



Short Communication

Phosphorylated ordered mesoporous carbon as a novel solid acid catalyst for the esterification of oleic acid



Lingtao Wang, Xiuqin Dong, Haoxi Jiang*, Guiming Li, Minhua Zhang*

Key Laboratory for Green Chemical Technology of Ministry of Education, Research and Development Center for Petrochemical Technology, Tianjin University, Tianjin 300072, China

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ABSTRACT

A novel phosphorylated ordered mesoporous carbon (POMC) solid acid catalyst has been prepared by modifying mesoporous carbon with phosphoric acid, and was employed to catalyze the esterification oleic acid with methanol. The effects of the carbonization temperature on the type of phosphorus species formed, the phosphorus content and the amount of acid in the POMC were investigated. A mechanism for the phosphorylation of the ordered mesoporous carbon is proposed. The POMCs have good catalytic activity for the esterification of oleic acid and showed good reusability.

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1. Introduction

Due to the increasing energy consumption and stringent regulations for environmental protection, the production of eco-friendly fuels has drawn extensive attention worldwide. Biodiesel is considered a promising alternative fuel for the replacement of petroleum-based fuels because of its biodegradability, non-toxicity and favorable combustion emission profile [1]. Generally, biodiesel is obtained from the transesterification of vegetable oil and animal fats in the presence of low molecular weight alcohols. In order to reduce the expense of the raw materials and avoid using food sources, some non-edible raw feedstock oils, such as *Jatropha* oils and waste cooking oils, are widely used in the production of biodiesel [2,3]. However, these non-edible oils contain large amounts of free fatty acids (FFAs), which results in the production of saponification materials in the product. This increases the difficulty of product separation and can also result in the deactivation of alkaline catalysts. Therefore, two-step methods that involve the pre-esterification of FFAs with methanol using acid catalysis before transesterification have been proposed [3–5]. Sulfuric acid has good catalytic performance for the esterification of FFAs, but it is non-reusable and corrodes the equipment. Consequently, the development of a green pretreatment process to reduce the content of FFAs in raw oils has become a key problem that urgently needs to be solved.

Ordered mesoporous carbon materials (OMCs), which can be obtained using the replication of mesoporous silicas with a nanocasting method or a self-assembly template method, have attracted great

interest due to their regular mesostructures, high surface areas and large pore volumes. Recently, acid functional OMCs have been reported as solid acid catalysts in acid catalysis of large molecule reaction [6,7]. The catalysts supply the effective active acid sites for the acid-catalyzed reaction, and the mesoporous structures make it easier for large molecules to access the active sites. In addition, for esterification, the hydrophobic surface of the OMCs inhibits the water product from adsorbing on the acid sites which effectively prevents the deactivation of the catalyst. Thus, functionalized OMC catalysts with acid groups are good candidates for the esterification of large molecules.

Sulfonic acid functionalized OMC catalysts have been obtained by direct modification of OMC with sulfuric acid and showed good catalytic performance for the acid-catalyzed reaction due to their high acid densities and large surface areas [8,9]. Feng and coworkers prepared a OMC based solid acid catalyst by attaching sulfonic acid functional groups to the OMC surface using diazonium chemistry in the presence of H_3PO_2 [6,10]. Although they have high acid amount, the well ordered mesoporous structure of OMC cannot suffer from sulfuric acid during the sulfonation process. Phosphoric acid as a functionalizing agent has been widely applied to the surface modification of carbon and mesoporous silica materials [11–14]. Compared with sulfuric acid, phosphoric acid as a functionalizing agent could considerably reduce the damage to the well ordered mesoporous structures of OMC because of its milder acidity. Mayes et al. [15] reported that phosphorylated mesoporous carbon obtained from phosphoric acid modification had good catalytic performance for the dehydration of isopropanol. In that case, the phosphorylated mesoporous carbon materials retained the pore structure of the carbon materials, but their phosphorus content was relatively low. This affected the number of acid sites in the catalysts which limits

* Corresponding authors. Tel./fax: +86 22 27406119.

E-mail addresses: hxjiang@tju.edu.cn (H. Jiang), mhzhang@tju.edu.cn (M. Zhang).

their applications for acid-catalyzed reactions. Therefore, a new functionalizing method is desired to obtain OMC catalysts with more active acid sites while maintaining the robust carbon structural frameworks which can withstand the phosphorylating conditions.

In this study, novel phosphorylated ordered mesoporous carbon (POMC) solid acid catalysts were prepared by modifying OMCs with phosphoric acid. The effects of the carbonization temperature on the mesoporous structure and surface properties of the POMCs were investigated. The type of phosphorus species and the acid density in the POMCs were determined. In addition, a mechanism for the phosphorylation of the OMC is proposed. The POMC catalysts were employed to catalyze the esterification of oleic acid in the presence of methanol, and the reusability was also studied.

2. Experimental

2.1. Catalyst preparation

The ordered mesoporous carbon materials were prepared by a soft template method at different carbonization temperatures under nitrogen for 5 h. The POMC catalysts were obtained POMCs by direct modification of OMCs with phosphoric acid at room temperature for 6 h, and are labeled as POMC- T_C , where T_C again represents the carbonization temperature. The detail preparation methods of OMCs and POMCs were reported in the Supporting information (SI).

2.2. Catalyst characterization

The magic-angle spinning (MAS) solid state NMR study was carried out on an Infinity-Plus 300 NMR spectrometer under ambient conditions. The ^{31}P NMR spectra were recorded at 121.38 MHz using 85% phosphoric acid as an external standard. The spinning rate was 8 kHz. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer PHI-1600 spectrometer equipped with an Mg K α radiation. The C1s binding energy of 284.6 eV was used as the reference. Ammonia temperature programmed desorption (NH $_3$ -TPD) was measured on a Micromeritics AutochemII 2920 chemisorption analyzer under a mixed stream of 1.0% ammonia in helium (10 mL/min). The phosphorus content in catalyst samples was estimated using a S4 Pioneer X-ray fluorescence (XRF) spectrometer equipped with a Rh target energized at 50 kV and 40 mA.

2.3. Catalytic activity measurement

Esterification reactions were carried out in a three-neck glass flask equipped with a reflux condenser at 80 °C. Oleic acid (0.06 mol) and methanol (0.9 mol) were heated to 80 °C with an accuracy of ± 1 °C, while being continuously stirred with a magnetic stirrer. The catalyst samples (0.85 g) were dried at 100 °C for 1 h before utilization in the reaction. After reaction, the oil phase products was extracted and diluted with n-hexane. The yield of methyl oleate was analyzed using an Agilent 7890N gas chromatograph equipped with a flame ionization detector and a capillary column HP-INNOWAX (15 m \times 0.25 mm \times 0.5 μm). The internal standard method was used for quantity analysis of methyl oleate using methyl salicylate as the internal standard. The conversion of oleic acid was defined as the fraction of the oleic acid removed, which was transform to methyl oleate [16].

3. Results and discussion

3.1. Catalyst characterization

The N $_2$ adsorption–desorption isotherms and pore size distribution curves, low angle XRD patterns and TEM images of the POMCs are depicted in Figs. S1, S2, and S3, respectively. Corresponding results and analysis were reported in the Supporting information.

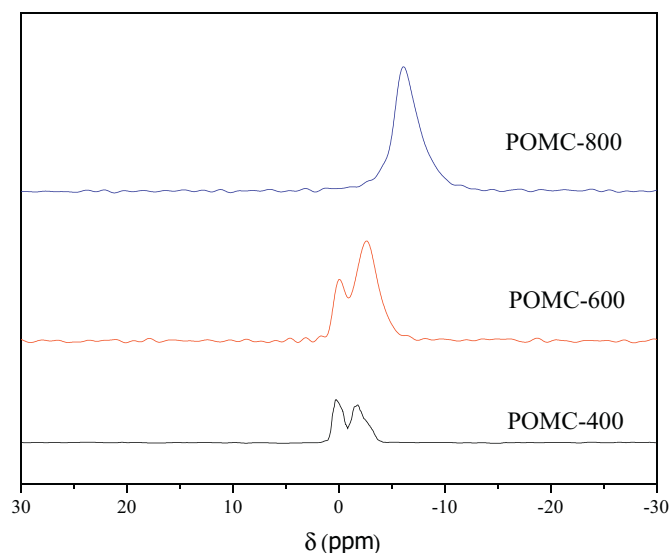


Fig. 1. ^{31}P MAS NMR spectra of POMCs.

The ^{31}P MAS NMR spectra of the POMCs are shown in Fig. 1. The resonance peaks around 0 ppm are attributed to phosphate-like structures (PO_4), such as phosphoric acid [17]. The peaks in the range from -0.4 to -6 ppm are assigned to phosphonates, such as C–P. These peaks shifted toward lower chemical shift values as the carbonization temperature increased, which is consistent with the results for phosphorylated phenol formaldehyde fibers reported by Fu et al. [18]. The POMC-400 and POMC-600 spectra have two resonance peaks, suggesting the existence of two phosphorous species on the carbon surface. In contrast, the POMC-800 spectrum has only one peak of at -6 ppm, which can be attributed to phosphonates with C–P bonds. This implies that the OMC-800 framework does not have available oxygen sites to interact with P

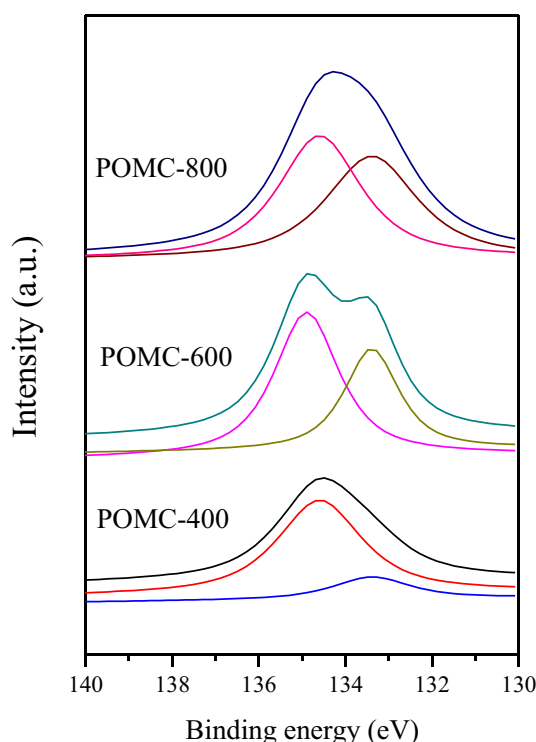


Fig. 2. XPS P2p spectra of POMCs.

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