Chinese Journal of Catalysis 37 (2016) 769–777

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journal homepage: www.elsevier.com/locate/chnjc

Article

Esterification of cyclohexene with formic acid over a peanut shell-derived carbon solid acid catalyst

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ARTICLE INFO

Article history:
Received 21 December 2015
Accepted 26 February 2016
Published 5 May 2016

Keywords:
Carbon solid acid
Peanut shell
Cyclohexene
Esterification
Cyclohexyl formate

ABSTRACT

A carbon solid acid catalyst was prepared by the sulfonation of partially carbonized peanut shell with concentrated H_2SO_4. The structure and acidity of the catalyst were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, and elemental analysis, which showed that it was an amorphous carbon material composed of aromatic carbon sheets in random orientations. Sulfonic acid groups were present on the surface at a density of 0.81 mmol/g. The carbon solid acid catalyst showed better performance than HZSM-5 for the esterification of cyclohexene with formic acid. At a 3:1 molar ratio of formic acid to cyclohexene, catalyst loading of 0.07 g/mL of cyclohexene, and reaction time of 1 h at 413 K, the cyclohexene conversion was 88.4% with 97.3% selectivity to cyclohexyl formate. The carbon solid acid catalyst showed better reusability than HZSM-5 because its large pores were minimally affected by the accumulation of oligomerized cyclohexene, which deactivated HZSM-5. The activity of the carbon solid acid catalyst decreased somewhat in the first two recycles due to the leaching of polycyclic aromatic hydrocarbon containing $-SO_3H$ groups and then it remained constant in the following reuse.

1. Introduction

In recent years, carbon solid acids (CSAs) have been studied by many researchers [1–21]. CSAs are amorphous carbon materials consisting of small polycyclic aromatic carbon sheets with attached SO_3H groups [1]. Due to the high density of SO_3H groups, simple separation process and environmentally friendly characteristics, CSAs are considered promising replacements for H_2SO_4, which is one of the most widely used liquid acid catalysts for the production of many industrially important chemicals [2]. CSAs exhibit high catalytic performance for many types of acid-catalyzed reactions, such as esterification [3–7], transesterification [8–10], hydration [2,11], dehydration [12], alkylation [13], hydrolysis [14–17], condensation [18], and rearrangement [19,20]. There are two routes for the preparation of CSAs [21]: one is the incomplete carbonization of sulfoaromatic compounds and the other is the sulfonation of partially carbonized organic matter, such as sucrose, D-glucose, starch, cellulose, or biomass. Most CSAs are prepared by the second route because of its convenience and safety.

Peanut shell is an agricultural waste and would be an excellent bio-resource for preparing CSAs because of its high supply,

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This work was supported by the National Natural Science Foundation of China (21236001, 21176056), the Programme for 100 Excellent Talents in Universities of Hebei Province (II) (BR2-208), and the Natural Science Foundation of Hebei Province (B2015202228).

DOI: 10.1016/S1872-2067(15)61076-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 5, May 2016

low cost, and easy sustainability. Several papers [22–24] have reported the preparation of CSAs by the sulfonation of the partially carbonized peanut shell and shown their high activity and excellent recyclability for biodiesel production and esterification reactions. Zeng et al. [24] found that the acid strength of the CSAs from peanut shell was stronger than that of HZSM-5 (Si/Al = 75), but weaker than that of 100% H_2SO_4. The CSAs produced from peanut shell do not have any Lewis acid sites on their surface.

Cyclohexyl formate is an important chemical used in the perfume and coating industries [25]. The most widely used method for the production of cyclohexyl formate is the reaction of formic acid with cyclohexanol over a mineral acid catalyst or an acidic heterogeneous catalyst. Due to the availability of cyclohexene on a large scale, the direct esterification of cyclohexene with formic acid has been of interest in recent years. Saha et al. [26] investigated the esterification of formic acid with cyclohexene in the presence of cation-exchange resins as the catalyst. Cyclohexene conversion reached 95.7% with 95.2% selectivity for cyclohexyl formate. The esterification of cyclohexene with acetic acid has been also studied over Hβ [27], ionic liquids [28], and ion exchange resins [25]. A propysulfonic acid modified mesostructured silica (SBA-15-SO_3H) was used as catalyst for the esterification of acrylic acid and cyclohexene [29], which gave good catalytic performance and stability. Other than use in the perfume industry, cyclohexyl formate can also be easily hydrolyzed to cyclohexanol [30], which is an important chemical intermediate in the synthesis of adipic acid and caprolactam for the production of nylon-6 and nylon-66 polymers [31]. In the 1990s, Asahi Chemical Industry Co. commercialized a process for the preparation of cyclohexanol by the direct hydration of cyclohexene [32]. However, this reaction is limited by the thermodynamics and extremely poor miscibility of water and cyclohexene, and the reaction rate was low. The once-through yield was only 10%, which led to high recycle amounts with high energy consumption. The synthesis of cyclohexanol from cyclohexene via cyclohexyl formate in the direct hydration of cyclohexene overcomes the drawbacks above [33]. Steyer et al. [30] studied the esterification of cyclohexene with formic acid and the subsequent hydrolyzation of the ester over Amberlyst 15 catalyst in a reactive distillation column. They concluded that it was possible to achieve an almost complete conversion of cyclohexene to cyclohexanol [34]. Du et al. [35] studied the one-pot synthesis of cyclohexanol from cyclohexene via cyclohexyl formate over HZSM-5 catalyst and obtained cyclohexanol in yields of up to 40%, which was far more than in the direct hydration of cyclohexene.

Concerning the two reactions in the synthesis of cyclohexanol from cyclohexene via cyclohexyl formate, the esterification of cyclohexene with formic acid should receive more attention because the hydrolyzation of cyclohexyl formate is much easier. Cyclohexyl formate conversion can reach nearly 60% with high cyclohexanol selectivity even without a catalyst [35]. Therefore, in this work, the catalytic performance of a CSA catalyst for the esterification of cyclohexene with formic acid was evaluated. The CSA catalyst was prepared by the sulfonation of partially carbonized peanut shell with concentrated H_2SO_4. The structure and acidic properties were characterized and the reusability of the catalyst was also studied.

2. Experimental

2.1. Catalyst preparation

Peanut shell was heated in a tube furnace for 10 h at 723 K under a N_2 flow. Then the partially carbonized peanut shell was ground into powder. To sulfonate this carbon material, 6 g of the carbonized peanut shell powder and 150 mL concentrated H_2SO_4 (98%) were mixed in a 250 mL flask and heated at 433 K for 8 h under N_2 flow. After sulfonation, the mixture was cooled to room temperature. Then the carbon material was filtered and washed repeatedly with hot deionized water (＞353 K) until the filtrate was free of SO_4^{2-}. Finally, the solid was dried at 353 K under vacuum overnight to obtain the peanut shell derived carbon solid acid catalyst. The catalyst was denoted as PSCSA.

2.2. Catalyst characterization

The Fourier transform infrared (FT-IR) spectrum of PSCSA with the KBr tablet method was recorded by a Thermo Nicolet Nexus 470 spectrometer. The results were used to determine the functional groups on the material. The morphology of PSCSA was characterized by scanning electron microscopy (SEM) using a Hitachi S-4800 field emission scanning electron microscope. X-ray diffraction (XRD) was carried out using a Rigaku D/Max-2500 X-ray diffractometer and Cu K_α radiation at 40 kV and 100 mA. Raman spectra were measured by a Renishaw inVia Reflex microspectrometer.

The thermostability of PSCSA was measured by thermogravimetric analysis (TGA) using a DuPont TA2000 TG analyzer. The temperature was increased from ambient temperature to 1273 K under air/N_2 flow at a heating rate of 10 K/min. X-ray photoelectron spectroscopy (XPS) measurements were performed with a PE PHI-1600 spectrometer with a Mg K_α source (1253.6 eV). The composition of the samples was determined by the elemental analysis of C, H, N, S and O using an Elementar Vario EL elemental analyzer. The content of S was used to calculate the acid density of $-SO_3H$. The specific surface area and pore structure of PSCSA were measured by N_2 adsorption using a Micromeritics ASAP 2020 instrument. The surface area was calculated by the BET method.

2.3. Catalytic activity test

The esterification of cyclohexene with formic acid was carried out in a 100-mL Teflon-lined stainless steel autoclave fitted with a magnetic stirrer. In a typical experiment, 15.0 mL cyclohexene (0.148 mol) and 16.8 mL formic acid (0.446 mol) were introduced into the autoclave together with 1.05 g PSCSA as catalyst. The autoclave was sealed and pressurized with N_2 for leak testing, then purged and the temperature set to 413 K to start the esterification. At the end of the reaction, the autoclave was cooled in an ice bath and vented. The catalyst was sepa-