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Sulfonated carbon materials with hydrophilic and lipophilic properties

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Abstract

Two acidic carbon materials (H-PRC and HS-C) were used as catalysts for the condensation reaction of methanol with formaldehyde to produce dimethoxymethane (DMM) in aqueous solution (hydrophilic system) and for the etherification of isopentene with methanol to produce tert amyl methyl ether (TAME) in toluene solution (lipophilic system). Microcalorimetric adsorptions of water and benzene showed that the HS-C was highly hydrophilic without the lipophilicity, while the H-PRC exhibited both the hydrophilicity and lipophilicity. Thus, the HS-C was well dispersed in aqueous solution and difficult to separate from it. On the other hand, the H-PRC was highly active, more active than the acidic resin (D008) and sulfuric acid, for the synthesis of DMM in aqueous solution. The H-PRC was also highly active, more active than the HS-C, for the etherification of isopentene with methanol to produce TAME in toluene solution, probably owing to its amphiphilic surface property as well as its strong surface acidity as measured by the microcalorimetric adsorption of NH_3.

Key words

acidic carbon materials; surface acidity; hydrophilicity; lipophilicity; condensation reaction of methanol with formaldehyde; etherification of isopentene with methanol

1. Introduction

The acid catalyzed reactions are widely used in the chemical industry. H_2SO_4 is an effective acid catalyst and frequently used for the acid catalyzed reactions. However, the liquid acid catalysts such as H_2SO_4 often lead to the environmental pollutions and separation problems. Thus, the search for solid acid catalysts has been the hot research area for a long time.

Ion exchange resins have been commercially available for over seventy years and have been used extensively in many fields [1], but they can not be used at temperatures higher than 423 K and may be easily crushed due to the swelling in organic solvents. Other solid acids, such as zeolites and solid superacids (e.g., SO_4^{2-}/ZrO_2, heteropoly acid) [2,3], have been widely studied [4]. However, they also have some shortcomings such as the fast deactivation. Thus, the development of new solid acid catalysts with high activity and long life at lower costs is always the goal of research in academic and industrial societies. Sulfonic acid groups (–SO_3H) have been introduced onto the solid materials for the formation of various solid acids, such as polystyrene-supported sulfonic acid (PS-SO_3H) [5], hybrid mesoporous ethenylene-slilica-SO_3H [6], sulfonated carbon nanotubes [7] and SO_3H-functionalized

FDU-type mesoporous polymers [8].

Recently, sulfonated acidic carbon materials attracted wide interests [9−20]. The preparation process generally involved two steps: (1) incomplete carbonization of the raw materials such as starch [13], glucose [14−17], cellulose [9,18] and naphthalene [19] in an inert atmosphere; (2) sulfonation of the carbonized precursors with concentrated H_2SO_4 or fuming H_2SO_4. It was also reported that a novel carbon functionalized with sulfonic acid groups was synthesized using the one-step hydrothermal carbonization of furaldehyde and hydroxyethylsulfonic acid in the aqueous solution [20].

Different precursors, carbonization and sulfonation processes gave rise to different properties of the acidic carbon materials. Recently we noticed that the sulfonated acidic carbon materials might possess the different hydrophilic and lipophilic properties, which might affect their catalytic activities in different acid catalyzed reactions. Only a few discussions on this issue appeared in literature up to now [14,15,18,21]. In our previous work [22], we prepared an acidic carbon material (HS-C) by the polymerization of glucose with *p*-hydroxybenzenesulfonic acid followed by the sulfonation in concentrated H_2SO_4. In addition, a lipophilic mesoporous carbon was prepared using $ZnCl_2$ as the template [23]. In this work, another new sulfonated carbon ma-

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terial (H-PRC) was prepared by the sulfonation of the meso-porous carbon. The hydrophilic/lipophilic properties of these two acid carbon materials were characterized and tested for the condensation reaction of methanol with formaldehyde to produce dimethoxymethane (DMM) in aqueous solution (hydrophilic system) and for the etherification of isopentene with methanol to produce tert amyl methyl ether (TAME) in toluene solution (lipophilic system). DMM has been taken as a potential diesel additive which might reduce the emission of particular materials (PM) and NO_x from the diesel engines [24], while TAME is a widely used gasoline additive which increases the octane number and the burning efficiency of gasoline.

2. Experimental

2.1. Preparation of catalysts

Using the methods reported by Benak et al. [13] and Huang et al. [23], 10 g phenolic resin (PR 2123, Taizhou Tiancheng Chemical Co., China) was dissolved in appropriate amount of ethanol, and then 0.9 g hexamethylenetetramine and 10.9 g $ZnCl_2$ were added under stirring to form a clear solution. The solution was warmed in a water-bath at 353 K for 12 h to evaporate the solvent, and then cured at 443 K for 2 h in a drying oven to form a solid. This solid was smashed to 60 mesh and introduced to a tubular furnace for the thermal treatment under flowing N_2. The furnace was heated from room temperature to 673 K at a rate of 5 K·min^{-1} and held at 673 K for 2 h. After cooling down, the carbonized residue was washed with diluted HCl (pH $\sim$ 3) and then boiling water to remove $ZnCl_2$. The carbon sample was dried at 393 K for 6 h and denoted as PRC. The PRC was mixed with concentrated H_2SO_4 (98%) with the ratio of 1 g : 20 mL and the mixture was boiled at 433 K for 12 h. Then, it was washed thoroughly and dried at 353 K overnight. The acidic carbon thus prepared was denoted as H-PRC.

Another acidic carbon (HS-C) prepared using the procedure reported by Zhao et al. [22] and a proton exchanged resin (D008) provided by the Kairui Chemical Co., Ltd. China were used as the references in this work.

2.2. Characterization of catalysts

Surface areas were measured by the adsorption of N_2 at 77.3 K using a Micromeritics Gemini V 2380 autosorption analyzer. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) equation. Samples were degassed in flowing N_2 for 5 h at 393 K (353 K for D008) before the measurements.

X-ray diffraction (XRD) patterns were collected on a Philips X'Pert Pro powder diffractometer using a Ni-filtered Cu K_α radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at the voltage of 40 kV and the current of 40 mA. The 2θ scans covered the range of 10º to 80º with a step of 0.02º.

The density of surface acid sites was measured by a neutralization titration method described in literature [22]. 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.

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

The microcalorimetric adsorptions of water, benzene and ammonia were performed on 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 dried at 353 K for 5 h and evacuated at 353 K for 12 h prior to the measurements. The microcalorimetric adsorptions of water and benzene were measured at 308 K, while the adsorption of ammonia was measured at 353 K.

The thermogravimetry (Netzsch STA 449C TG-DSC) combined with the mass spectrometry (Pfeiffer Thermostar Mass Spectrometer) (TG-MS) 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 quadrupole. 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.

2.3. Catalytic tests

The catalytic activities of different materials (H-PRC, HS-C, D008 and H_2SO_4) were compared for the condensation reaction of methanol with formaldehyde and the etherification of isopentene with methanol.

The condensation of methanol with formaldehyde to DMM was carried out in an autoclave equipped with a magnetic stirrer. The reaction was performed at 333 K and 0.2 MPa (autogenous pressure) with the methanol to formaldehyde mole ratio of 2.1 : 1. Specifically, a 100 mL Teflon-lined autoclave was charged with 20.6 g methanol, 24.2 g aqueous solution of formaldehyde (38 wt%) and 0.5 g of a catalyst. The reactor was sealed and purged with N_2 for three times. It was then heated to 333 K and remained at this temperature for 2 h under stirring. The reaction products were analyzed by a gas chromatograph equipped with a SE-30 capillary column and a FID detector. DMM and DMM2 ($CH_3O(CH_2O)_2CH_3$) were detected in the products. The conversion of formaldehyde and the selectivity to DMM were calculated according to the following formulae: