Editor's choice paper

The effect of hierarchical pore architecture on one-step catalytic aromatization of glycerol: Reaction routes and catalytic performances

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ABSTRACT

One-step aromatization of glycerol to value-added aromatics is a very promising way not only owing to the growing byproduct of glycerol in biodiesel manufacturing but also due to the imperious demands to provide a sustainable route for aromatics production to alleviate the dependence on fossil fuels. Different hierarchical HZSM-5 catalysts with diverse sizes of intramesoporosity and similar size of microporosity are prepared by desilication with different alkali. The occurrence of deoxygenation and dehydration reactions among the GTA process brought about a noticeable drop in the oxygen content of the organic products and as a consequence, resulted in a superior quality in liquid products, in which aromatics, such as benzene, toluene, xylene, trimethylbenzene, tetramethylbenzene, et al., were the major components. Liquid route during the GTA reaction was suppressed while the gas route was enhanced over the desilicated HZSM-5 samples, leading to the increment of BTX light aromatics yields and reduction of the heavier aromatics yields (trimethylbenzene, tetramethylbenzene). It was found that smaller intramesopores (3–5 nm) together with well-preservation of parent HZSM-5 microporosity exhibited better shape-selective BTX yields and slower carbon deposition rate during the GTA procedure than larger ones (6–16 nm).

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1. Introduction

The increasing global attention on environmental pollution and energy crisis has given rise to the new utilization of alternative bioenergy [1]. Glycerol is a main coproduct stemmed from the production of biodiesel [2,3], which is manufactured from sustainable resources such as palm, canola, soya bean and rape seed oil [4]. The huge boom in biodiesel production over the last fifteen years has resulted in a surplus in the current glycerol market and a sharp decrease in the price of glycerol [5], which makes glycerol an inexpensive and renewable feed for producing other value-added chemicals and materials, such as acrolein (acrylic acid and acrylic resins precursor) [6], acrylic acid [7], 1,2-propanediol [8] and dihydroxyacetone [9], etc.

Aromatization of glycerol is an alternative process that could replace the current BTX (benzene, toluene and xylene) production, which is mainly based on petrochemical processes derived from fossil fuels [10]. BTX are important feed stocks for various polymers and petrochemicals. The production of glycerol to aromatics (GTA) is economically feasible since it integrates the whole biodiesel

industrial chain enabling surplus glycerol plants to add value. However, investigation on the glycerol to aromatics could be scarcely ever ascertained in literature. Hoang et al. [11] investigated the catalytic conversion of glycerol to gasoline-range alkyl-aromatics on a series of zeolites (HZSM-5, HY, Mordenite, and HZSM-22) and found that glycerol can be converted to high yields of alkyl-aromatics, mainly C_8-C_{10} over three-dimensional HY and HZSM-5. Luo et al. [12] studied the effects of reacting temperature, glycerol addition and reaction time on the catalytic performance of methanol and glycerol to gasoline (MGTG) process and found that with increasing additions of glycerol in methanol, lower oil-phase yield was obtained, while relatively more oxygenate compounds were produced. Jang et al. [13] diluted glycerol with different solvents such as water, methanol, ethanol, isopropanol or isobutanol and investigated the aromatization of glycerol solution. The result showed the carbon fraction of aromatic products depends upon the alcohol mixed with glycerol. Nevertheless, these reports are mainly based on the utilisation of microporous HZSM-5 zeolite, which suffer from rapid deactivation with time on stream caused by micropore blockage of carbon deposits during the reaction due to the mass transfer limitation of the zeolite micropores. Recently, enormous studies have been reported that the hierarchical structured zeolites, which can facilitate molecular diffusion in the pores of HZSM-5 zeolites by incorporated mesopores while keeping the aromatization per-

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formance of micropores in HZSM-5, could effectively improve the zeolite stability during the aromatization process [14–17]. Post-treatment method of the desilication in alkaline aqueous solution has become the most powerful tool to introduce hierarchical micro-mesoporous system by selective removal of framework silicon [18], as a result of the inexpensive and convenient operation and effective micro-mesoporous production. In our previous work [14], we have also investigated aromatization of glycerol using NaOH-treated HZSM-5 catalysts, which exhibited better performance than the parent HZSM-5 catalyst in terms of aromatics yield and stability. Nevertheless, most of these studies only paid attention to the introduction of hierarchical porous structure, but ignored the influence of different intramesopore sizes on the catalytic performance.

The aim of this work is to demonstrate the impact of various hierarchical HZSM-5 with diverse sizes of intramesoporosity generated by desilication with different alkali on the GTA performance, including the catalytic activity and stability, the distribution of the products in GTA process and reaction route of GTA procedure.

2. Methods

2.1. Catalysts preparation

A commercial HZSM-5 with a Si/Al ratio of 25 was purchased from Nanjing refinery Co., Ltd in China and used as starting material. Prior to treatments, the as-received sample was calcined at 550 °C for 4 h. The parent sample was designated as HZSM-5-P.

The desilication treatment was carried out in an aqueous alkaline solution. Typically, 7.5 g HZSM-5 was vigorously stirred in 150 ml of aqueous alkaline solution (including sodium methoxide (CH$_3$ONa), sodium hydroxide (NaOH), tetrapropylammonium hydroxide (TPAOH), tetramethyl guanidine (TMG), sodium bicarbonate (NaHCO$_3$) and ammonium hydroxide (NH$_4$OH)) with the concentration of 0.3 M and 0.9 M at 80 °C for 2 h. Subsequently, the slurry was cooled down immediately using an ice bath, followed by filtration and thorough washing with deionized water until pH neutral. All the Na-form zeolites were converted to H-form via a twice conventional ion exchange with 0.8 M NH$_4$NO$_3$ solution at 80 °C for 8 h, followed by calcination in air at 550 °C for 4 h before the reaction. The prepared samples were referred as x y/HZSM-5, where y stands for the name of alkaline while x represents the molar concentration of alkaline solution during the post-treatment (e.g., 0.3 M CH$_3$ONa/HZSM-5).

2.2. Characterization

Nitrogen adsorption-desorption isotherms were obtained using a physical adsorption apparatus (Beishide 3H-2000). Before measurements the samples were evacuated at 200 °C under vacuum for 12 h. The bulk Si/Al ratios of the prepared samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, Optima 7300 DV). X-ray diffraction (XRD) patterns of the catalysts were collected on an X-ray diffractometer (Bruker AXS D8 Focus, 40 kV, 40 mA) using a Cu Kα radiation source in the 2θ range of 5°–60°. The transmission electron microscope (TEM) images were taken using a Philips CM-100 microscope. The acidity of the prepared samples was determined by temperature-programmed desorption of ammonia (NH$_3$-TPD) and FT-IR spectra of adsorbed pyridine. NH$_3$-TPD was conducted on an automated adsorption system (TP-5076, Tianjin city industry and Trade Development Co. Ltd.) equipped with an online thermal conductivity detector (TCD). 0.1 g of the sample was loaded in a small quartz tube and preheated at 400 °C under a He flow of 30 ml/min for 1 h. After saturation with NH$_3$ at 100 °C for 30 min, the sample was flushed with He at a rate of 30 ml/min for 1 h to remove excessive NH$_3$. The

NH$_3$-TPD profile was measured from 100 °C to 600 °C at a constant heating rate of 10 °C/min using a TCD detector. Fourier transform infrared (FTIR) measurements of pyridine adsorption were performed by a Nicolet FTIR 360 spectrometer. The samples were pressed into thin wafers with a diameter of approximately 13 mm. Before pyridine adsorption, all samples were evacuated for 2 h at 400 °C. The background spectrum was recorded after cooling the samples to room temperature. Then, the samples were exposed to pyridine vapors until saturation. Finally, the samples were heated to 150 °C under vacuum for 2 h to remove the physisorbed pyridine, and the corresponding spectra were then recorded. Temperature programmed oxidation (TPO) measurements of all spent samples was carried out on the same TPD apparatus. Typically, 100 mg of deactivated catalyst was treated in a He stream at 200 °C for 60 min and then heated in a 50 ml/min flow of 5%O$_2$/He from 50 °C to 800 °C at a ramp rate of 10 °C/min to obtain the TPO profile.

2.3. Catalytic testing

GTA reactions were achieved at 400 °C and atmospheric pressure in a vertical fixed-bed reactor equipped with a stainless steel tube (inner diameter 8 mm). 1.6 g of the pressed catalyst (40–60 mesh) was sandwiched in the middle section of the reactor, with quartz wool packed at both ends. Prior to the reaction, the catalyst was pretreated at 400 °C for 1 h under N$_2$ flow (25 ml/min).

The solution of 40 wt% glycerol in methanol (the pure glycerol was too viscous to be pumped effectively) was fed by a syringe pump at WHSV = 0.71 h^{-1}. Before sending the reaction mixture to reactor, the mixture was evaporated in a preheater at 300 °C. The reaction products were condensed in an ice water trap and gathered every 0.5 h for analysis using a GC-7890 (Shanghai Techcomp Ltd.) gas chromatograph equipped with a FID detector connected to a capillary column (SE-30). The reactant conversion and product yield were calculated according to the following equations:

$$Conversion\,(wt\%) = (1 - \frac{Mass\ of\ \text{methanol or glycerol (out)}}{Mass\ of\ \text{methanol or glycerol (in)}})$$

$$Product\ Yield\,(wt\%) = \frac{Mass\ of\ a\ specific\ product}{Mass\ of\ the\ feed}$$

$$Conversion\,(C\%) = \frac{Moles\ of\ carbon\ in\ converted\ reac\tan ts}{Moles\ of\ carbon\ in\ the\ feed}$$

$$Product\ Yield\,(C\%) = \frac{Moles\ of\ carbon\ in\ specific\ products}{Moles\ of\ carbon\ in\ the\ feed}$$

Detail gaseous analysis was not performed in this study since liquid products, specifically aromatics, were the main focus.

3. Results and discussion

3.1. Textural properties of zeolites

The elemental composition measured by ICP-AES and textural data derived from the nitrogen adsorption/desorption on parent and modified HZSM-5 zeolites are listed in Table 1. The elemental composition revealed that the Si/Al ratio of HZSM-5 was reduced after alkali treatment, which could be interpreted as that the Si—O—Al bond is relatively more difficult to fission than the Si—O—Si bond in HZSM-5 zeolite under alkaline environment due to the existence of adjacent negatively charged AlO$_4^-$ tetrahedral [19]. It should be noted that the degree of desilication differs depending on the intrinsic nature and concentration of alkali solution. The Si/Al ratio remained essentially unchanged when the pristine HZSM-5