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Roles of texture and acidity of acid-activated sepiolite catalysts in gas-phase catalytic dehydration of glycerol to acrolein

Chun Hui Zhou[a,b,*], Gui Li Li[a], Xiao Yu Zhuang[a], Peng Peng Wang[a], Dong Shen Tong[a], Hui Min Yang[c], Chun Xiang Lin[d,*], Li Li[d], Hao Zhang[a], Sheng Fu Ji[e], Wei Hua Yu[a]

[a] *Research Group for Advanced Materials & Sustainable Catalysis (AMSC), State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Discipline of Industrial Catalysis, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China*
[b] *Centre for Future Materials, University of Southern Queensland, Toowoomba, QLD 4350, Australia*
[c] *Key Laboratory of High Efficient Processing of Bamboo of Zhejiang Province, China National Bamboo Research Center, Hangzhou 310012, China*
[d] *Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, QLD 4072, Australia*
[e] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029 China*

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ABSTRACT

In the search for novel solid acid catalysts for the gas-phase catalytic dehydration of glycerol to acrolein, sepiolite clay minerals were activated with hydrochloric acid to produce acid-activated sepiolite catalysts. The effects of the activation process on the texture and acidity of acid-activated sepiolite, and their roles in gas-phase catalytic dehydration of glycerol to acrolein, were then investigated. A series of acid-activated sepiolite catalysts were made from purified natural sepiolite treated with hydrochloric acid of different concentrations (0–8 mol/L) at 80 °C, followed by drying at 100 °C. The acid-activated sepiolite catalyst samples were characterized using X-ray diffraction, X-ray fluorescence analysis, scanning electronic microscopy, thermogravimetric analysis, N_2 adsorption-desorption isotherms, NH_3-temperature-programmed desorption. Fourier transform-infrared spectroscopy and pyridine adsorption followed by in situ infrared spectroscopy. The catalytic performances in gas-phase catalytic dehydration of glycerol to acrolein were studied using a vertical fixed-bed reactor. Typically, a glycerol conversion of 92.9%, an acrolein selectivity of 59.4%, and a yield of acrolein of 55.2% were achieved when the gas-phase catalytic dehydration of glycerol was conducted over HCl (2 mol/L) acid-activated sepiolite catalyst at 320 °C with an aqueous glycerol solution (20 wt.%) at a rate of 0.10 ml/min as the feedstock and air as the carrier gas at a flow rate of 20 ml/min. The activation of the sepiolite with hydrochloric acid followed by drying can eliminate a portion of the zeolitic water in the tunnels, remove part of the magnesium and aluminum cations in the octahedral sheets of sepiolite, unbundle aggregated sepiolite fibers, and partly break the Si-O-Si in the tetrahedral sheets of sepiolite. These factors increased the porosity, the specific surface area and the acidity of the sepiolite. The partial leaching of magnesium and aluminum ions in the octahedral sheet generated octahedral vacancies and created Mg—O—Al^+ sites in the octahedral sheets, thereby increasing the amount of Lewis acid sites. Along with penetration of H^+ cations into the interlayered space of the sepiolite by an ion-exchange reaction and physicochemical surface adsorption, some breakage of the Si—O—Si bonds in the tetrahedral sheets generated more Si—O—H^+, thus increasing the quantity of Brønsted acid sites. Furthermore, the strength of acidity of the hydrochloric acid-activated sepiolite was significantly changed after the acid activation. The medium-strong Brønsted acid sites (Si—O—H^+ and H^+ adsorbed on the surface) appeared to be beneficial for the high conversion of glycerol and the selectivity to acrolein. Lewis acid sites could facilitate the formation of acetol. Under the reaction conditions mentioned above, the coking on the hydrochloric acid-activated sepiolite catalysts readily occurred, rapidly leading to the decrease of the yield of acrolein.

1. Introduction

Glycerol is an unavoidable by-product from the industrial soap-making processes [1], the transesterification of fatty oil with

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* Corresponding author.
E-mail addresses: clay@zjut.edu.cn, Chun.Zhou@usq.edu.au (C.H. Zhou).

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alcohol to biofuel [2], and the production of fatty acids [1]. It can also be produced from microbial fermentation of cellulose and glucose [3]. Glycerol is now considered a platform chemical to produce value-added chemicals, polymers and fuel additives [4–6]. Catalytic dehydration of glycerol produces acrolein, which is used to produce acrylic acid, methionine, 1,3-propanediol, glutaraldehyde, and pyridine [7–10]. The catalytic dehydration of glycerol is a typical acid-catalyzed reaction. Namely, it usually needs to be conducted over homogeneous or heterogeneous acid catalysts. Homogeneous catalytic liquid-phase dehydration of glycerol with liquid acid as catalysts, for example sulfuric acid and hydrochloric acid, causes equipment corrosion, catalyst separation, and leads to waste management challenges [11]. Comparatively, the heterogeneous catalytic gas-phase dehydration of glycerol over solid acid catalysts can substantially avoid these concerns.

The acidity and texture of solid acid catalysts are crucial factors in the catalytic dehydration of glycerol [4–6]. For example, Chai et al. [12] found that the strong Brønsted acid of solid acid catalysts appeared to be beneficial for a high yield of acrolein. A glycerol conversion of 70% and an acrolein selectivity of 60–70% were obtained at 315 °C over WO_3/ZrO_2 and $H_3PW_{12}O_{40}/\alpha\text{-}Al_2O_3$ catalysts with H_0 between −8.2 and −3.0. Moreover, the detailed investigation into the type of acidity suggested that the catalytic dehydration of glycerol to acrolein should proceed via the protonation of the secondary hydroxyl group over Brønsted acid sites, then forming 3-hydroxypropanal with the elimination of a water molecule. It subsequently undergoes a second dehydration step, thereby leading to the formation of acrolein [13]. Alhanash et al. [14] used $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ with strong Brønsted acidity as a solid catalyst for the catalytic gas-phase dehydration of glycerol to acrolein. At 275 °C, the conversion of glycerol was 100% and the selectivity of acrolein was ca. 98% after 1 h. Nevertheless, the strong Brønsted acid sites caused severe coke deposition and hence rapidly decreased the activity of the catalyst.

In addition to the acidity, the texture and porosity of the solid acid catalyst affects the mass transfer, selectivity, and coke formation during glycerol dehydration. Many studies indicated that acidic aluminosilicate zeolite catalysts, with a microporous structure, have transport limitations, which adversely affect catalytic performances of the catalyst, particularly when bulky molecules are involved. In view of this limitation, Decolatti et al. [15] treated zeolitic material H-ZSM5 with an aqueous sodium hydroxide solution to enhance the porosity for the catalytic dehydration of glycerol to acrolein. Such a treatment of H-ZSM-5 with an aqueous sodium hydroxide solution led to the development of mesopores and accordingly increased its porosity and specific surface area. Over the meso-microporous H-ZSM5 catalyst, the conversion of glycerol was 77.6% and the selectivity of acrolein was 58.6% after 5 h. In our previous work, Zhao and Zhou et al. [16] treated montmorillonite clay minerals with acid and used acid-activated montmorillonite as a solid acid catalyst for the catalytic dehydration of glycerol. As a result, the acid-activated montmorillonite catalyst possessed high mesoporosity. The mesoporosity and H^+ in the interlayer space were ascribed to the catalytic dehydration of glycerol. The findings implied that the conversion of glycerol and selectivity of acrolein could be further improved by finely tuning both texture and acidity of clay minerals.

Compared with layered montmorillonite clay mineral, sepiolite ($Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4{\cdot}8H_2O$, it is possible that Mg is partly replaced by Al) possesses additional exposed tunnel-like structures (openings) on the outer surface, additional to channels (pores) in the structure [17–26]. Such a structure allows sepiolite to have surface acidity and to be used as a solid acid catalyst. For example, sepiolite-based catalysts have been used in catalytic dehydration of 1-phenylethanol [17], transesterification of oil to biodiesel [18] and Suzuki reaction [19]. In particular, it is worth nothing that the discontinuous octahedral sheets of sepiolite provide available open tunnels (10.6 Å in width) with the edges of broken bonds at either side. (Fig. 1(A), (B)) [21,22]. In consideration of the catalytic dehydration of glycerol, such open tunnels are far larger than the size of a glycerol molecule (*ca.* 6.2 Å) and the acidic sites on the tunnel surface are readily approachable for glycerol reactants. Specifically, both the silanol groups (—Si—O—H^+) at the edges of the tetrahedral sheets and the unsaturated Al^{3+} ions in the octahedral sheets are exposed, as are active acid sites [23]. The amount and type of such acid sites can be increased if more tunnels, edges and broken bonds are created by proper acidic activation [24], primarily because the acid activation of sepiolite under judiciously-chosen conditions can remove the zeolitic water and partly dissolve the layer framework of sepiolite. This enhances both the porosity and the specific surface area, and changes the type and strength of acidity [24,25]. To our knowledge, the effects of acid activation of sepiolite on the texture and acidity of sepiolite has not been investigated as much as that for montmorillonite. It has not yet been touched that acid-activated sepiolite catalysts act as catalysts for the catalytic dehydration of glycerol to acrolein.

In the present work, we attempt to investigate the effects of texture and acidity of hydrochloric acid-activated sepiolite catalysts and coke deposit on the performances of the acid-activated sepiolite catalysts in the catalytic dehydration of glycerol to acrolein. To this end, sepiolite was treated with hydrochloric acid of different concentrations to yield a series of hydrochloric acid-activated sepiolite catalysts. The resultant hydrochloric acid-activated sepiolite catalyst samples were then characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electronic microscopy (SEM), thermogravimetric analysis (TGA), N_2 adsorption-desorption, NH_3-temperature-programmed desorption (NH_3-TPD), Fourier transform-infrared (FT-IR) spectroscopy, and pyridine adsorption followed by in situ infrared spectroscopy. The performances of the acid-activated sepiolite catalysts were evaluated in the catalytic dehydration of glycerol to acrolein. Moreover, the state of coke formation on the catalysts and its effects on the deactivation of the catalysts were preliminarily investigated.

2. Experimental

2.1. Catalyst preparation

Purified natural sepiolite was obtained from a Sepiolite Co., Ltd, Xiangtan, China. Hydrochloric acid activation was carried out using an aqueous HCl solution and distilled water; concentrations varied from 0.5 mol/L to 8 mol. For each activation reaction, a mixture at a solid sepiolite/liquid (aqueous HCl solution) ratio of 1:10 (mass/volume) was used. The slurry was stirred magnetically for 4 h at 80 °C, and after cooling down to room temperature, the suspensions were centrifuged and filtered, the collected solid was washed several times with distilled water until the filtrates were neutral. The as-obtained hydrochloric acid-activated sepiolite samples were then dried at 100 °C for 48 h. The dried solids were crushed and sieved to obtain a uniform particle with a size of 40–60 mesh (0.250–0.425 mm). The catalyst samples were denoted as SP-X, where “X” represents the concentration of hydrochloric acid used (mol/L). The concentration of the aqueous hydrochloric acid solution is 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0 and 8.0 mol/L, respectively. For investigating the possible influence of diffusion, SP-2 catalysts were also sieved between 20 and 40 mesh (0.425–0.840 mm), and 60–80 mesh (0.180–0.250 mm).