



Direct conversion of glycerol to acrylic acid via integrated dehydration–oxidation bed system

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ARTICLE INFO

Article history:

Received 3 August 2011

Received in revised form 25 October 2011

Accepted 30 October 2011

Available online 6 November 2011

Keywords:

Glycerol

Acrolein

Acrylic acid

HZSM-5

Vanadium–molybdenum oxides

Dehydration

Oxidation

ABSTRACT

Acrylic acid can be successfully produced in a single reactor via subsequent oxidation of the glycerol-dehydrated products. Selective dehydration of glycerol to acrolein was studied at 275–400 °C over HZSM-5, HBeta, HMordenite and HY. The V–Mo oxides (15–70 mol%V) on silicic acid support (20–100 wt% mixed oxides loading) were then included as a second bed for subsequent oxidation of the dehydrated products. Over the acid zeolites, acrolein and acetol are mainly generated, together with acetaldehyde, propionaldehyde, pyruvaldehyde and other oxygenates as secondary products. A complete conversion of glycerol with high selectivity to acrolein (up to 81 mol%) can be obtained when medium pore zeolites (HZSM-5) and low glycerol concentration (10–30 wt%) was used at 300 °C. A separated-sequential bed system provides high selectivity for acrylic acid with small amount of acetic acid and acetaldehyde (~15 mol%). The catalyst with high V content promotes total oxidation of the dehydrated products to CO while that with highly dispersed V–Mo–O phases affords 98% selectivity to acrylic acid with 48% acrolein conversion.

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1. Introduction

Nowadays, attempts to replace the petroleum resource by biomass have been increasingly focused for the production of both liquid fuel and petrochemical feedstock. In particular, the use of alkyl ester as biodiesel via trans-esterification between vegetables oil and alcohol [1,2], becomes increasingly attractive for the countries with agriculture-based economics. However, a large amount of glycerol, the by-product, is continually produced, while its current demand remained unchanged. Despite efforts are made to utilize glycerol as alternative fuel, its combustion emits toxic gases [3]. Alternatively, glycerol is a sustainable feedstock that can be used for manufacture of some C₃ derivatives. Several processes, so called “deoxygenation”, were applied to eliminate its oxygen content. These include hydrogenolysis [4,5] and dehydration [6,7]. For example, conversion of glycerol to propylene glycol [8] has been widely investigated. However, most of the process consumes large amount of hydrogen and high pressure is generally applied.

In an economic point of view, deoxygenation of glycerol via dehydration become more attractive since more than 60% oxygen content can be simply eliminated without hydrogen consumption under relatively mild reaction condition [9]. Moreover, the dehydrated product, acrolein, can be readily converted to other

C₃ petrochemicals, namely acrylic acid [10–12], acrylonitrile [13], allyl alcohol [14], etc. The dehydration can be generally promoted over acid catalysts at 275–350 °C. The common acid oxides such as η -Al₂O₃, SiO₂/Al₂O₃ [15] and TiO₂ [16] have been applied but they did not provide a satisfied selectivity to acrolein. Improved selectivity can be obtained from the reactions over Nb₂O₅ (~50%) [17], WO₃/ZrO₂ (75%) [18], phosphoric-doped metal oxides (i.e. Al₂O₃–PO₄, TiO₂–PO₄ [19]), heteropoly acids (i.e. HSiW, HPW, HPMo on silica supports [16]) and zeolites (i.e. ZSM-5, Y, Beta [20–22], and SAPOs [19]). However, low selectivity is typically obtained at high conversion and the catalysts usually possess low stability. This is presumably because acrolein is highly reactive and undergoes secondary reactions to form other products during the dehydration process. Accordingly, a subsequent conversion of acrolein to a desirable and more stable product, immediately after its formation, would not only enhance the designed product selectivity, but also eliminate handling problems of acrolein storage and transportation.

Major industrial use of acrolein is for production of acrylic acid that is widely used for in adhesive, paint, plastic and rubber synthesis. Typical oxidation catalysts involve vanadium–molybdenum mixed oxides on alumina or silica supports due to their high selectivity to acrylic acid [23]. It was also report that Mo:V ratio and oxygen partial pressure play important role on the catalyst performance [23]. In general, selective oxidation competes against total combustion and the TPR experiment showed that CO₂ could be minimized at temperature below 400 °C [24]. While acrylic acid

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