for functionalizing carbon materials. The process generates sulfate radicals (SO_4^-) in the liquid phase, primarily from reactions between OH radicals and HSO_4^- ions, leading to the formation of sulfonic, sulfate, and oxygen-containing groups on the carbon surface. DC plasma-treated CNTs achieved 34.6% cellulose conversion with a 22.5% glucose yield in cellulose hydrolysis.

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