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Preparation of a novel sulfonated carbon catalyst for the etherification of isopentene with methanol to produce *tert*-amyl methyl ether

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ABSTRACT

A novel method for the preparation of acid carbon catalyst from glucose and 4-hydroxybenzenesulfonic acid (*p*-HBSA) was reported. Glucose was first hydrolyzed to hydroxymethylfurfural that reacted with *p*-HBSA (a phenol compound) to form a phenolic (PF)-like resin containing $–SO_3H$ groups. The resin was carbonized and sulfonated further in concentrated sulfuric acid at 443 K to form an amorphous carbon material with a surface area of 22 m^2/g. This acidic carbon contained 3.1 mmol/g of strong surface acid sites ($–SO_3H$), and thus exhibited good catalytic activity for the etherification of isopentene with methanol to produce *tert*-amyl methyl ether.

1. Introduction

The acid catalyzed reactions are important in chemical industry [1]. Sulfuric acid is frequently used for various acid catalyzed reactions, such as alkylation, esterification, isomerization, hydration and etherification [2]. However, the problems of pollution and separation are always there when sulfuric acid and other inorganic acids are used as catalysts. Thus, enormous efforts have been made in the academic and industrial communities in order to find solid acid catalysts to replace them. Various solid acids have been studied, including proton exchanged resins [3], solid superacids (e.g., SO_4^{2-}/ZrO_2) [4] and sulfonated carbon materials [5]. The acidic resins are widely used as catalysts in industry, but they cannot be used at temperatures higher than 423 K and may swell in an organic solvent resulting in the crush of catalyst bed. On the other hand, acidic carbon catalysts do not swell and exhibited much better thermal stability. Recently, Hara, et al. prepared a series of acidic carbon catalysts through the direct carbonization of raw materials such as sugar [6,7] and cellulose [8,9] followed by the sulfonation of resulted carbons, and found that such acidic carbon materials exhibited good catalytic behavior. Their work promoted the development of acidic carbon catalysts. However, the acidic carbons prepared by Hara et al. possessed low surface areas (~2 m^2/g).

Recently, a method was developed in our group for the synthesis of mesoporous carbons from carbohydrates such as fructose, glucose, sucrose and so on [10]. The carbohydrates were found to be first hydrolyzed into hydroxymethylfurfural (HMF) catalyzed by an acid and then the resulted HMF was polymerized into a resin, which could be subsequently carbonized to mesoporous carbon materials. The same method might be used for the preparation of acidic carbon materials with some appropriate modifications.

Accordingly, a new strategy for the synthesis of acidic carbon materials was proposed in this work. Glucose and 4-hydroxybenzenesulfonic acid (*p*-HBSA) were used as the raw materials. Glucose was first hydrolyzed into HMF which reacted with *p*-HBSA (a phenol compound) to form a phenolic (PF)-like resin. Since the use of *p*-HBSA, great amount of $–SO_3H$ groups were introduced into the PF-like resin. The resin was then carbonized and further sulfonated in concentrated sulfuric acid, resulting in an acid carbon enriched with surface sulfonic groups. This synthesis process is schematically shown in Fig. 1.

Since no high temperature treatment process was involved in this new method, the surface area of and surface sulfonic groups on the acidic carbon thus prepared would not be very low. The catalytic activity of this acidic carbon material was evaluated by the reaction of etherification of isopentene with methanol to produce *tert*-amyl methyl ether (TAME). TAME is an important additive in gasoline [11]. This reaction is typically catalyzed by Brønsted acids catalysts such as sulfuric acid and proton exchanged resin [12].

2. Experimental

2.1. Preparation of the catalyst

In a typical synthesis, 10 g glucose and 20 g *p*-HBSA (65% aqueous solution) were dissolved in 30 ml de-ionized water in a beaker to form

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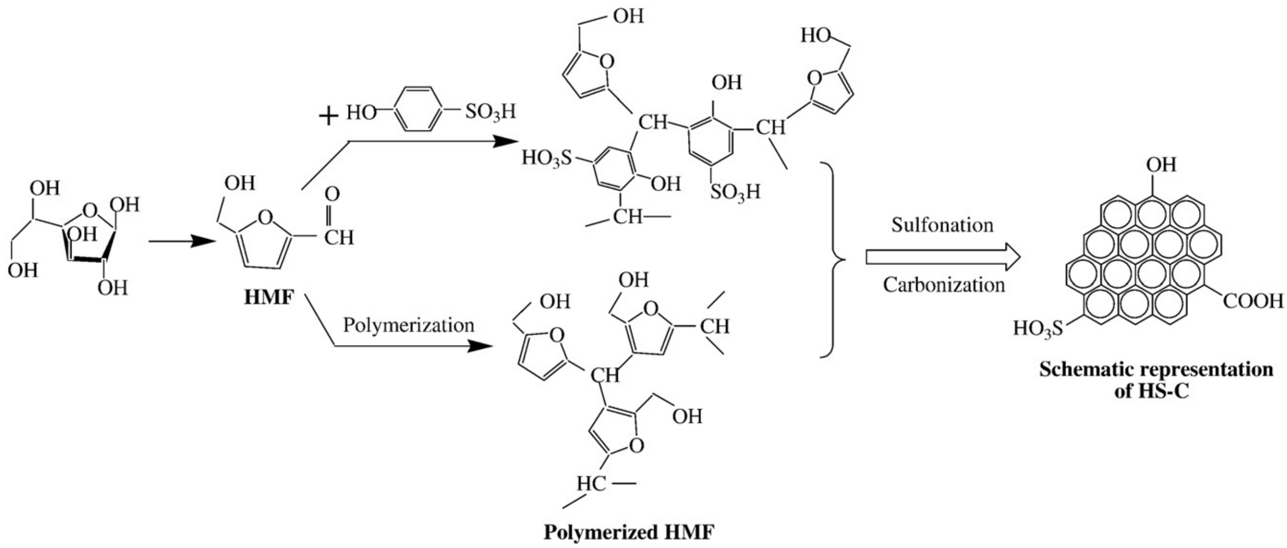

Fig. 1. Schematic diagram for the synthesis of acidic carbon materials from glucose and 4-hydroxybenzenesulfonic acid.

a clear brownish red solution. The solution was heated at 358 K under stirring for about 2 h during which water was simultaneously evaporated and a black viscous paste was formed. The paste was then cured at 303 K for 1 h to form a black solid (resin). It was washed with de-ionized water for several times until the filtrate was neutral and no sulfate ions were detested, and then dried at 353 K. The resin thus prepared was denoted as HS-R, and further heated in concentrated sulfuric acid (98%) at 443 K for 12 h, during which carbonization and sulfonation processes occurred. Afterwards, the carbonized sample was washed thoroughly by de-ionized water, and dried at 353 K overnight. The acidic carbon thus prepared was denoted as HS-C.

For comparison, an acidic carbon (denoted as Hara-C) was also prepared according to the method reported by Hara, et al. [6]. In this method, glucose was carbonized in N_2 at 673 K for 15 h. The carbonized sample was ground to a powder and then heated in sulfuric acid at 423 K for 15 h. Afterwards, the black powder was washed thoroughly and dried at 353 K.

2.2. Catalyst characterizations

Surface areas were measured by the adsorption of N_2 at 77.3 K using a Micromeritics ASAP 2000 surface area analyzer and the specific areas were calculated according to the Brunauer–Emmett–Teller (BET) equation. Samples were degassed in flowing N_2 for 5 h at 383 K before the measurements.

X-ray diffraction (XRD) patterns were collected on a Philips X'Pert Pro powder diffractometer using a Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The 2θ scans covered the range of 10 to 80° with a step of 0.02°.

The density of surface acid sites was measured by a neutralization titration method described in [13]. In short, the sample was added into an aqueous solution of NaCl (in excess), and HCl formed due to the exchange of Na^+ with proton on sulfonic groups was titrated by a standard solution of NaOH. In this way, the density of strong surface acid sites or the number of sulfonic groups was determined. On the other hand, when the sample was added into a standard solution of NaOH (in excess), all the surface acid sites could be reacted with NaOH and the remaining NaOH was titrated by a standard solution of HCl. In this way, the total number of surface acid sites was measured.

The microcalorimetric adsorption of ammonia was performed by using a Setaram Tian–Calvet C-80 heat-flux microcalorimeter, connected to a gas-handling system equipped with a Baratron capacitance manometer for precise pressure measurements. Samples were evacuated at 353 K for 12 h before the measurements at 353 K.

The thermogravimetry-mass spectrometry (TG-MS) coupling technique employing Netzsch STA 449C TG-DSC and Pfeiffer Thermostar Mass Spectrometer was used to probe the surface function groups and their stabilities. The quartz capillary tube was used as the interface between the thermal analyzer and quardrupole. The different *m/z* mass numbers were monitored in the multiple ion detection (MID) mode. The measurement was carried out under flowing N_2 with a linear ramp of temperature from room temperature to 873 K at a rate of 10 K/min.

FTIR spectra were obtained on a Thermo Fisher Scientific Nicolet-iS10 spectrometer. Samples were palletized with KBr.

2.3. Catalytic tests

The etherification of isopentene with methanol to produce TAME was carried out in an autoclave equipped with a magnetic stirrer. The reaction was performed at 353 K and 0.3 MPa (autogenous pressure) with the alkene to alcohol ratio of 1:1. Specifically, a 100 ml Teflon-lined autoclave was charged with 10 g isopentene, 4.57 g methanol, 35.43 g solvent (toluene) and 0.5 g catalyst. The reactor was sealed and purged with N_2 for 3 times. It was then heated to 353 K and remained at the temperature for 20 h under stirring. The reaction products were analyzed by a gas chromatography equipped with a SE-30 capillary column and a FID detector.

3. Results and discussion

3.1. Textural and structural properties

Table 1 shows the surface areas and acid densities of catalysts. It is seen that both the surface area and acid density were significantly higher for HS-C than for Hara-C. The Hara-C was prepared according to Hara et al. and possessed similar surface area and acid density as they reported [6]. The sample HS-R possessed a low surface area ($1\ m^2/g$). When it was treated in sulfuric acid at 443 K, the acidic carbon material (HS-C) was formed with the reactions of carbonization and sulfonation. The HS-C thus formed exhibited a surface area of $22\ m^2/g$.

Fig. 2 shows the XRD patterns of HS-C and HS-R. The HS-R exhibited a broad and weak peak in the range of 10°–30°, a typical XRD pattern for a polymer. This diffraction peak was significantly enhanced after it

Table 1
Surface area and acid density of the catalysts.

Catalysts	Acid density (mmol/g)		Surface area (m^2/g)
	–SO_3H	Total	
HS-C	3.1	6.3	22
HS-R	1.8	4.2	1
Hara-C	0.9	1.7	1
H_2SO_4	20.4	20.4	–
D001	4.7	4.7	12

Note: D001 is a proton exchanged styrene resin.

was treated in concentrated sulfuric acid at 443 K, indicating the formation of a carbonized material. In fact, the carbonization of organic compounds in sulfuric acid has been documented [14]. The diffraction peak round 24° belongs to the C (002) face. Since the peak is narrow for crystalline carbon (the full width at half maximum (FWHM) is 1.85° ± 0.05°), while it is broad for amorphous carbon (FWHM is 7.00° ± 0.50°) [15], the XRD pattern of HS-C shown in Fig. 2 clearly showed that it was an amorphous carbon.

3.2. Surface acidity

The surface acid densities of the samples determined by the titration method are presented in Table 1. The data showed that the sample HS-R possessed 1.8 mmol/g strong acid sites, indicating the polymerization of HMF and *p*-HBSA for the formation of a resin containing sulfonic groups. The total acid density reached 4.2 mmol/g for HS-R, indicating the presence of acidic sites other than –SO_3H in the resin. These acidic sites might be hydroxyl groups on *p*-HBSA polymerized into the resin. After treated in sulfuric acid at 443 K, HS-R was converted into HS-C, which possessed sulfonic groups of 3.1 mmol/g. Apparently, the sulfonation reaction occurred simultaneously with the carbonization process of HS-R.

Microcalorimetric adsorption of NH_3 was also used to determine the surface acidity of HS-C and compared with that of Hara-C. Fig. 3(a) shows the isotherms for the adsorption of NH_3 over the two samples. Apparently, the uptake of NH_3 was significantly higher on HS-C than on Hara-C, indicating more acidic sites on HS-C than on Hara-C, agreeing with the results of titration. Fig. 3(b) shows the heat of adsorption versus coverage for the adsorption of NH_3. The initial heat was low for the adsorption of NH_3 over the two carbon samples. The heat increased and passed a maximum with the increase of coverage. Since it is known that the adsorption of NH_3 on the pyrosulfuric group is an endothermic process [16], the low initial heat indicated the endothermic process for the adsorption of NH_3 on the carbon samples, and thus some pyrosulfuric groups might be formed on the HR-C and Hara-C from the dehydration of sulfonic groups. Without the endothermic process, the initial heat should be the highest, and the surface acidity might be descried by the initial heat and coverage for the adsorption of ammonia. Owing to the endothermic process, the initial heat could not be used to judge the strength of acidic sites. However, the results in Fig. 3(b) seemed to indicate that the strength of strong acidic sites due to sulfonic groups was stronger on Hara-C than on HR-C. This was probably due to the high density of –SO_3H on Hara-C, which was so high (5.4 –SO_3H/Å^2) that it might be taken as being similar to oleum (SO_3–H_2SO_4). On the other hand, the density of –SO_3H was much lower on HS-C (0.85 –SO_3H/Å^2).

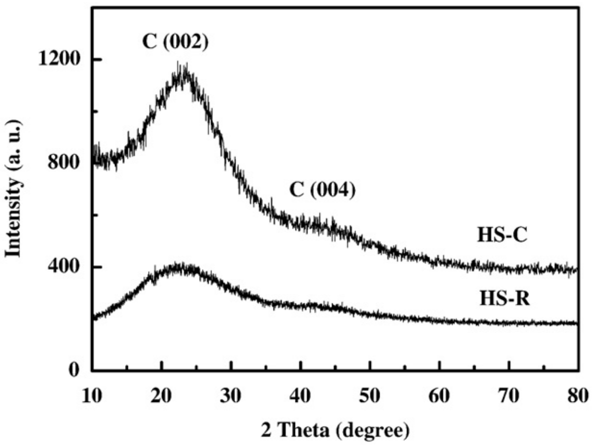

Fig. 2. X-ray diffraction patterns of HS-R and HS-C.

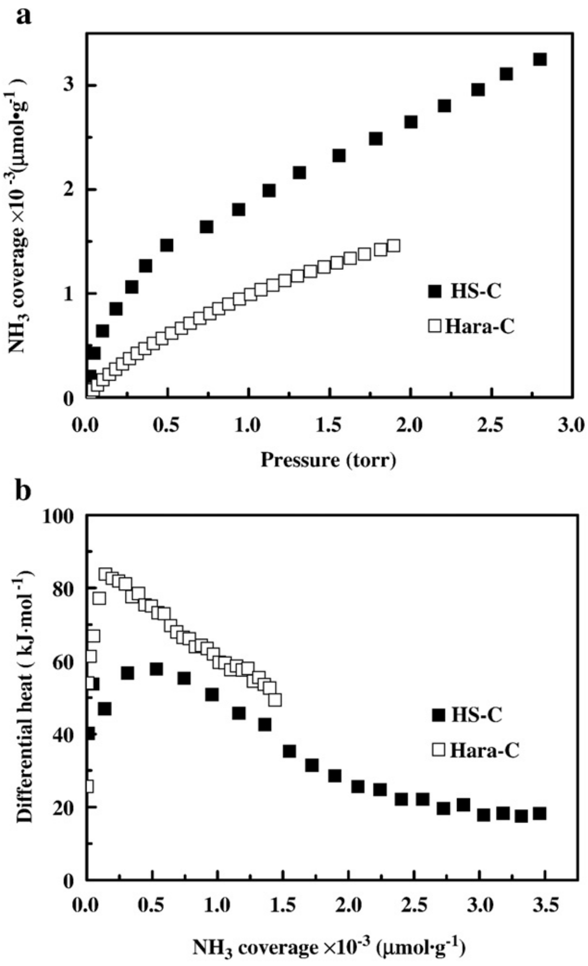

Fig. 3. Microcalorimetric adsorption of NH_3 at 353 K over HS-C and Hara-C.

3.3. Thermal stability of surface functional groups

The surface sulfonic groups were decomposed upon the heat treatment, releasing SO_2 ($m/z = 64$) and SO_3 ($m/z = 80$) that could be detected by TG-MS. Fig. 4 shows the results. It is seen that SO_2 began to evolve around 453 K and a great amount of SO_2 was evolved until 823 K. SO_3 was evolved simultaneously, but was much less than SO_2. These results clearly indicated the presence of a great amount of –SO_3H on the surface of HS-C, which were stable at the temperatures not higher than 453 K. The presence of –SO_3H was also confirmed by FTIR results (see Fig. S1 in Supplementary material). A band around 1032 cm^{-1} was clearly seen for –SO_3H groups on HS-C [17]. In addition, a great amount of CO_2 ($m/z = 44$) was detected at the temperatures higher than 423 K, demonstrating the presence of a substantial amount of –COOH groups on the surface of HS-C, which might be attributed to the weak surface acid sites.

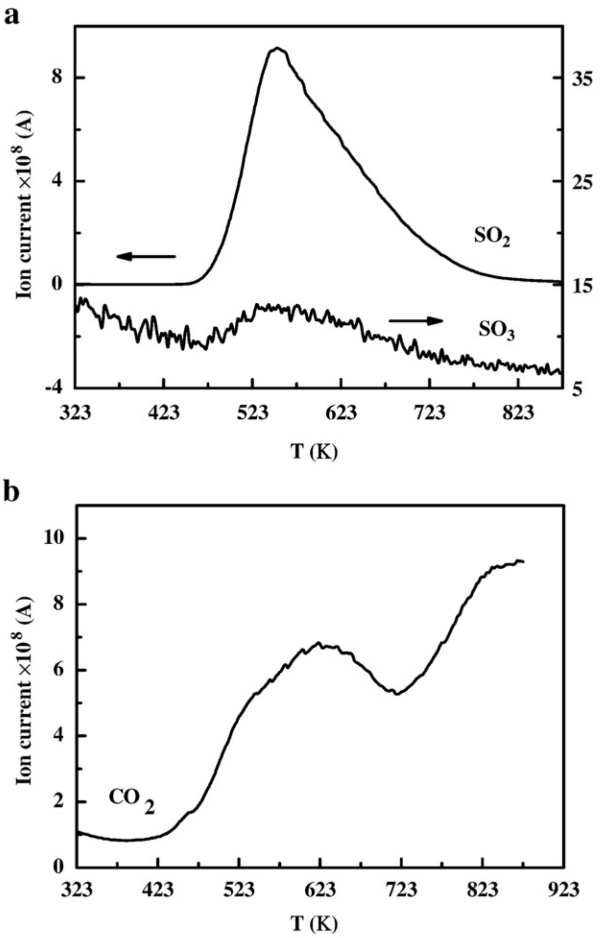

Fig. 4. Evolution of SO_2, SO_3 and CO_2 from HS-C when it was linearly heated in N_2 during the TG-MS measurement.

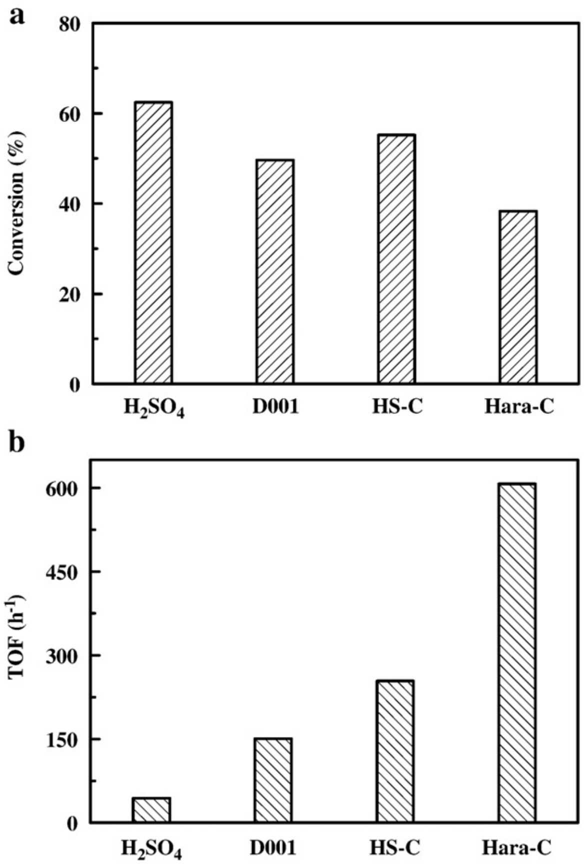

Fig. 5. Conversion of isopentene and rate of formation of TAME (TOF) for the reaction of isopentene with methanol at 353 K after 20 h.

3.4. Catalytic activity

The catalysts were used for the etherification of isopentene with methanol to produce TAME. This is a typical Brønsted acid catalyzed reaction, in which the mechanism has been documented [18]. Under the reaction conditions employed in this work, TAME was the only product and no by-products were detected. Fig. 5 compares the catalytic activity of H_2SO_4, HS-C, Hara-C and a proton exchanged styrene resin D001. The conversion of isopentene was found to be 62.4, 55.2, 38.3 and 49.6% with the catalysts H_2SO_4, HS-C, Hara-C and D001, respectively. Sulfuric acid was the most active for the reaction.

The HS-C exhibited high activity for the etherification reaction. Although it was slightly less active than H_2SO_4, it was significantly more active than Hara-C. The high activity of HS-C might be due to its high density of strong acid sites and high surface area. Since the amount of a catalyst used for the reaction was 0.5 g, the number of protons related to $–SO_3H$ groups in the reactor was calculated to be 10.2, 1.55, 0.45 and 2.35 mmol, and thus the rate in TOF (turnover frequency) for the production of TAME was correspondingly calculated to be 44, 254, 607 and 150 h^{-1} for H_2SO_4, HS-C, Hara-C and D001, respectively. Thus, protons in HS-C and Hara-C seemed much more active than those in liquid H_2SO_4 and D001 for the etherification reaction, indicating the structure and acidic strength of sulfonic groups in the two acidic carbons might be different from those in sulfuric acid and proton exchanged resin.

The catalytic stability of HS-C was also studied. It was used successively for three cycles of the reaction and the conversion of isopentene was found to be nearly the same (55.2, 55.9 and 54.3%, respectively). The FTIR spectrum of HS-C after the three cycles of use for the reaction showed that the band around 1032 cm^{-1} for $–SO_3H$ remained (see Fig. S1 in Supplementary material), indicating the stability of HS-C under the conditions employed for the reaction.

4. Conclusions

A resin containing a great amount of $–SO_3H$ groups was obtained by heating glucose with 4-hydroxybenzenesulfonic acid (*p*-HBSA) at 353 K, since glucose was first converted to hydroxymethylfurfural (HMF) which was then polymerized with *p*-HBSA to form the resin. The resin was carbonized and further sulfonated in concentrated sulfuric acid (98%) at 443 K to obtain an acidic carbon material (HS-C) with the surface area of 22 m^2/g and $–SO_3H$ density of 3.1 mmol/g. This acidic carbon exhibited excellent catalytic activity and stability for the etherification of isopentene with methanol to produce TAME, due to its relatively high surface area and density of sulfonic groups. The new method seemed better than the sulfonation of directly carbonized carbohydrates for the preparation of acidic carbon catalysts.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2010.03.001.

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