



## Mixed alcohol dehydration over Brønsted and Lewis acidic catalysts

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### ABSTRACT

Mixed alcohols are attractive oxygenated products of biomass-derived syngas because they may be catalytically converted to a range of hydrocarbon products, including liquid hydrocarbon fuels. Catalytic dehydration to form olefins is a potential first step in the conversion of C<sub>2</sub>–C<sub>4</sub> alcohols into longer-chain hydrocarbons. We describe here the physical and chemical characterization along with catalytic activity and selectivity of 4 Brønsted and Lewis acidic catalysts for the dehydration of two mixed alcohol feed streams that are representative of products from syngas conversion over K-CoMoS type catalysts (i.e., ethanol, 1-propanol, 1-butanol and 2-methyl-1-propanol). Specifically, a Lewis acidic Zr-incorporated mesoporous silicate (Zr-KIT-6), a commercial Al-containing mesoporous silicate (Al-MCM-41), a commercial microporous aluminosilicate (HZSM-5), and a commercial microporous silicoaluminophosphate (SAPO-34) were tested for mixed alcohol dehydration at 250, 300 and 350 °C. The zeolite materials exhibited high activity (>98% ethanol conversion) at all temperatures while the mesoporous materials only displayed significant activity (>10% ethanol conversion) at or above 300 °C. The turnover frequencies for ethanol dehydration at 300 °C decreased in the following order: HZSM-5 > SAPO-34 > Al-MCM-41 > Zr-KIT-6, suggesting that Brønsted acidic sites are more active than Lewis acidic sites for alcohol dehydration. At 300 °C, SAPO-34 produced the highest yield of olefin products from both a water-free ethanol rich feed stream and a C<sub>3+</sub>-alcohol rich feed stream containing water. Post-reaction characterization indicated changes in the Brønsted-to-Lewis acidic site ratios for Zr-KIT-6, Al-MCM-41 and HZSM-5. Ammonia temperature programmed desorption indicated that the acid sites of post-reaction samples could be regenerated following treatment in air. The post-reaction SAPO-34 catalyst contained more aromatic, methylated aromatic and polyaromatic compounds than its zeolite counterpart HZSM-5, while no aromatic compounds were observed on post-reaction Al-MCM-41 or Zr-KIT-6 catalysts. Olefin yield at 300 °C over SAPO-34 (>95%) was comparable to published values for the methanol-to-olefins process, indicating the potential industrial application of mixed alcohol dehydration. Furthermore, the olefin product distribution over SAPO-34 was tunable by the composition of the alcohol feed mixture.

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### 1. Introduction

In recent years, significant effort has been placed on the cost competitive production of transportation fuels from non-food biomass [1–5]. The gasification of lignocellulosic biomass to produce syngas followed by additional chemical transformations is one approach for producing hydrocarbons for chemical and fuel

use [6,7]. This process has also been referred to as indirect liquefaction [8]. A variety of products can be produced from syngas, including hydrogen, alkanes, methanol, and mixed alcohols [9]. The methanol-to-olefin (MTO) process is an industrial example of olefin production from syngas-derived methanol, but suffers from limitations in the ethylene to propylene product ratio [10]. The MTO process is typically operated between 450 and 525 °C and 34–345 kPa [11]. The ability to target precise ratios of a more diverse olefin product would be advantageous for the downstream production of hydrocarbons with a greater carbon number distribution via oligomerization.

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Previous research from the National Renewable Energy Laboratory has demonstrated the ability to convert biomass-derived syngas to a mixed alcohol product containing primarily ethanol, with lesser amounts of methanol, 1-propanol, isobutanol, 1-butanol, methyl formate, ethyl formate, ethyl acetate, acetaldehyde, and propionaldehyde [7]. Transforming a mixed alcohol product into liquid fuel-range hydrocarbons using a moderate-temperature, low-pressure process remains a challenge. Catalytic dehydration is a potential first step in the conversion of C<sub>2</sub>–C<sub>4</sub> alcohols into longer-chain hydrocarbons. Following dehydration, the resulting olefins can be oligomerized to produce naphtha and distillate fuels, providing an option for producing hydrocarbons from syngas.

SAPO-34 is the preferred catalyst for converting methanol to ethylene and propylene [10,12,13], and has demonstrated high activity for ethanol, 1-butanol and 2-butanol dehydration [14,15]. Other solid acid zeolite catalysts such as HZSM-5 have also been studied extensively for alcohol dehydration reactions [16–21]. In addition to zeolite materials, metal-containing mesoporous silica-based materials (e.g., Ni-MCM-41 and Zr-KIT-6) are capable of dehydrating a variety of alcohols to the corresponding olefin products [22–26]. The nature of the acid sites (type and strength) has also been shown to effect alcohol dehydration performance. Strong Brønsted acidic zeolites often suffer from poor selectivity to desired products [16,27,28] and are prone to coke deposition and short operable lifetimes [27,29,30]. There is evidence that materials with lower Brønsted to Lewis acid ratios exhibit higher selectivity and stability in alcohol dehydration reactions [23,31]. Despite the extensive analyses of alcohol dehydration to olefins, a performance comparison of zeolite and mesoporous silica catalysts for dehydration of mixed alcohols has not been reported.

Here we report a comparison of the performance of a Lewis acidic Zr-incorporated mesoporous silicate [Zr-KIT-6 (Si/Zr = 20)], a commercial Al-incorporated mesoporous silicate [Al-MCM-41 (Si/Al = 78)], and two commercial zeolites (HZSM-5 and SAPO-34) for dehydration of mixed alcohols. Two mixed alcohol feeds, representative of products of mixed alcohol synthesis from syngas over K-CoMoS type catalysts [7], were tested between 250 and 350 °C. The mixed alcohol feeds were composed of varying concentrations of ethanol, 1-propanol, 1-butanol, 2-methyl-1-propanol and water. Product selectivity and olefin yields achieved from mixed alcohol dehydration are compared to those from the MTO process. Catalyst samples were analyzed before and after reaction for evidence of coking, acid site modifications and crystalline structural changes. The results suggest that olefin yields comparable to the MTO process are achievable at lower temperature, and that the olefin composition is tunable by the alcohol feed composition.

## 2. Experimental section

### 2.1. Catalyst characterization

#### 2.1.1. BET surface area

Nitrogen physisorption data were collected at –196 °C using a Quantachrome Quadrasorb SI instrument. Samples were pre-treated under vacuum for 20 h at 200 °C. Surface areas were determined using the Brunauer–Emmett–Teller (BET) method, and pore volumes were determined from the adsorption isotherm data using the Barrett–Joyner–Halenda (BJH) method. For zeolite materials (SAPO-34 and HZSM-5), the  $P/P_0$  range of 0.01–0.08 was used to determine the BET surface area. For mesoporous silica-based materials (Al-MCM-41 and Zr-KIT-6), the  $P/P_0$  range of 0.05–0.30 was used to determine the BET surface area. Pore diameters for Zr-KIT-6 and Al-MCM-41 were determined from the adsorption isotherm using the BJH method, by taking the maximum point on

the plot of  $dV(\log d)$  versus pore diameter ( $d$ ). For zeolite materials, the micropore sizes are reported based on the crystalline parent structures of MFI (HZSM-5) and CHA (SAPO-34) zeolites according to the International Zeolite Association Database of Zeolite Structures [32].

#### 2.1.2. X-ray diffraction

Powder X-ray diffraction (PXRD) data were collected using a Rigaku Ultima IV diffractometer with a Cu K $\alpha$  source using a D/teX Ultra high-speed detector. Diffractograms were collected in the  $2\theta$  range of 5–80° at a scan rate of 5°/min. Samples were prepared by supporting the powdered catalyst onto a glass slide having a 0.5 mm recession and pressing with a glass slide to create a uniform  $z$ -height. Small Angle X-ray Scattering (SAXS) diffractograms were collected in the  $2\theta$  range of 0.5–4.0 degrees at a scan rate of 0.05°/min and a scan width of 0.005° using a scintillation counter. The diffractometer was operated at 40 kV and 44 mA for PXRD and SAXS measurements.

#### 2.1.3. Total acid site titration: NH<sub>3</sub>-TPD

The total number of acid sites was determined by NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD) using an Altamira Instruments AMI-390 system with gas flow rates of 25 mL/min. Catalyst samples (ca. 200 mg) were loaded into a quartz U-tube reactor and held as a fixed bed between plugs of quartz wool. All catalyst samples were first heated to 500 °C at 2 °C/min in 10% O<sub>2</sub>/Ar and held for 5 h. Following pretreatment, samples were cooled to 120 °C in flowing He and then saturated with flowing 10% NH<sub>3</sub>/He for 3 h. Excess and/or physisorbed NH<sub>3</sub> was removed by holding the samples at 120 °C in flowing He for 0.5 h. NH<sub>3</sub>-TPD was performed by heating the sample from 120 °C to 500 °C at 30 °C/min, and then holding at 500 °C for 0.5 h in flowing He. Desorbed NH<sub>3</sub> was measured with a thermal conductivity detector, and calibration was performed after each experiment by introducing 10 pulses of 10% NH<sub>3</sub>/He from a 5 mL sample loop into a stream of flowing He. The quantification of surface sites was done assuming adsorption stoichiometry of one NH<sub>3</sub> molecule per acid site [33,34].

#### 2.1.4. Brønsted and Lewis acid site titration: pyridine DRIFTS

The relative amounts of Lewis and Brønsted acidic sites were determined using pyridine adsorption diffuse-reflectance FT-IR spectroscopy (py-DRIFTS), which was recorded on a Thermo Nicolet iS50 FT-IR spectrometer operating at 4 cm<sup>–1</sup> resolution equipped with a Harrick praying mantis reaction chamber and Si windows. For analysis of fresh catalysts, samples were loaded into the chamber and pretreated in flowing air at 2 °C/min to 500 °C for zeolites and 10 °C/min to 500 °C for silica materials, and held at this temperature for 3 h. Post-reaction samples were pre-treated in flowing nitrogen at their reaction temperature (250, 300, or 350 °C), and held at this temperature for 0.5 h. After cooling to 150 °C, the sample was purged with nitrogen for 0.5 h, and pyridine vapor was introduced. After 3 min of pyridine exposure, the sample was heated to 300 °C at 10 °C/min and held for 0.5 h under flowing nitrogen to remove excess and/or physisorbed pyridine. The pressure throughout the pre-treatment, dosing, and desorption procedures was atmospheric. The absorption bands near 1445 cm<sup>–1</sup> (Lewis) and 1545 cm<sup>–1</sup> (Brønsted) and their relative absorption coefficients ( $\epsilon_B/\epsilon_L = 0.76$ ) were used to determine the relative Brønsted/Lewis acidic site ratios [35,36].

#### 2.1.5. Post-reaction organic species: solution <sup>1</sup>H NMR

The amount of soluble organic material remaining on the catalyst surface after reaction was determined using <sup>1</sup>H NMR spectroscopy. Solution-phase <sup>1</sup>H NMR spectra were recorded using a Varian Inova 400 MHz spectrometer. Spectra were collected for 16

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