Acid Site Properties of Tungstate Zirconia in Alcohol Dehydration Reactions

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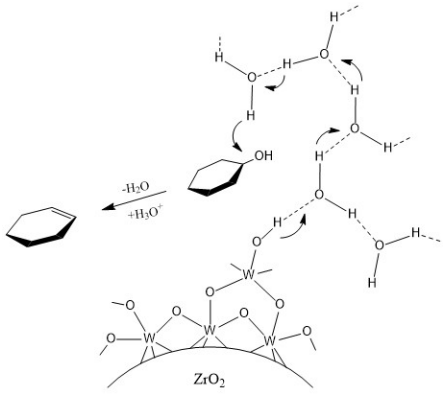
Abstract

Bio-oil generated by pyrolysis of biomass can be upgraded in (hydro)deoxygenation reactions such as dehydration, an acid-catalyzed step. We focus on alcohol dehydration in this work, because they are hydrogenation products of phenolics and acids, components of lignin-derived bio-oils. Tungstated zirconia (WO_x-ZrO_2) comes with a comparable intrinsic acid strength to zeolites, but is considered to be more stable at conditions that induce structural degradation to zeolites (e.g., in water).



Key parameters for this class of materials include the surface W density, which remarkably affects the acid site properties. While the effects of WO_x loading and annealing temperature have been studied in several gas phase acid-catalyzed reactions [1,2], those aspects have not been investigated in aqueous phase where BAS, which are considered to be the active sites, are effectively in the form of hydrated hydronium ions. In this work, we prepared a series of WO_x-ZrO_2 catalysts with varying surface densities and domain sizes of the WO_x entities by applying different annealing temperatures, characterized their bulk and surface structures, performed titration of catalytically active acid sites (using organic bases with similar kinetic diameters as the reactant) under working conditions, and compared the site-normalized activities among these catalysts. Depending on the W density and the solvent used, not only catalytic rates drastically differ, but also the concentration of active sites widely vary. For example, pyridine titration of cyclohexanol dehydration in aqueous phase showed active site concentration to be ~250 μmol/g_{cat} for a WO_x-ZrO_2 catalyst containing ~650 μmol/g_{cat} W atoms. Gas phase titration using pyridine, instead, showed <30 μmol/g_{cat} BAS, a value comparable to that obtained from similar titration experiments in apolar solvents. An understanding of the observed kinetic phenomena and the state of active site during reaction will be presented, and a comparison with zeolite catalysts [3] will be reported.

Reference

[1] J. Macht, C. D. Baertsch, M. May-Lozano, S. L. Soled, Y. Wang, E. Iglesia, *Journal of Catalysis* **2004**, *227*, 479-491.
[2] C. D. Baertsch, S. L. Soled, E. Iglesia, *The Journal of Physical Chemistry B* **2001**, *105*, 1320-1330.
[3] Y. Liu, A. Vjunov, H. Shi, J. A. Lercher, *Nature Communications* **2017**, *14113*