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Aqueous-phase fructose dehydration using Brønsted acid zeolites: Catalytic activity of dissolved aluminosilicate species

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ABSTRACT

We show that in the aqueous-phase dehydration of fructose to 5-hydroxymethyl furfural (HMF) with zeolite catalysts, about 1–2 wt% of the zeolite dissolves, resulting in a solution of aluminosilicate species with Al 1.2–26.2 mg/L and Si up to 226 mg/L. The actual concentration of these species depends on the zeolite type used and on its Si/Al ratio. These species homogeneously catalyze side reactions of fructose and sequential reactions of HMF, but not glucose–fructose isomerization. This is in contrast to what has been observed using zeolites and several Al^{3+} salts. Fructose conversion to glucose, HMF, and levulinic acid was observed with several dissolved Al and Si salts (e.g., aluminum formate, $Al(HCO_2)_3$, aluminum lactate, $Al(C_3H_5O_3)_3$, and $AlCl_3$). Detailed characterization using NMR, FTIR, DLS and XRD suggests that the active species dissolved from the zeolites are probably oligomeric aluminosilicate fragments in which the Al—O—Si and Si—O—Si connectivity is similar to that of amorphous aluminosilicate solids that do not catalyze hexose isomerization reactions.

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1. Introduction

We recently reported [1] that catalytically active dissolved species are generated in the dehydration of aqueous fructose solutions using zeolites. In particular, species dissolved from the zeolite can increase fructose conversion and decrease selectivity to desired products, such as 5-hydroxymethyl furfural (HMF). Scheme 1 shows how these dissolved species fit into a generalized reaction network for fructose dehydration in the presence of zeolites. Briefly, fructose can react in the zeolite or in the aqueous phase to form HMF, but also undesirable polymeric side products known as humins. HMF can further react, either in the aqueous phase or on the catalyst sites, to produce similar side products, or on the catalyst sites to produce formic and levulinic acids through rehydration. These and other acidic products, as well as the aqueous solvent, induce a minor degree of zeolite dissolution, and the dissolved species can also catalyze side reactions.

The susceptibility of zeolites, and in general of aluminosilicate materials, to partial dissolution in carbohydrate dehydration reactions is especially important because they frequently serve as supports for other novel catalysts, including functionalized micro- and mesoporous materials [2–11]. Although the stability of the catalyst active sites is frequently explored, the underlying support

material (or oxide catalyst itself, in the case of zeolites) is often assumed to be stable [12,13]. Furthermore, catalyst dissolution could be a contributing factor to the inconsistent trends reported by different groups with respect to catalyst performance in aqueous sugar dehydration systems [14,15].

The stability of zeolites in aqueous acidic and basic solutions has been explored in several previous studies [16–30], but typically at extreme pH values with strong acids and bases, or for naturally occurring mineral forms with impurities and minor phases not found in commercial synthetic zeolites. Results of these studies typically showed that Al was removed preferentially at low pH, while Si was dissolved primarily at high pH. Earlier work on the stability of zeolites and related materials (Al_2O_3 and SiO_2) in pure water at high temperatures ($\geq 130\,^\circ$C) revealed that the relative roles of OH^--catalyzed Si dissolution and H^+-catalyzed Al dissolution depend on framework structure, SiO_2/Al_2O_3 ratio, and the presence of carbohydrates, which can form dissolution-inhibiting carbonaceous deposits on the oxide surface [31–34]. In carbohydrate dehydration using zeolite catalysts, moderately acidic pH values are encountered, and the primary acidity comes from carboxylic acids produced by carbohydrate fragmentation or furan hydration. Thus, we were motivated to adapt previous work on zeolite stability to carbohydrate dehydration conditions, especially regarding the catalytic activity of zeolite dissolution products.

We present here further characterization of the species dissolved from zeolite catalysts during fructose dehydration that we discovered in our previous work [1], investigate several classes

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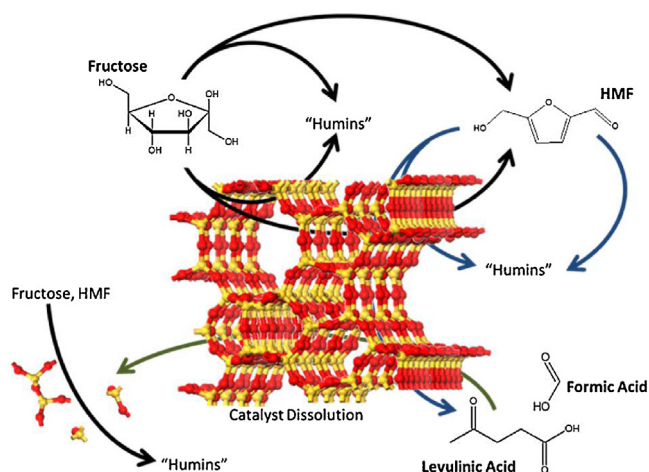
Scheme 1. Simplified reaction network for dehydration of fructose to HMF and rehydration of HMF to formic and levulinic acids in aqueous systems catalyzed by zeolites.

of potential candidate molecules, and propose a general structure for these species. In particular, we compare solutions containing species dissolved from zeolites of varying framework type and SiO_2/Al_2O_3 ratio via ICP-AES, NMR, and product selectivity in fructose dehydration using these solutions as solvents. We also use FTIR and XRD to characterize solids recovered from these solutions and potential candidate molecules.

2. Materials and methods

2.1. Materials and catalyst preparation

Fructose (BioXtra, ≥99%), glucose (BioUltra, ≥99.5%), HMF (≥99%), formic acid (Fluka, 98%), levulinic acid (98%), furfural (98%), hydrochloric acid (1.0 M), and tetraethyl orthosilicate (98%) were purchased from Sigma–Aldrich. All zeolites (BEA-18, BEA-38, BEA-360, MOR-20, and FAU-Y-30, where the number indicates the SiO_2/Al_2O_3 ratio) were purchased from Zeolyst in the ammonium form, except for the BEA-360, which was purchased in the protonated form.

To generate the acidic form of the zeolite, ammonium-form zeolites were calcined in ambient air with the following temperature program: ramp temperature at 2 °C/min to 90 °C, hold for 1 h, ramp at 2 °C/min to 450 °C, hold for 8 h, cool to room temperature. The BEA-360 was also calcined by the same procedure prior to use. We denote the resulting acidic forms by adding H-, e.g., H-BEA-18.

2.2. Reaction procedure

The fructose dehydration reaction procedure was previously described in detail [1]. Briefly, reactors consisted of 5 mL glass vials fitted with a triangular magnetic stir vane. Fructose dehydration experiments were performed at 130 °C, using aqueous solutions of

10 wt% fructose. Zeolite was added to give fructose-to-zeolite mass ratios F/Z = 3 or, equivalently, water-to-zeolite mass ratio W/Z = 27. Vials were quenched in water, cleaned of oil residue on their external surface and weighed to 0.1 mg precision to ensure their mass had not decreased during the reaction. A final pH measurement was taken and the reaction liquid was filtered through a 0.20 μm nylon syringe filter. Filtered solids were rinsed and dried by vacuum through Whatman No. 1 filter paper.

The solvents for these reactions were either water (atmosphere-equilibrated at pH = 5.6) or a zeolite filtrate (ZF) solution, which was generated by suspending zeolite in water (atmosphere-equilibrated, pH ∼ 5.6, or pH = 3, adjusted using formic acid or HCl) at W/Z = 27, heating to 85 °C for 5 h, and filtering through a 0.2 μm filter to separate the zeolite. Fructose was added to the filtrate to produce a 10 wt% solution, and the homogeneous dehydration reaction was performed as above. This experiment is labeled as "ZF" and represented graphically in Scheme 2. To generate zeolite filtrate (ZF), a 125 mL stainless steel Parr reactor was used to facilitate catalyst recovery. To test the generality of this methodology, the same procedure was repeated with several zeolites of different Si/Al ratio and framework structure. Because the initial pH of the zeolite filtrate solution was lower than the original homogeneous experiment, 10 wt% fructose was also dehydrated in water with formic acid and HCl at initial pH = 3 for comparison. All experiments are summarized in Table 1.

Conversion, selectivity, and yield were calculated respectively as

$$X_{Fru} = \frac{[Fru]_0 - [Fru]_t}{[Fru]_0} \times 100\%$$

$$S_i = \frac{[i]_t n_{c_i}}{([Fru]_0 - [Fru]_t) n_{C_{fru}}} \times 100\%$$

$$Y_i = \frac{[i]_t}{[Fru]_0} \times 100\%$$

Here i denotes a species other than fructose, n_{c_i} is the number of carbon atoms in species i, Fru denotes fructose, subscript t denotes reaction time, subscript 0 denotes initial time (i.e., $t = 0$), and terms in brackets are concentrations in mol/L.

2.3. Analytical methods

Reaction liquids were analyzed on a Waters 2695 HPLC system with 2414 Refractive Index and 2998 Photodiode Array (UV) Detectors. Analytes were separated on a BioRad Aminex HPX-87H column at 65 °C with 0.005 M H_2SO_4 mobile phase at 0.65 mL/min.

XRD was performed on a Philips X'Pert X-ray diffractometer with Cu Kα source, 45 kV tension, and 20 mA current. Scan step size was 0.01° with a dwell time of 2 s. Before measuring XRD spectra, zeolites were dried at 95 °C for 1.5 h and then stored over a 42 wt% solution of aqueous $CaCl_2$ for at least 24 h to maintain an environment of 35% relative humidity (RH) [35]. Relative crystallinity was calculated by integrating the XRD peaks at 2θ = 15.9°, 19.0°, 20.7°,
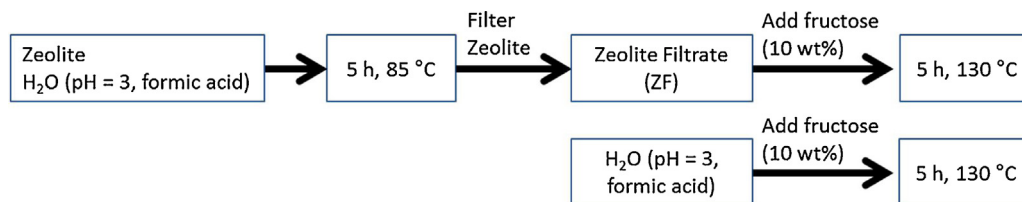
Scheme 2. Representative flow chart of zeolite filtrate (ZF) preparation procedure and pH = 3 formic acid experiments.

Source: Adapted from Kruger et al. [1].