



Mechanistic study of the catalytic conversion of 2,3-butanediol to butenes

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ABSTRACT

The reaction kinetics of 2,3-butanediol (2,3-BDO) and other key intermediates, including methyl ethyl ketone (MEK), 2-methylpropanal, acetoin, 2-butanol and 2-methyl-1-propanol, were investigated over acidic zeolites (ZSM-5, and Y-type zeolite), Cu/ZSM-5, Cu/Y and Cu/SiO₂ to elucidate the roles of acid and metal sites in the process of hydrodeoxygenation of 2,3-BDO to butene. Hydrogenation and dehydrogenation reactions occur on Cu sites, while dehydration reactions take place on acid sites. At low space time, 2,3-BDO can readily be converted to acetoin by dehydrogenation over supported Cu catalysts, however, with increasing space time, the formed acetoin is hydrogenated back to 2,3-BDO. DFT (density functional theory) calculations suggest that the cage structure of Y zeolite allows the formation of larger Cu clusters, potentially blocking acid sites and preventing access of C₄ alcohols (2-butanol, 2-methyl-1-propanol) to the acid sites for dehydration. This effect results in lower selectivity to butenes over Cu/Y than on Cu/ZSM-5.

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1. Introduction

Recently 2,3-butanediol (2,3-BDO) has attracted substantial interest as a potential renewable feedstock for the production of fuels and chemicals. Zhang et al. [1] investigated the dehydration of 2,3-BDO over zeolite HZSM-5 and HZSM-5 modified with boric acid, and they reported that high Si/Al ratio was beneficial to low-temperature activation of 2,3-BDO and the methyl migration to 2-methylpropanal, and the addition of boric acid enhanced the catalytic stability. Duan et al. [2] investigated the dehydration of 2,3-BDO over monoclinic ZrO₂ and the result showed that 3-buten-2-ol was produced with a maximum selectivity of 59.0% along with major byproducts such as methyl ethyl ketone (MEK) and 3-hydroxy-2-butanone (acetoin). Duan and coworkers [3] also investigated dehydration of 2,3-BDO to 1,3-butadiene over Sc₂O₃ and the maximum butadiene selectivity they obtained was 94% with 100% 2,3-BDO conversion on a two-bed catalyst system (Sc₂O₃ + Al₂O₃) [3]. More recently, Liu et al. [4] used γ -alumina to catalyze the direct production of 1,3-butadiene from 2,3-BDO and they suggested that under the optimized kinetic reaction conditions (trace amount of γ -alumina, high flow rate), the production of MEK and 2-methylpropanal was significantly reduced, while the

selectivity of 1,3-butadiene could be obtained up to 80%. Harvey et al. [5] developed a pathway to selectively convert 2,3-BDO by acid catalyst Amberlyst-15 to a complex mixture of 2-ethyl-2,4,5-trimethyl-1,3-dioxolanes and 4,5-dimethyl-2-isopropyl dioxolanes, which can be used as a gasoline-range fuel and diesel oxygenate due to an anti-knock index of 90.5, high combustion value, low solubility in water and full miscibility with both gasoline and diesel fuel. Our previous work has shown that bifunctional catalyst Cu/ZSM-5 can convert 2,3-BDO to butenes with high selectivity (~70%) in the presence of H₂ at 250 °C, and the optimal performance is the result of a balance between copper and acid catalytic functions [6].

The functionalized nature of 2,3-BDO means that a variety of reactions can occur, especially when multiple catalyst functionalities are present. For example, our recent work to produce butenes from 2,3-BDO in the presence of hydrogen over an acid-metal bifunctional catalyst involved complex chemistry where 2,3-BDO could be dehydrogenated to acetoin and butanedione, dehydrated to MEK and 2-methylpropanal which could in turn be hydrogenated to butanol which can then be dehydrated to butenes [6]. Even further reactions are possible from the butenes [7]. This complicated reaction scheme suggests a need for a systematic measurement of reaction kinetics for 2,3-BDO and its products over catalysts of interest. Such work could impact not only our approach

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of producing butenes from 2,3-BDO, but also other research to produce butadiene and MEK.

This research studies the reaction kinetics of 2,3-BDO and other key intermediates in 2,3-BDO chemistry (including MEK, 2-methylpropanal, acetoin, 2-butanol, and 2-methyl-1-propanol) over acidic zeolites (ZSM-5 and Y-type), supported copper zeolites, and copper supported on silica. Through these experiments, the roles of acid and metal sites can be elucidated and possible reaction pathways to specific products can be proposed.

2. Experimental

2.1. Materials

Commercial zeolites NH₄⁺-ZSM-5 (CBV 2314, SiO₂/Al₂O₃ = 23; CBV 5524G, SiO₂/Al₂O₃ = 50; CBV 28014, SiO₂/Al₂O₃ = 280, Zeolyst International), H-ZSM-5 (Zeocat PZ-2/500H, SiO₂/Al₂O₃ = 500, Zeochem), H-ZSM-5 (HSZ-890HOA, SiO₂/Al₂O₃ = 1500, Tosoh Corporation), HY (CBV 400, SiO₂/Al₂O₃ = 5.1; CBV 760, SiO₂/Al₂O₃ = 60, Zeolyst International), HY (HSZ-390HUA, SiO₂/Al₂O₃ = 500, Tosoh Corporation) and commercial fumed SiO₂ (Cab-O-Sil EH-5, Cabot Corporation) were employed as supports or catalysts. ZSM-5 and HY are referred to as ZSM-5(n) and HY(n), respectively, where n stands for the SiO₂/Al₂O₃ ratio. Cu(NO₃)₂·3H₂O (99%, Fisher Scientific) was used as metal precursor. 2,3-BDO (>97%, TCI America), acetoin (96%, Fisher Scientific), methyl ethyl ketone (>99%, Fisher Scientific), 2-methylpropanal (>99%, Fisher Scientific), 2-butanol (99.5%, Sigma-Aldrich) and 2-methyl-1-propanol (99.5%, Sigma-Aldrich) were used as reactants to investigate the reaction rate of each reaction. As acetoin exists as a solid dimer (2,3,5,6-tetramethyl-1,4-dioxane-2,5-diol) at room temperature, acetoin was used in the reaction as an aqueous solution with concentration of 85 wt% in order to avoid clogging the pump. Quartz sand (40–60 mesh, X-fine, Quartz Plus, Inc.) was used as an inert to dilute the catalysts.

2.2. Catalyst preparation

Preparation of catalysts has been described in the previous report [6]. To make ~20 wt% of CuO loading catalysts, typically, 36.24 g of Cu(NO₃)₂·3H₂O was dissolved in 100 mL of deionized water at room temperature, followed by adding ammonia hydroxide (28–30 wt%, Fisher Scientific) until the pH reached 9.1 to form a dark blue cupric ammine complex [Cu(NH₃)₄(H₂O)₂]²⁺, and then water was added to make 250 mL of a copper-ammonia complex solution. 20 g of ZSM-5 zeolite (or SiO₂) was added to the solution and then the container was capped to avoid the evaporation of ammonia and stirred for 4 h at room temperature. After that, the container was transferred to an oil bath and heated to 60 °C for 2 h. For Cu/Y zeolites, 20 g of Y zeolite was added to the complex solution and stirred for 6 h at room temperature without heating to 60 °C to avoid the collapse of structure. Then the solid was recovered by filtration, washed, dried at 110 °C, and calcined in air at 550 °C for 4 h. Finally, the calcined catalyst was pelletized, crushed and sieved to obtain a particle size distribution in the range 40–60 mesh. The content of CuO was determined (shown in Table 2) by the inductively coupled plasma (ICP) method. The copper catalysts were named as Cu/ZSM-5(n), Cu/Y(n) and Cu/SiO₂, where n is the SiO₂/Al₂O₃ ratio.

2.3. Catalyst characterization

BET surface area and porosity of catalysts were determined from Brunauer–Emmett–Teller (BET) gas (N₂) adsorption method

measured on Quantachrome Autosorb-1 instrument at –196 °C and analyzed with Autosorb-1 software. Before measurement, the samples were evacuated at 350 °C for 4 h. The acid properties of samples were investigated by temperature programmed desorption of ammonia (NH₃-TPD) in an Altamira AMI-200 system equipped with a thermal conductivity detector. Powder X-ray diffraction (XRD) patterns of the samples were recorded using Rigaku Miniflex II desktop X-ray diffractometer. Scans of two theta angles were from 5° to 90° for all catalysts with a step size of 0.02° and scan speed of 0.75°/min. The reducibility of the calcined catalysts was determined by temperature programmed reduction (H₂-TPR), which was carried out on the same system as NH₃-TPD. Copper surface area and dispersion were determined by the dissociative N₂O adsorption method at 90 °C [8,9] using the same system as H₂-TPR and NH₃-TPD. The detailed procedures of all characterization are described in previous report [6].

2.4. Catalytic reaction

The catalytic reactions were performed in a conventional continuous flow fixed-bed reactor made of stainless steel (id = 8 mm) under atmospheric pressure [6]. Prior to reaction, the catalyst sample was reduced in the reactor in the H₂/N₂ flow (flow rate of H₂/N₂ = 1/5) at 300 °C for 2 h. The H₂ flow of 24 cm³ min^{–1} (standard ambient temperature and pressure, SATP) and the N₂ flow of 120 cm³ min^{–1} (SATP) were controlled with mass-flow controllers (Brooks). Different chemicals, such as 2,3-BDO, acetoin, MEK, 2-methylpropanal, 2-butanol and 2-methyl-1-propanol, were employed as reactants to investigate the reaction rate of each reaction over various catalysts (or supports). Typically, the reactant was fed via a micropump (Eldex 15MP) at 3 mL h^{–1} together with a H₂ flow of 67.2 cm³ min^{–1} (SATP) and N₂ flow of 15.4 cm³ min^{–1} (SATP). The reaction temperature was set at 250 °C according to the previous report [6]. For the kinetic study, the catalyst was diluted with inert quartz sand to a total weight of 1 g to adjust the conversion to a comparable level (30–80%). Product compositions were analyzed by an on-line gas chromatograph (SRI 8610C) equipped with an MXT-1 column (nonpolar phase, 60 m, ID 0.25 mm, film thickness 0.25 μm), TCD and FID detectors for the analysis of hydrocarbons and oxygenated chemicals, and quantified by injecting calibration standards to the GC system. As reported in the previous paper [6], the MXT-1 column is not capable of separating 1-butene and isobutene. For this reason, we only report the summation of butenes (1-butene, trans-2-butene, cis-2-butene and isobutene) here. The previous paper should be consulted for information on the typical distribution of the four isomers. The temperature of the tubing from the bottom of the reactor to the inlet of GC was maintained at 230 °C to avoid the condensation of liquid products. For the detailed procedure, see the previous report [6]. To confirm the identification of products, GC–MS analyses were also carried out by using an Agilent 7890A GC system equipped with an Agilent 5975C MS detector and HP-1 capillary column. The carbon selectivity [10,11] and conversion were calculated according to Eqs. (1) and (2).

$$\text{Carbon selectivity} = \frac{\text{Moles of carbon in specific product}}{\text{Total carbon atoms in identified products}} \times 100\% \quad (1)$$

$$\text{Conversion} = \frac{(\text{moles of reactant})_{\text{in}} - (\text{moles of reactant})_{\text{out}}}{(\text{moles of reactant})_{\text{in}}} \times 100\% \quad (2)$$

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