



Research paper

Catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalysts



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ABSTRACT

For the development of efficient solid acid catalysts for the catalytic dehydration of glycerol to acrolein, catalysts made from montmorillonitic clay activated by sulfuric acid were investigated. Montmorillonite was activated in diluted sulfuric acid in the concentration range of 5–40 wt.%. The effects of sulfuric acid treatment on the structure of the montmorillonite were characterized by X-ray diffraction, measurements of acidity, N₂ adsorption-desorption isotherms, and Fourier transform infrared spectroscopy. The catalytic behavior of sulfuric acid-activated montmorillonite catalysts in the gas-phase dehydration of glycerol were investigated under varying conditions, including the reaction temperature, the feed rate, and the concentration of glycerol. After montmorillonitic clay was activated by sulfuric acid, the layered structural features of montmorillonite remained nearly intact. Ca²⁺-montmorillonite was changed to H⁺-montmorillonite by ion exchange reaction during activation. The optimal catalytic glycerol dehydration reaction conditions were found to be: temperature at 320 °C, liquid hourly space velocity (LHSV) = 18.5 h⁻¹, concentration of glycerol solution = 10 wt.%, and the flow rate of N₂ carrier gas = 10 mL/min. A conversion of 54.2% of glycerol and a yield of 44.9 wt.% acrolein were achieved over the montmorillonite catalyst activated by an aqueous 10 wt.% sulfuric acid solution. The H⁺ in the interlayer space of acid-activated montmorillonite catalysts played a critical role in the catalytic dehydration of glycerol. The temperature, the LHSV, and the concentration of glycerol affected the performance of the catalysts through their influence on the reaction mechanism, the contact time, and the reaction equilibrium.

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1. Introduction

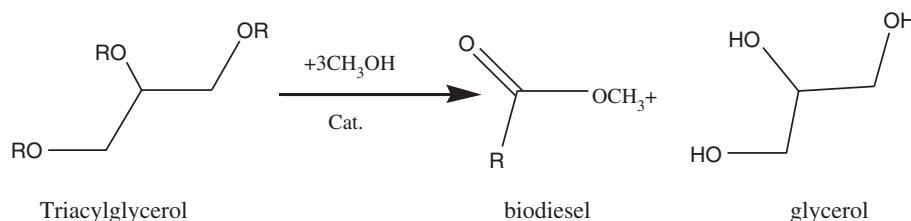
With dwindling petroleum reserves, growing demand for fuels, and increased global warming caused by the emission of greenhouse gases, the use of biomass, a sustainable and renewable alternative source, has recently received much greater attention for the production of a new-generation of fuels, chemicals and materials in sustainable and environmentally friendly ways than ever before (Corma et al., 2007; Gallezot, 2007; Zhou et al., 2011b, 2012). In particular, many attempts have been made at the production of biofuels and chemicals from the catalytic conversion of bio-renewable feedstocks, including lignocellulosic bioresources (Zhou et al., 2011b), lipids (e.g., vegetable oil) (Behr and Gomes, 2010), starch (Huber and Corma, 2007), sugarcane (Alves et al., 2011), and municipal solid wastes (Li et al., 2011). The chemical reaction of vegetable oils with methanol produces fatty acid methyl esters (FAME). Such products, also known as biodiesel, can be used in pure form or blended with petrodiesel at any concentration in standard diesel engines (Johnson and Taconi, 2007). In

addition, biodiesel can be used as an alternative to heating oil with, theoretically, little carbon emission. Hence, the past decade has witnessed a rapid expansion of biodiesel processes. It is expected that these would continue to increase with the increasing availability of the feedstock of lipids from non-food plants (e.g. *Jatropha*) (da Silva Freire et al., 2012). However, the transesterification of lipids with methanol (Scheme 1) to biodiesel simultaneously produces significant amounts of glycerol as a by-product (Sharma et al., 2008). Therefore the utilization of glycerol is an issue that needs to be addressed by the biodiesel industry. An attractive solution is to develop novel catalytic chemical processes that convert glycerol to useful fuels, polymers, or value-added fine chemicals (Pagliareo et al., 2007; Zhou et al., 2008). While many potential reactions have been reported to convert glycerol to useful fine chemicals, for example hydrogenation (Coll et al., 2011) and catalytic oxidation (Zhou et al., 2011a), only a few of these catalytic reactions for glycerol conversion have been developed to commercial application (Holladay et al., 2009; Werpy and Petersen, 2004).

Catalytic dehydration of glycerol offers an alternative route to the production of acrolein (Scheme 2). The product, acrolein, is a versatile intermediate used in the synthesis of pharmaceuticals, detergents and polymers (Corma et al., 2008). For the dehydration reaction of glycerol,

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Scheme 1. Transesterification of lipids with methanol to biodiesel with by-product glycerol.

so far many acid catalysts have been examined. In the liquid-phase batch reaction, these include homogeneous and heterogeneous acid catalysts, such as benzenesulfonic acid (Waldmann and Petru, 1950), sulfonic acid (Ramayya et al., 1987), metal phosphates (Takanori and Masayuki, 2009), alumina (Yang et al., 2008), zeolite (de Oliveira et al., 2011) and metal sulfates (Lehr et al., 2007). The application of liquid-phase catalytic dehydration of glycerol on an industrial scale, however, is hampered by tedious separation, equipment corrosion, operational safety, and the large quantity of liquid waste produced (Dubois et al., 2008). A preferred alternative approach is a continuous process in which glycerol undergoes catalytic gas-phase dehydration over a heterogeneous solid acid catalyst.

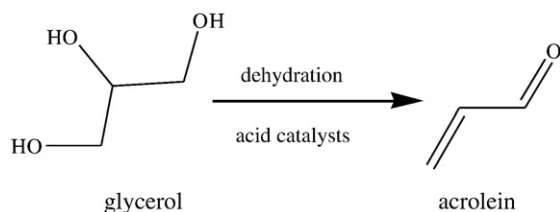
For the gas-phase dehydration of glycerol, the solid acid catalysts which have been examined are metal phosphates (Wang et al., 2009), metal sulfates (Chai et al., 2007), metal oxides (Yang et al., 2008), supported heteropolyacids (HPAS) (Tsukuda et al., 2007), and zeolites (Yoda and Ootawa, 2009). It is worth noting that acidic clay minerals and their derivatives are one class of heterogeneous solid acid catalysts that have yet to be investigated for the gas-phase dehydration of glycerol.

Montmorillonite is a member of the smectite clay group with a 2:1 layer structure consisting of a dominantly Al–OH octahedral sheet sandwiched by two Si–O tetrahedral sheets. The clay mineral can be modified and engineered to give various solid acid catalysts that make use of its special properties of nanometer-scale platelets and interlayer space (Zhou, 2011a). The peculiar structural features of montmorillonite not only allow versatile methods for modifying the composition on their layers and within their interlayer space (Tong et al., 2009), but also the Brønsted and Lewis acidity of montmorillonite can be tuned through surface adsorption (Santhi et al., 2010), and ion exchange reaction, intercalation, pillaring and surface grafting (Joshi et al., 2009; Zhou, 2011). The acid catalytic performance of raw montmorillonite is usually poor. Acid treatments, however, can substantially increase the catalytic activity of montmorillonite. Here the modification of montmorillonite by acid activation was done with varying concentrations of H₂SO₄ and the catalytic performance in the dehydration of glycerol was investigated.

2. Experimental

2.1. Catalyst preparation

The montmorillonite (MMT) clay was obtained from a bentonite deposit in north China, and was used without further purification.



Scheme 2. Acid-catalyzed dehydration of glycerol to acrolein.

The cation exchange capacity (CEC) of the raw clay was 80.0 mmol/100 g_(MMT). Concentrated H₂SO₄ (98.0%) was a commercially available chemical. The dried montmorillonite was crushed and ground to a fine power. Batches of montmorillonite powder were activated in an aqueous solution of sulfuric acid at 80 °C with constant stirring for 4 h. The concentration of sulfuric acid was varied in the range of 5–40 wt.% H₂SO₄. The ratio of solid montmorillonite powder to liquid sulfuric acid solution was 1:4 (w/w), based on the weight of dry clay. After reaction, the acid-activated solid was separated by filtration, then washed three times with distilled water, and dried at 100 °C for 2 days. The solids were then ground with a mortar and pestle to produce fine powder catalysts for further use. The catalyst samples were labeled as MMT-5, MMT-10, MMT-15, MMT-20, MMT-30 and MMT-40, respectively, where the number referred to the concentration of sulfuric acid used.

Regenerated catalysts were made by calcination of the used catalysts at 500 °C in a muffle furnace. In this way, the unknown by-products and coke deposited onto the catalysts were burned off. Here the used catalysts were those that had been used in the catalytic reaction with glycerol for 6 h. The regenerated sample was denoted as MMT-10R.

2.2. Catalytic reaction

The evaluation of catalysts in the dehydration of glycerol was carried out in an upright fixed-bed quartz reactor with a dimension of 8 mm inner diameter and 500 mm length. A diagrammatic representation of the process is shown in Fig. 1. All reactions were operated at atmospheric pressure. For each run, 0.5 g of catalyst was loaded into the reactor, and the space beneath the catalyst bed was filled with quartz beads. Before pumping the feedstock into the reactor the catalyst bed was heated at an incremental rate of 10 °C/min in a flow of pure N₂ (10 mL/min) to the required temperature and then kept at the temperature for 3 h. Typically, an aqueous solution with a ratio of glycerol to water at 10:90 (w/w) was fed into the reactor at a flow rate of 0.30 mL min^{−1} by a Kontron Instruments 422 HPLC pump. Reaction products together with unconverted glycerol were collected half-hourly in an ice trap (0 °C). The analysis of the collected species was done using a gas chromatograph

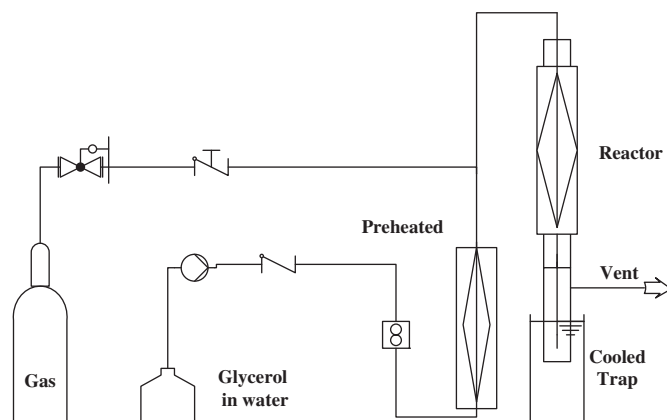


Fig. 1. Schematic of the experimental set-up for catalytic dehydration of glycerol.

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