Rational Design of Zn,Zr,O₃ Catalysts for the Conversion of Ethanol to Isobutene with Improved Selectivity and Stability

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Introduction

With increases in availability and decreases in its production cost, ethanol has become an attractive platform molecule for the production of value-added chemicals [1]. With infrastructure already in place for bio-derived ethanol production and limits on ethanol levels in gasoline blending, favorable economic conditions for ethanol as a feedstock are expected. Isobutene (IB) is a highly valued industrial chemical that can be used as solvents, fuel additives, and precursors for synthetic rubber. In order to become less dependent on finite fossil fuel resources, sources other than crude oil are needed for isobutene.

Mixed metal oxides are promising catalysts due to their dual acid-base functionality for multi-solvent reduction and reactions converting ethanol to IB. For ethanol to IB (ETIB), acetone, formed via acetaldehyde kettone formation, has been identified as a key intermediate. We have previously reported that basic sites are needed for acetaldehyde and acetone formation [2]. It was also found that both Brønsted acid sites [3] and Lewis acid-base pairs are active for aldol-condensation of acetone at <100°C [4]. At temperatures higher than 350°C, only Brønsted sites were found to be selective to IB. In our previous work, IB yield – as high as 83% – from bio-ethanol was achieved over Zn,Zr,O₃ catalysts [2]. Further work revealed that weak Brønsted acid sites were responsible for increased IB yield [3]. However, the Zn,Zr,O₃ catalyst prepared by a hard template method (Zn,Zr,O₃-1*gen.) suffered from deactivation and produced undesired C₃ isomers with the IB stream due Brønsted sites. To mitigate these two issues, a new catalyst (Zn,Zr,O₃-2*gen.) with only Lewis sites was designed and synthesized. In this presentation, steady state and kinetic experiments, and pyridine-infrared spectroscopy (Py-IR) have been used to correlate the acidic sites with the activity of Zn,Zr,O₃ catalysts. Insight has been provided on which reaction steps are catalyzed by Brønsted and Lewis acidic sites. By pinpointing each type of acidity's role in ethanol conversion, higher IB selectivities can be achieved and fundamental understanding of acidic site requirements can be applied to the rational design of catalysts for the conversion of other bio-derived compounds.

Materials and Methods

Zn,Zr,O₃ catalysts were prepared via two methods – (1) hard-template (Cabot Black Pearl 2000) for Zn,Zr,O₃-1*gen. [2] and (2) incipient wetness of Zn(NO₃)₂·6H₂O onto Zr(OH)₄ for Zn,Zr,O₃-2*gen. Catalytic activity testing was conducted in a fixed-bed stainless steel reactor equipped with a K-type thermocouple for temperature monitoring and a Cole-Parmer single syringe infusion pump for liquid reactant introduction. An online Shimadzu GC-2014 equipped with an auto-sampling valve, and a HP-Plot Q column was used to analyze gas products. Py-IR experiments were conducted using a Bruker 27 FTIR spectrometer.

Results and Discussion

Zn,Zr,O₃-1*gen. and Zn,Zr,O₃-2*gen. catalysts displayed similar surface areas (124 vs. 91 m²/g). Py-IR revealed the presence of Brønsted (1544 cm⁻¹) and Lewis acid sites (1445, 1574, and 1608 cm⁻¹) of varying strength on fresh Zn,Zr,O₃-1*gen. Meanwhile, only Lewis sites were found on fresh Zn,Zr,O₃-2*gen. For ETIB reactions, Brønsted acid sites were found to catalyze undesired ethanol dehydration and secondary acetone reactions leading to the formation of side products such as ethylene and propylene. Brønsted acid sites also facilitated the isomerization of IB to form C₃ isomers, which is consistent with literature [4]. This is confirmed by acetone to IB experiments (Fig. 1, inset). Formation of C₃ isomers would make isobutene separation difficult. Although an 83% IB yield was achieved with Zn,Zr,O₃-1*gen., formation of C₃ isomers and rapid catalyst deactivation are major issues for this catalyst.

The redesigned Zn,Zr,O₃-2*gen. catalyst, with only Lewis acid-base pairs, showed not only high selectivity to IB without other C₃ isomer formation, but also high stability (no noticeable deactivation for >200 hours of TOS) (Fig. 1). Reaction pathway studied using isotope labeling and characterization work to elucidate acidic sites roles of Zn,Zr,O₃-2*gen. will be presented.

Significance

This study provides insight for the rational design of highly stable and selective catalysts with acid-base functionality for the conversion of commercially available bio-derived feedstocks to value added chemicals.

Figure 1. (Left) Zn,Zr,O₃-2*gen. exhibits improved catalyst stability for ETIB and (inset) lack of formation of C₃ isomers in acetone to IB reaction contrasts with Zn,Zr,O₃-1*gen.’s performance. (Right) Py-IR characterization of catalysts (desorption at 250 °C) shows the absence of Brønsted on Zn,Zr,O₃-2*gen.

References