



Zeolite H-USY for the production of lactic acid and methyl lactate from C₃-sugars

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ABSTRACT

Lactic acid is an interesting platform chemical with many promising applications. This includes the use as a building block for the production of biodegradable plastics and environmentally friendly solvents. A study of the liquid-phase conversion of the triose-sugars, glyceraldehyde and dihydroxyacetone directly to methyl lactate and lactic acid catalyzed by inexpensive commercially available zeolites is presented. One particular zeolite, H-USY (Si/Al = 6) is shown to be quite active with near quantitative yields for this isomerization. Deactivation of the H-USY-zeolite was studied by correlating the catalytic activity to data obtained by TPO, XRD, N₂-sorption, and NH₃-TPD on fresh and used catalysts. Coking and irreversible framework damage occurs when lactic acid is produced under aqueous conditions. In methanol, methyl lactate is produced and catalyst deactivation is suppressed. Additionally, reaction rates for the formation of methyl lactate in methanol are almost an order of magnitude higher as compared to the rate of lactic acid formation in water.

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1. Introduction

Lactic acid is currently emerging as a building block in a new generation of materials such as biodegradable plastics and solvents [1–3]. These new materials can be produced from biomass-derived precursors and have the potential to replace existing petroleum-based materials by displaying comparable and even superior properties [4]. Lactic acid also has the potential to become a central chemical feedstock for the chemical industry in the production of acrylic acid, propylene glycol, and different useful condensation products [5–8].

However despite its high potential, the major obstacle in a wider implementation of lactic acid-based materials and a lactic acid platform in the chemical industry is the high cost associated with the expensive and cumbersome manufacturing route of lactic acid. The large-scale production of lactic acid relies on the batch-wise fermentation of aqueous glucose under anaerobic conditions [9,10]. The fermentation reaction typically takes 2–4 days and requires calcium hydroxide to be added continuously to maintain a neutral pH-level in order for the bacteria to function optimally, thereby resulting in the formation of calcium lactate. Crystalliza-

tion of calcium lactate, followed by acidification with sulfuric acid releases the crude lactic acid and gypsum. Typically, one ton of gypsum is formed for every ton of lactic acid produced [1]. Further purification of lactic acid is done by esterification to methyl lactate followed by distillation and hydrolysis to release pure lactic acid.

Lactic acid is an isomer of the triose sugars dihydroxyacetone (DHA) and glyceraldehyde (GLA). The relative stability of the three isomers are in the order of lactic acid ≫ DHA > GLA. The triose sugars can be formed by aerobic oxidation of glycerol using both homogeneous and heterogeneous catalysts [11–14] or by fermentation of glycerol using the *Gluconobactor suboxydans* strain [15–18].

Homogeneous catalysts such as sulfuric acid and sodium hydroxide are known to catalyze the isomerization of DHA and GLA in very hot water (250–300 °C) to give low yields of lactic acid [19,20]. A more effective isomerization catalyst is zinc sulfate, which is reported to give a 75–86% yield of lactic acid in 300 °C hot water [21]. However, the use of a homogeneous isomerization catalyst is problematic from an environmental point of view and the purification of lactic acid can be problematic. Furthermore, the use of very hot water as the reaction media requires expensive pressure resistant equipment which will make a large-scale process unattractive. Homogeneous metal chlorides are active in this isomerization–esterification reaction. In particular, tin

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chloride has been found to be able to form methyl lactate in a high 89% yield [22]. However, a high catalytic amount (10 mol%) of tin chloride is used in this case.

Currently, very limited work has been done using acidic zeolites for the conversion of biomass to value added chemicals. Acidic zeolites have been demonstrated to catalyze the conversion of DHA in ethanol to form ethyl lactate, although in a moderate 65% yield [23]. Very recently Lewis acidic beta zeolites were shown to be highly active in the isomerization reaction of DHA and GLA with excellent selectivity toward methyl lactate/lactic acid [24]. These hydrophobic zeolites were made by incorporating Ti, Zr, and Sn into the framework. In particular the Sn-Beta zeolite appears to be an exceptionally promising catalyst in the DHA/GLA conversion. However, application may be limited due to long synthesis time and to the use of tin. Thus an investigation using commercially available solid acids, mainly zeolites containing only silicon and aluminum and sulfated zirconia was undertaken in batch reactors. The most promising of these catalysts, the proton form of an ultra stable Y-zeolite with a Si/Al = 6 (H-USY-6) showed very good activity with near quantitative yields at appropriate conditions. This zeolite was tested under continuous flow within a plug flow reactor to determine the kinetics of the isomerization network and to study the deactivation of the system. A discussion of the catalytic behavior is coupled to the results from XRD, NH₃-TPD, N₂-sorption, FT-IR, and TPO of the fresh and spent zeolite.

2. Experimental

2.1. Chemicals

Dihydroxyacetone (97%), pyruvic aldehyde dimethyl acetal (PADA) (97%), glyceraldehyde (95%), anhydrous pyridine (99.8%), and methanol (99.9%) were purchased from Sigma-Aldrich. Methyl lactate (97%) was obtained from Fluka. Pyruvic aldehyde (PA) was obtained from SAFC Supply as a 40 wt.% aqueous solution while lactic acid was obtained from Fluka and Riedel-de Haën. All the commercially available zeolites used throughout this study were kindly provided by Zeolyst International. The zeolites are pure and do not contain any binder material. Some of the zeolites were received in the NH₄-form. In these cases the zeolites were calcined at 550 °C in air for 6 h prior to use in order to produce the acidic form.

2.2. Catalytic tests

Batch experiments were performed in an Ace pressure tube with magnetic stirring. In these runs, 80 mg of catalyst, 1.25 mmol of substrate (calculated as monomer), and 4 g of water or methanol were added and mixed in the pressure tube using magnetic stirrer ring. The ace pressure tube was then dipped into an oil bath having a temperature of 140 °C for experiments with water and 120 °C for experiments with methanol. The internal temperature during reaction as recorded with an internal thermocouple was 125 °C and 115 °C, respectively.

In the flow reactor set-up, the feed was introduced into the system by either a Waters 501 HPLC pump, or by a Knauer K-120 HPLC pump. The catalyst was held in place in a stainless steel reactor tube by quartz wool on both sides of the catalyst. The reactor tube was heated by a Carbolite oven while a type E thermocouple attached to the external surface of the reactor tube was used to monitor the reactor temperature. The effluent was collected in a stainless steel collector tube. The system was pressurized to 20 bar of pressure with Argon before each run. Feeds were created by placing a measured amount of substrate in a volumetric flask and filling to the set volume. For concentrated solutions, the mix-

tures were heated to 69 °C under stirring for 1–2 h to help dissolve the substrate.

Effluent concentrations for batch and flow experiments were characterized by an Agilent 1200 Series HPLC with an R.I. detector and a Biorad Aminex HPX-87H column and an Agilent 6890N GC with an HP-5column and an FID detector. Species were quantified with standards and confirmed with GC-MS, Agilent 6850 GC system coupled with Agilent 5975 C MSD.

2.3. Zeolite characterization

The degree of carbon deposition on used catalysts was determined using temperature-programed oxidation (TPO). Prior to analysis the used zeolites were dried at 110 °C. The TPO was carried out by heating a premeasured amount of used catalyst to 650 °C at 3.5 °C min⁻¹ in a gas flow of 20 mL min⁻¹ consisting of 5% oxygen in helium. The release of CO and CO₂ was quantified using a BINOS detector. The TPO data are shown in Table 4 as the weight percent of carbon present on the coked catalyst.

NH₃-TPD, N₂-sorption, and XRD were performed on calcined catalyst samples. The procedures used were either as described for the TPO or calcination at 550 °C for 4 h in static air, heated at a ramp of ~2 °C/min. Nitrogen physisorption was measured on a Micromeritics ASAP 2020 after the samples had been degassed in vacuum at 300 °C for 2 h.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS powder diffractometer. The XRD data are shown in Table 4 as a relative crystallinity, calculated by integrating the peak area of eight characteristic reflections and comparing to the un-used zeolite. The reflections used along with the respective 2θ values given in parenthesis were 331 (15.97), 511 (19.01), 440 (20.71), 533 (24.06), 642 (27.52), 822 (31.29), 555 (31.95), and 664 (34.69) [25].

NH₃-TPD measurements were performed on a Micromeritics Autochem II equipped with a TCD detector. Dry weights of the samples were found after evacuation at 300 °C for 1 h. After saturation with ammonia, the weakly bound ammonia was desorbed prior to measurement at 150 °C for 1 h in a He flow of 25 mL min⁻¹. The desorption curve was then attained at a heating ramp of 15 °C per minute to 550 °C at a He flow rate of 25 mL min⁻¹.

FT-IR operated in transmission mode was used to analyze the zeolites on a BioRad FTS 80 spectrometer equipped with a MCT detector. Self-supporting wafers of the zeolites were pressed and were prior to analysis dehydrated under evacuation at 400 °C for 4 h. The absorbance spectra were obtained after the samples were allowed to cool to RT. Pyridine adsorption was done by saturating the zeolite at RT and subsequently heating the sample to 200 °C for 30 min under evacuation. The sample was once again allowed to cool to RT before the spectrum was recorded.

3. Results and discussion

3.1. Reaction pathway

We have investigated the isomerization of the two three-carbon sugars dihydroxyacetone (DHA) and glyceraldehyde (GLA) into methyl lactate and lactic acid over an acidic zeolite catalyst. When the solvent used is methanol, the resulting product becomes methyl lactate and if water is used, lactic acid is formed. Scheme 1 gives the proposed reaction path of the isomerization reaction in either alcohol or water [22–24]. Pyruvaldehyde (PA) is believed to be an initial product formed by the dehydration of DHA/GLA. After addition of water/methanol the resulting hydrate/hemiacetal can isomerize into lactic acid/methyl lactate (path A). The reaction

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