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Carbon-coated mesoporous silica functionalized with sulfonic acid groups and its application to acetalization

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ABSTRACT

The inner surface of mesoporous silica SBA-15 was coated by a homogeneous polycyclic carbon layer through controlled carbonization of furfuryl alcohol. The composite was subsequently functionalized with sulfonic acid ($-\text{SO}_3\text{H}$) groups to form a strong solid acid material, with a tunable acid site density in the range of 0.38–0.84 mmol/g by varying the thickness of the carbon layer. Structural analysis and reaction data revealed that the solid acid catalyst exhibited high reactivity towards the acetalization of aldehydes or ketones with alcohols because of the uniform carbon coating of the mesopores, high acid site density, and its mechanical stability.

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1. Introduction

Solid acid catalysts have been widely applied in petroleum refining and fine chemical production processes because of a number of advantages, including their convenient reuse, long-term activities, and low environmental pollution. Solid acids such as metal oxides [1,2], heteropoly acids [3,4], sulfonic acid group-functionalized materials [5,6], and acidic ion exchange resins [7,8] can effectively replace homogeneous acids, including sulfuric acid, fatty acid salts [9], and organic sulfonic acid [10], in various acid-catalyzed reactions, such as the Beckmann rearrangement [11,12], alkylation [13], esterification and hydrolysis [5,6], acylation [14], etherification [15], addition reaction of the epoxides and olefin adducts as well as the dehydration of the alcohols [16,17], condensation [18,19], and hydrogenation reforming [20].

Recently, heterogeneous acids containing sulfonic acid

groups, including ionic liquids [21], organic-inorganic hybrid porous materials [22,23] and sugar derived carbon catalysts [24], have been intensively investigated, because of their abundant acid content and effective activities. Xing et al. [25] reported a sulfonated mesoporous carbon material with a classical CMK-3 type mesostructure, applying SBA-15 as a hard template filled with sucrose, which was subsequently carbonized incompletely to a polycyclic aromatic carbon. The aromatic system is rich in benzene rings that can be controllably grafted by sulfonic acid groups, leading to a novel mesoporous solid acid CMK-3- SO_3H . Compared with the sulfonated sugar carbon acid (2 m²/g) from Nakajima et al. [26], it possesses a large specific surface area of nearly 1000 m²/g and 1.0 mmol/g Brønsted acid sites and shows an excellent catalytic activity towards the liquid phase Beckmann rearrangement. However, the carbon framework of CMK-3- SO_3H is fragile in practical applications, especially during sulfonation because the frame-

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work tends to collapse with over-carbonation by the sulfuric acid. Accordingly, Fang et al. [6] further simplified the synthetic procedure to make a sulfonic functionalized carbon-silicon composite, which exhibited high stability and chemical reactivity for esterification and transesterification in biodiesel synthesis after several recycles because of pillaring of silica in the composites. Increasing the carbon loading in a carbon-silica composite can provide more benzene rings for functionalization by sulfonic acid groups but, nevertheless, the bulk aromatic carbon is randomly distributed in the pores or on the channel entrance of SBA-15, which significantly limits the diffusion of large molecules in confined nanospaces.

As is well known, acetalization is generally used to protect the carbonyl group of aldehydes and ketones and, moreover, the acetal is the main raw enantiomeric compound used in the production of anabolic steroids, pharmaceuticals, paint, and perfumes, which often involves large molecules. The reaction is usually catalyzed by homogeneous acids to obtain high yield and selectivity [27]. Although heteropoly acids [21] and ionic liquid catalysts give high yields, greater than 90%, long reaction times are necessary because of their low acidity [28]. Sulfonated nano silica fibers with high acidity are a good candidate; however, their low surface area and small pore volume dramatically reduce the reaction rate [29].

Here, based on a method to synthesize CMK-5 with furfuryl alcohol [30], we prepared a carbon-silica composite with an aromatic carbon layer decoration on the pore walls of mesoporous silica, using furfuryl alcohol as the carbon source. A SBA-15 silica support was pretreated by incorporation of Al^{3+} , which modifies the silica wall with a dispersion of acid sites that then catalyze the carbonization of furfuryl alcohol. The resultant Al-SBA-15 was loaded by furfuryl alcohol, which was then converted to a polycyclic benzene ring carbon coating on the silica wall under a sequence of vacuum extraction and appropriate thermal treatment. Finally, the composite was sulfonated to obtain a mesoporous carbon-silica solid acid, reserving the hollow channels to retain a large surface area and accessible acid sites. This material exhibits a high catalytic reactivity towards the acetalization of aldehydes or ketones with alcohol and is stable during recycled usage.

2. Experimental

2.1. Material preparation

Mesoporous SBA-15 was synthesized by the conventional approach using poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyl-eneoxide) (P123, $M_w \approx 5800$, Sigma-Aldrich) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich) in acidic media [6]. One gram of calcined SBA-15 was treated with Al^{3+} in a 25 ml anhydrous alcohol (China National Medicines Corporation Ltd.) solution containing 0.12 g AlCl_3 (China National Medicines Corporation Ltd.) at a Si/Al molar ratio of 20:1 [31]. After stirring at room temperature for 14 h, the Al-incorporated SBA-15 was filtered, washed three times with anhydrous alcohol, and then dried at 80 °C, followed by calcination at 550 °C in air for 6 h. The resultant white solid product was named Al-SBA-15 and

had a Si/Al molar ratio of 19.2, determined by elemental analysis.

Subsequently, the aluminosilicate was filled with furfuryl alcohol (>98.0%, China National Medicines Corporation Ltd.) at room temperature using an incipient wetness method. The amount of furfuryl alcohol was varied over a furfuryl alcohol/Al-SBA-15 mass ratio of 0.5-5, respectively. The filled aluminosilicate was heated at 80 °C for 1 h to polymerize the furfuryl alcohol and then exposed to extraction under vacuum at the same temperature for 1 h to remove the excess alcohol. Finally, calcination was continued under N_2 at 550 °C for 6 h to obtain the carbon-silica composite, which was named SC- x (x = mass change due to the carbon compound according to the thermogravimetric analysis profile, e.g. $x = 15$ indicates a 15% mass change). The SC- x was mildly sulfonated at 80 °C in an atmosphere of fuming sulfuric acid (50% $\text{SO}_3/\text{H}_2\text{SO}_4$, China National Medicines Corporation Ltd.), with a ratio of solid/liquid = 1:20 g/ml for 12 h. To extract the physically adsorbed $-\text{SO}_3\text{H}$ group, the solid acid was finally washed with water at >80 °C until no white precipitate could be detected in the filtrate with BaCl_2 ($\geq 98.0\%$, China National Medicines Corporation Ltd.), and dried to obtain the surfonated carbon-silica composite SC- x - SO_3H .

The SC- x and SC- x - SO_3H were liberated from the silica template by treatment with 15% HF ($\geq 40\%$, China National Medicines Corporation Ltd.) solution at a ratio of solid/liquid = 1:20 g/ml under stirring at room temperature overnight, followed by washing with ionized water and drying to obtain CMK-5 type materials, named C- x and C- x - SO_3H , respectively.

Sulfonated carbon-silica composites using sucrose were prepared according to the method reported by Fang et al. [6].

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). N_2 adsorption isotherms were measured at -196 °C on a Quantachrome Autosorb-3B instrument after activating the sample at 120 °C under vacuum for 6 h. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 microscope. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Fourier transform infrared spectrometer (NEXUS 670) using KBr. The spectra of pyridine adsorption were measured by first treating the sample wafers at 150 °C under vacuum for 5 h and then exposing them to pyridine vapor at 110 °C for 0.5 h. Desorption of pyridine was carried out at 150 °C. Thermogravimetric (TG) analysis curves were obtained on a Mettler analyzer (TGA/SDTA 851e/5FL1100). The acid density was quantified by acid-base titration whereby 0.15±0.01 g solid acid was ion-exchanged in 60 ml saturated NaCl solution at room temperature for 12 h and then filtered, followed by titration of the filtrate against NaOH solution, which had been standardized by potassium acid phthalate.

2.3. Catalytic test

The aldehyde or ketone 0.04 mol, alcohol 0.048 mol (cyclo-

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