

# Active solid acid catalysts prepared by sulfonation of carbonization-controlled mesoporous carbon materials

Rong Xing, Yueming Liu, Yong Wang, Li Chen, Haihong Wu, Yongwen Jiang, Mingyuan He, Peng Wu \*

*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, China*

Received 21 December 2006; received in revised form 4 June 2007; accepted 25 June 2007  
Available online 13 July 2007

## Abstract

A novel sulfonic acid group-functionalized mesoporous carbon was prepared through vapour-phase transfer sulfonation of CMK-3 type mesoporous carbon with the controllable carbonization degree. The method of vapour-phase sulfonation, that is, through contacting the sample powders with the vapor from fuming sulfuric acid in a closed autoclave, proved to be more effective than both the direct dipping of the carbon in concentrated or fuming H<sub>2</sub>SO<sub>4</sub> and the treatment with pure SO<sub>3</sub> gas. The influence of carbonization temperature on the sulfonation was investigated, suggesting an optimum temperature of 823 K. The SO<sub>3</sub>H group-functionalized mesoporous carbon, CMK-3-SO<sub>3</sub>H, was characterized by means of XRD, SEM, TEM, N<sub>2</sub> adsorption–desorption, <sup>13</sup>C NMR, FTIR and elemental analysis, which indicated that it had uniform mesopores together with an extremely high surface area, and also contained an amount of acid sites as high as 1.3 mmol g<sup>-1</sup>. CMK-3-SO<sub>3</sub>H catalyzed efficiently the liquid-phase Beckmann rearrangement of cyclohexanone oxime and condensation reactions involving bulky aromatic aldehydes.

© 2007 Elsevier Inc. All rights reserved.

**Keywords:** Mesoporous carbon; Sulfonation; CMK-3; Solid acid; Sulfonic acid group

## 1. Introduction

The discovery of mesoporous materials with extremely high surface areas, large-pore volumes and uniform nano-sized pores has opened up new opportunities for converting large molecules into valuable petrochemicals, fine chemicals and pharmaceuticals from the viewpoint of catalysis [1–6]. It is of particular importance and research interests to develop new heterogeneous solid acid catalysts applicable to Beckmann rearrangement, alkylation, acylation, esterification, condensation, oligomerization, hydration, dehydration, etc., because most of which are currently operated in environmentally unfriendly ways owing to using liquid acid catalysts such as H<sub>2</sub>SO<sub>4</sub>, HF and H<sub>3</sub>PO<sub>4</sub> [3,7].

To prepare mesoporous solid acid catalysts, many works in last decade have focused on the functionalization and modification of silica-based and organosilica hybrid materials with trivalent aluminum cations and sulfonic acid groups. The incorporation of Al into mesoporous silica can be realized by direct hydrothermal synthesis or post-synthesis, while the SO<sub>3</sub>H group-functionalized mesoporous silicas are usually prepared from the oxidation with H<sub>2</sub>O<sub>2</sub> of SH groups post-grafted or directly incorporated onto the silica walls [8–11]. However, the silica walls are organically modified only by a limited fraction of SH groups due to the hydrophobic nature of silanes agents. Furthermore, a possible Si–C bond cleavage is needed to avoid during the direct synthesis and surfactant removal processes. Accordingly, the SO<sub>3</sub>H-functionalized mesoporous silica materials have relatively low SO<sub>3</sub>H densities, resulting in restricted utility in practical acid-catalyzed reactions. Mesoporous organosilicas with a high

\* Corresponding author. Tel./fax: +86 21 6223 2292.  
E-mail address: [pwu@chem.ecnu.edu.cn](mailto:pwu@chem.ecnu.edu.cn) (P. Wu).

functionality, on the other hand, are possibly subject to a direct sulfonation [12]. They, however, suffers the problem of using costly organic silica sources.

Another family of pure carbon-based mesoporous materials, the replication of mesoporous silicas with nanocasting method, are promising in energy storage or supporting for noble metals [13,14] but they are catalytically inactive owing to a neutral framework. To introduce sulfonic acid groups into these mesoporous carbons would obtain new solid acids of high surface area, stable framework, high hydrophobicity and activity.

CMK-type carbons are generally prepared by introducing carbon sources into the mesopores of silica scaffolds followed by a complete carbonization at 1173 K [13]. The high temperature-carbonization is helpful to form an interconnected rigid carbon framework but lacking the functionality. We report here with CMK-3 as a first example that it is possible to develop by controlling carbonization temperature the polycyclic aromatic carbon atoms available for the sulfonation. Partially carbonized mesoporous carbons then are converted to catalytically active solid acids successively through a prudent sulfonation.

## 2. Experimental

### 2.1. Synthesis of mesoporous CMK-3-S<sub>3</sub>OH

The synthesis of the CMK-3 mesoporous carbon was performed according to the procedure reported elsewhere [13]. In a typical synthesis of SBA-15, the hard template for the preparation of CMK-3 mesoporous carbon, 15 g of TEOS was dissolved in a solution containing 7 g of triblock copolymer (Pluronic 123), 47 g of hydrochloric acid and 187 g of H<sub>2</sub>O. The mixture was stirred with magnetic stirring at 308 K for 20 h, followed by further aging statically at 363 K for 24 h. The product was filtered, dried without washing, and calcined at 823 K for 6 h in air. Then, 2.1 g of thus calcined SBA-15 was impregnated with 2.6 g of sucrose which has been dissolved in 0.25 g of 98% H<sub>2</sub>SO<sub>4</sub> and 4.2 g of deionized water in advance. The resultant mixture was kept in an oven at 373 K for 6 h. Subsequently, the oven temperature was raised to 433 K and maintained there for 6 h to allow a partial carbonation. This thermal treatment was repeated after the sample was impregnated again with 1.7 g of sucrose, 0.2 g of 98% H<sub>2</sub>SO<sub>4</sub> and 3.2 g of deionized water. The SBA-15 silica/carbon composite was then pyrolyzed under vacuum at 673–1173 K for 6 h to induce a deep carbonation. The mesoporous carbon replica, CMK-3-*T* (*T* denotes the carbonization temperature), was obtained after removing the silica framework in a 5 wt.% HF solution followed by filtration, washing with deionized water and drying at 373 K. The sulfonation was carried out in a Teflon container set in a Teflon-lined autoclave where 0.3 g of CMK-3-*T* powder was contacted with the vapor from 5 mL 50 wt.% SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at 333 K for 48 h. The sulfonated sample, denoted as CMK-3-*T*-SO<sub>3</sub>H, was washed with hot deionized water

(>353 K) to remove any physically adsorbed species until the sulfate ions were no longer detected in the filtration water (sulfate ions were detected with 6 mol L<sup>-1</sup> BaSO<sub>4</sub> solution). After the filtration, the samples were dried at 373 K overnight in air.

For control experiment, proton-type zeolites such as USY (Si/Al = 7), ZSM-5 (Si/Al = 15) and Beta (Si/Al = 20) were obtained commercially or hydrothermally synthesized. All the zeolites were converted into proton-type by ion-exchanged with NH<sub>4</sub>NO<sub>3</sub> solution followed by calcination at 773 K for 6 h. The acid-type resin of Dowex 50 was purchased from the ACROS ORGANICS.

### 2.2. Characterization methods

The small angle powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 ADVANCE instrument using Cu-K<sub>α</sub> radiation ( $\lambda = 1.5418$ ). Nitrogen adsorption–desorption isotherms were measured at 77 K on a Quancachrome Autosorb-3B instrument after the samples were outgassed at 473 K in vacuo at least for 10 h prior to investigation. The SEM images were taken on a Hitachi S-4800 microscope, while the TEM images were taken on a JEOL-JEM-2010 microscope. FT-IR spectra were recorded on a Nicolet Fourier transform infrared spectrometer (NEXUS 670) using KBr technique. <sup>13</sup>C solid-state MAS NMR spectra were recorded on a Bruker DSX300 spectrometer. The sulfur amount of sulfonated mesoporous carbon was determined by elemental analyses on a Perkin–Elmer series II 2400 CHNS analyzer, while the amount of acid sites was quantified by acid–base titration following previous reported procedures [15]. The amount of Al in the zeolites was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

### 2.3. Catalytic reactions

The CMK-3-873-SO<sub>3</sub>H catalyst was not further pretreated before the reactions. The liquid-phase Beckmann rearrangement of cyclohexanone oxime was performed in a 50 mL glass flask equipped with a reflux condenser and a magnetic stirrer under atmosphere. In a type experiment, 0.1 g of cyclohexanone oxime and 10 g solvent of benzonitrile was mixed and kept at 403 K under vigorous stirring, and then 0.1 g catalyst was rapidly added into the reactor at 403 K for 2 h. The condensation of benzaldehyde or 1-pyrenecarboxaldehyde (PYC) with ethylene glycol was performed in liquid-phase. The reactions were conducted in glass flasks and initiated by adding 0.01 g catalyst to a mixture of benzaldehyde (15 mmol), ethylene glycol (15 mmol) and 5 g cyclohexane solvent or to a mixture of PYC (1 mmol), ethylene glycol (1 mmol) and 5 g toluene solvent, respectively. After the reactions were conducted under vigorous stirring at 363 K for 1 h, the products were determined by using authentic chemicals commercially available or identified on a gas chromatograph-mass spectrometer

Download English Version:

<https://daneshyari.com/en/article/77096>

Download Persian Version:

<https://daneshyari.com/article/77096>

[Daneshyari.com](https://daneshyari.com)