



Study on the influence of channel structure properties in the dehydration of glycerol to acrolein over H-zeolite catalysts

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ABSTRACT

Systematic studies have been conducted over several selected H-zeolites, namely HZSM-5, H-Beta, HY, nano HZSM-5, HZSM-11 and nano HZSM-11, aimed to investigate influence of the channel structure on catalytic performance for gas phase dehydration of glycerol to acrolein. Compared to H-Beta and HY, improved catalytic performance was discovered over HZSM-5, which demonstrated that H-zeolites with smaller channels, the ones marginally larger than the molecular diameter of glycerol, were preferential for the reaction. HZSM-11, with lower channel complexity, was more likely to obtain superior catalytic performance due to enhanced diffusion. Nano HZSM-11 (300–500 nm) exhibited excellent catalytic performance with 81.6 mol% glycerol conversion and 74.9 mol% acrolein selectivity at GHSV as high as 873 h⁻¹ (TOS = 8 h). BET and TEM experiment results indicated that coke was initially deposited at channel intersections of H-zeolites, and when the channel blockage came up to a certain extent, there arrived the onset of coke deposition on the external surface.

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1. Introduction

With the rapidly growing energy demand, more attention has been devoted to biomass and the conversion of biomass related materials into fuels and chemicals, such as biodiesel. The advancing development of biodiesel production had provided a surplus supply of glycerol with reasonably lower prices [1], which currently has become a suitable feedstock for production of high value chemicals through catalytic conversions, including oxidation, reduction, etherification, etc. [2]. One of the most promising ways of glycerol application is through double-dehydration to produce acrolein, which is an important chemical intermediate for production of acrylic acid, acrylic acid esters and DL-methionine [3]. Acrolein is now commercially produced by selective oxidation of petroleum-derived propylene over mixed metal oxides based on BiMoOx [4].

The glycerol dehydration process is conducted either in liquid phase or in gas phase, with liquid or solid acid as catalyst [5]. In liquid phase reaction, sub- or supercritical conditions are necessary to enhance the catalytic activity of homogeneous catalysts [6–9]. However, the harsh conditions together with the presence of liquid acids will generate an extremely corrosive medium, resulting in high equipment investments and maintenance costs. As a result, it is unfeasible to produce acrolein commercially from glycerol in

liquid phase due to certain technical and environmental problems, such as reactor anticorrosion, catalyst/reaction mixture separation and waste management.

Recently, more and more researchers have been focusing on gas phase reaction over solid acid catalysts [10–46], including phosphates, zeolites, supported heteropolyacids, metal oxides, sulfates, and among others. Although supported heteropolyacids exhibited very promising results, the water solubility and poor thermal stability of heteropolyacids restrict their application.

H-zeolites possess large surface area and sufficient acid sites, which are necessary conditions for glycerol dehydration to acrolein. Yoda and Ootawa observed that acrolein was selectively formed over H-MFI zeolite at a relatively lower temperature (353 K) by FT-IR [22]. Recently, Jia et al. investigated catalytic performances of nanocrystalline HZSM-5 and bulk HZSM-5 with similar Si/Al ratio and proposed that H-zeolites with smaller particle size were more suitable for glycerol dehydration [20]. Nanocrystalline zeolites could provide large external surface area and short diffusion distance in the channels of particles, thereby facilitating access to active sites and reducing deactivation. However, currently it is hard to tell the predominant factor that controls the reaction process, external surface area or zeolite channels.

Kim et al. conducted the dehydration reaction of glycerol over several H-zeolites, and observed a good linear correlation between glycerol conversion and external surface area of catalysts [23]. Therefore, they concluded that external surface area was the main factor controlling glycerol conversion. The disappeared micropore

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