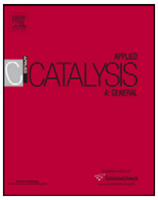
Applied Catalysis A: General 400 (2011) 148–155

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Dehydration of 1,2-propanediol to propionaldehyde over zeolite catalysts

Dazhi Zhang, Sami A.I. Barri, David Chadwick*

Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 11 November 2010
Received in revised form 19 April 2011
Accepted 21 April 2011
Available online 28 April 2011

Keywords:
1,2 Propanediol
Dehydration
Propionaldehyde
Glycerol
Zeolite
Catalyst

ABSTRACT

Dehydration of 1,2-propanediol has been investigated over a range of zeolite catalysts with different pore structures and acidity. The reaction forms part of a two-step process for the conversion of glycerol to propionaldehyde. The effects of reaction temperature, concentration, space velocity, and SiO_2/Al_2O_3 ratio have been studied. The medium pore size, unidirectional channel zeolites ZSM-23 and Theta-1 showed high activity and selectivity to propionaldehyde (exceeding 90 wt% at 300–350 °C). Selectivity to the intermolecular dehydration product 2-ethyl-4-methyl-1,3-dioxolane was high at lower temperatures for all the zeolites, but decreased to a low value at higher temperatures and lower GHSV. The results are discussed in relation to the reaction mechanism and zeolite structures. Significant deactivation was observed for higher 1,2-propanediol partial pressures, which was partially mitigated by the addition of steam.

1. Introduction

Biomass conversion to fuels and chemicals has been developing quickly [1–3]. The utilization of biomass improves security of energy supply and as a renewable resource it benefits the environment by lowering the overall CO_2 emissions. Nowadays glycerol is produced on significant scale as a by-product of biodiesel manufacture and as such it is a promising alternative feedstock for the manufacture of valuable bulk chemicals from a bio-derived source [3]. Many processes for glycerol utilisation have been investigated in the last few years [3–6]. Derived chemicals include: glycerol carbonate, telomers, selective oxidation products, branched alkyl ethers, propanediols, epoxides, hydrocarbons and syngas, which can be converted to bulk chemicals and fuels. Glycerol hydrogenolysis to produce 1,2-propanediol has been widely studied [7–14]. Cu based catalysts are reported to show very high selectivity to 1,2-propanediol [11–14] and both gas phase and liquid phase processes for glycerol hydrogenolysis have been claimed [15]. These processes have the potential to provide a renewable and economic source of 1,2-propanediol.

Propionaldehyde is an important chemical intermediate used extensively in the manufacture of rubbers, plastics, paints, and pesticides. Currently, propionaldehyde is produced by petroleum-derived processes such as ethylene hydroformylation, propylene oxide isomerisation, and acrolein hydrogenation or as a by-product of acetone [16–19]. The ready availability of a process to produce 1,2-propanediol from glycerol, provides the opportunity for a two-step process to propionaldehyde from glycerol.

1,2-Propanediol dehydration readily occurs over electrophilic, nucleophilic and lanthanide oxide catalysts [20–31]. This reaction has been studied in the gas phase and in sub-, or supercritical water. Different products are obtained over the various catalysts according to the corresponding reaction mechanisms. Electrophilic catalysts are active in 1,2 elimination and favour propionaldehyde and acetone. Examples are catalysts such as heteropoly acids, Nafion-H, and NaHX. Mori et al. reported 100% conversion and 93 mol% selectivity to propionaldehyde for 1,2-propanediol dehydration over silica supported silicotungstic acid [24]. Nucleophilic catalysts can dehydrate 1,2-propanediol to propene oxide by attack on the primary hydroxyl proton. For example, 70% selectivity to propene oxide was reported over alkali metal loaded silica. In sub- and supercritical water, 80 mol% propionaldehyde yield was reported for 1,2-propanediol dehydration at 360 °C and 34 MPa with the addition of $ZnSO_4$. Zeolite catalysts as solid acid catalysts have been widely studied for the dehydration of alcohols especially methanol and ethanol [32–35]. More recently, we have shown that zeolites are effective catalysts for dehydration of n-butanol [36], and in particular that the product distribution can be controlled by the shape selectivity arising from the unidirectional channel structure of ZSM-23 and Theta-1 (ZSM-22). In the context of glycerol conversion, zeolites have been used for dehydration to acrolein [37], and it has been reported recently that Theta-1 is also a highly selective catalyst for this reaction [38]. However, zeolite catalysts have not been studied previously for the dehydration of 1,2 propanediol to propionaldehyde although it is to be expected that they would prove to be efficient catalysts for this reaction.

---

* Corresponding author. Tel.: +44 0 20 7594 5579; fax: +44 0 20 7594 5637.
E-mail address: d.chadwick@imperial.ac.uk (D. Chadwick).

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.04.028

The present paper reports a study of the catalytic dehydration of 1,2-propanediol over a range of zeolite catalysts with different pore structures and acidities. Medium pore zeolites with unidirectional channels (ferrierite, Theta-1, ZSM-23) are compared with ZSM-5, which has 10-ring two-dimensional intersecting channels, and Y-zeolite, mordenite, and silica–alumina. All the zeolite catalysts are shown to be highly active for 1,2-propanediol dehydration. However, only the medium pore zeolites with unidirectional channels, namely Theta-1 and ZSM-23, are found to be highly selective for propionaldehyde.

2. Experimental

2.1. Catalysts

The H-form or NH_4 form of ferrierite ($SiO_2/Al_2O_3 = 20$ and 55), ZSM-5 ($SiO_2/Al_2O_3 = 50$ and 280), Y ($SiO_2/Al_2O_3 = 60$) and Mordenite ($SiO_2/Al_2O_3 = 20$) were purchased from Zeolyst. ZSM-23 ($SiO_2/Al_2O_3 = 68$) and Theta-1 ($SiO_2/Al_2O_3 = 63$) were synthesized according published literature [39,40]. The as-synthesised samples were calcined at 550 °C using a very slow temperature ramp rate, exchanged with ammonium nitrate solution three times, and calcined again at 550 °C to convert to the H-form. XRD was used to confirm the zeolite structures. These zeolite samples contained no binder and were granulated for the catalytic testing reported below. XRF was used to confirm the SiO_2/Al_2O_3 ratios. Silica–alumina and mordenite ($SiO_2/Al_2O_3 = 3.3$) were commercial catalysts containing binder.

The SiO_2/Al_2O_3 ratio of each of the zeolites was confirmed directly on the powder using a Bruker S4 explorer X-ray Fluorescence spectrometer. Surface areas and pore volumes were measured on a Micromeritics TriStar instrument using BET method. The pore volumes were calculated according to the procedure of Remy and Poncelet utilising the Dubinin and Radushkevich equation [41].

Ammonia temperature program desorption (TPD-NH_3) was carried out using a mass spectrometer detector. The desorbing ammonia was identified by $m/z = 16$. 0.1 g catalyst granules were loaded in a stainless steel reactor and pre-treated at 660 °C in 40 ml/min He for 30 min. The temperature was decreased to 110 °C, and ammonia was adsorbed to saturation over the catalyst. Ammonia was desorbed from 110 to 660 °C at 10 °C/min in 40 ml/min He.

2.2. Catalyst activities

The catalysts were evaluated in a fixed-bed continuous flow microreactor system operating at ambient pressure. The zeolite powders were pressed (without addition of binder or lubricant) and sieved to form granules between 0.50 and 0.85 mm. A certain amount of the catalyst granules (0.05 g or 0.5 g) were diluted with inert silicon carbide granules of approximately the same size to make up a volume of 7.0 ml. The diluted catalyst was loaded into a tubular reactor (11 mm internal diameter), sandwiched between beds of inert granules. SiC was used as diluent because of its inertness and heat transfer properties, and the particle size, dilution ratio and pre/post packing were used to maintain plug flow and isothermality. The reaction was carried out between 200 and 400 °C. The reactant was fed into the catalyst bed via an evaporator at 160 °C, through which the gas diluent (argon) was passed. In some cases, a flow of steam was added to the inlet gas to the reactor. GHSV was defined with respect to the total gas volumetric flow and the undiluted catalyst volume. The WHSV of 1,2-propanediol, where given, was defined as mass flow of 1,2-propanediol/weight of undiluted catalyst. After passing through the catalyst, the product was collected in a condenser kept at 0 °C and the gas effluent was analysed by GC/FID using a Plot Al_2O_3 capillary column. The liquid product was collected and analysed by GC/FID using a HP-FFAP capillary column. A blank reaction at 300 °C with only SiC diluent found a conversion of less than 1%. Carbon balances were ±5%.

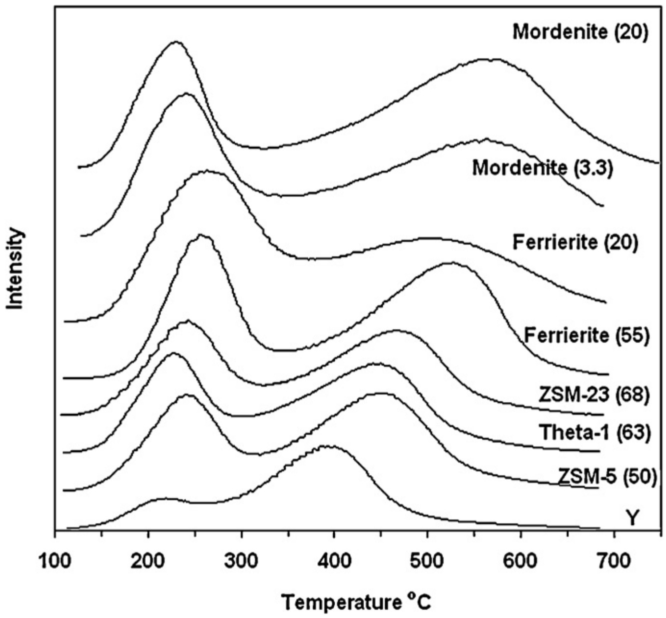


Fig. 1. Ammonia temperature programmed desorption (TPD NH_3) from the acid form of the zeolites.

3. Results and discussion

The catalysts and their properties are listed in Table 1. In general, the zeolites used had SiO_2/Al_2O_3 ratios in the range of 50–68. Samples outside this range were included for the purposes of comparison. The mordenite and amorphous silica–alumina (ASA) compositions were as supplied commercially. The zeolites used were in the form of granulated powder and contained no binder, except for the mordenite (3.3) and the ASA which were commercial samples and contained a binder. The surface areas of the zeolites reported in Table 1 are consistent with literature values and the supplier data sheets. The micropore volumes are consistent with the structure of the zeolites and their framework densities [42–44].

The acid site densities were calculated from the SiO_2/Al_2O_3 ratios and are given in Table 1. The strength of the acid sites was determined by TPD-NH_3. Profiles of the H-forms of the zeolites are shown in Fig. 1. All the zeolites exhibited two peaks, one at low temperature (LT) and the other at high temperature (HT). The HT was due to ammonia adsorbed on the Bronsted acid sites on the surface of the frameworks. The LT corresponded to ammonia hydrogen bonded to those adsorbed and contained within the micropores of the channels [45]. The temperatures corresponding to the HT peaks were characteristic of the strength of the acid site. As seen, the strength of the acid sites from TPD-NH_3 had the following trend: Mordenite $\gg$ Ferrierite > ZSM-23 $\geq$ ZSM-5 $\approx$ Theta-1 > Y.

The zeolite composition and structural properties along with the reaction conditions strongly influenced the observed selectivities and thus the yield of propionaldehyde, which dominated at temperatures of 300 °C and higher. 1,2-Diols are known to undergo the pinacol rearrangement to give the corresponding aldehyde [30]. A mechanism for 1,2-propanediol dehydration over acidic catalysts via E1 elimination is presented in Scheme 1. Protonation of either of the hydroxyl groups and rearrangement can produce three reactive carbenium intermediates (I, II, and III, Scheme 1), which yield ace-