Consequences of Composition and Acid Strength for Catalysis on Polyoxometalate Keggin Clusters

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Introduction

Keggin polyoxometalates (POM) comprise a class of model metal oxides aptly suited to develop rigorous composition-function relationships, because they maintain a constant and well-defined atomic connectivity over a broad range of composition. We describe here the use of acid POM clusters with W addenda atoms and central atoms of different valence and number of charge-balancing protons ($H_{8-n}X^{n+}W_{12}O_{40}$; $X^{n+} = P^{5+}$, Si^{4+}, Al^{3+}, Co^{2+}). These clusters are used to probe the effects of acid strength on the rate of alkanol elimination and alkane isomerization catalysis. We describe intrinsic acid strength in terms of deprotonation energy (DPE), a property of the solid acid accessible by theory for acids with known structure. These POM clusters are deposited onto inert supports without structural degradation to avoid the formation of secondary structures with uncertain accessibility and are compared with acid zeolites. For alkane isomerization, these samples are used as physical mixtures with Pt/Al_2O_3 to maintain constant and known alkene concentrations. The rates of these elimination and isomerization reactions were shown by kinetic, isotopic, and theoretical studies to be controlled by elimination from H-bonded alkanols and isomerization of bound alkoxides, respectively [1-3]. These elementary steps involve late ion-pair transition states [1,4] (Figure 1a), a common feature of acid catalysis.

Materials and Methods

Rates were measured using gas phase reactants in a plug-flow differential reactor. The reactor effluent was analyzed by gas chromatography and flame ionization detection. POM clusters were characterized by NMR and TEM methods and the number of accessible protons was determined by titration with hindered pyridine during catalysis. Density functional calculations were carried out using the Gaussian 03 program. Geometries were optimized and energies calculated at the B3LYP/6-31+G(d,p) level of theory.

Results and Discussion

Elementary step rate constants (per H^+) for elimination and isomerization showed an exponential decrease with increasing DPE on polyoxometalate structures and H-BEA, suggesting DPE determines the relevant activation barriers. These data are consistent with thermochemical treatments of transition state stabilities, which we use here to probe the effects of the properties of reactants (enthalpy of dehydration; proton affinity), catalysts (DPE), and ion-pairs (interaction energy, E_{int}) [4]. Activation barriers change with composition by a smaller value than the concurrent DPE changes, apparently because of compensation effects that depend on the specific reaction (Figure 1b). The slope in Figure 1b is smaller for elimination than for isomerization. The thermochemical descriptions of activation barriers led to the definition of this sensitivity to DPE as the derivative of the activation barriers with respect to DPE, a property that depends solely on the effects of DPE on transition state interaction energies (E_{int}). This relation between E_{int} and DPE reflects electrostatic interactions at the transition state, which become stronger for weaker acids, with their more highly charged conjugate anions. Electrostatic interactions depend on the ability of the cation and the anion to delocalize their respective charges spatially, a property that is reminiscent of the concepts of hardness and softness in liquid phase acid-base chemistry [5]. The correlations reported here between activation barriers and acid strength (DPE) can be used to estimate DPE values for solid acids of unknown or uncertain structure, such as sulfate or tungstate domains on zirconia and sulfonic acid resins. This approach involves measurement of rate constants for elimination or isomerization reactions and the interpolation of these values onto the relations obtained for POM and zeolitic acids of known structure and DPE values accessible by theory. These DPE values, measured during catalysis, can be used as reliable benchmarks of the fidelity of structures proposed for these materials and also as a probe of the subtle solvation effects of reaction environment on the structure and strength of Brønsted acid sites. For example, our DPE estimated for sulfated zirconia from n-hexane isomerization is 1110 kJ mol^{-1} versus 1165 kJ mol^{-1} during 2-butanol elimination, indicating weaker acid sites in an alkanol environment.
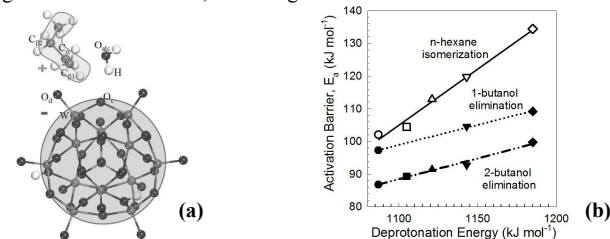

Figure 1. DFT elimination ion-pair transition state for 2-butanol dehydration on $H_3PW_{12}O_{40}$ (a) and (b) 1-butanol and 2-butanol elimination (full symbols) and n-hexane isomerization (open symbols) activation barriers vs. deprotonation energy. ($H_3PW_{12}O_{40}/SiO_2$ (●), $H_4SiW_{12}O_{40}/SiO_2$ (■), $H_5AlW_{12}O_{40}/SiO_2$ (▲), $H_6CoW_{12}O_{40}/SiO_2$ (▼), and H-BEA (♦))

Significance

We show here a method for relating reactivity in acid catalysis to properties of reactants and catalysts using thermochemical cycles and materials with known structure. Specifically, we identify the critical role of electrostatic stabilization in ion-pair transition states, its relation to hardness-softness acid-base concepts, and a method to estimate the acid strength of materials with uncertain structure during their use as catalysts. The financial support by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science US Department of Energy under grant number DE-FG02-03ER15479 is gratefully acknowledged.

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