447a Theoretical Insights into Alkylation Catalysis over Polyoxometalates

Michael J. Janik, Robert J. Davis, and Matthew Neurock

Acid catalysis is at the heart of many hydrocarbon conversion processes including catalytic cracking, isomerization, oligomerization, and alkylation. The first three of these processes are typically carried out over solid acids. The alkylation of isobutane with n-butene, however, is predominantly carried out using homogenous HF and H_2SO_4 which are highly corrosive and lead to waste disposal and catalyst separations issues. Despite the nearly 30 years of research, there are still no ideal solid acid alternatives. Catalyst deactivation remains one of the foremost challenges in finding acceptable solid acid replacements. The deactivation of solid acid catalysts correlates with the loss of the ability to catalyze the intermolecular hydride transfer between the adsorbed alkyl product and solution-phase isobutane. Understanding the mechanism for acid catalyzed hydride transfer has thus been proposed as "mandatory for the rational search for improved solid catalysts" for this reaction.[1] Determination of the mechanism, including the transition state(s) for the hydride transfer step over acid catalysts will help to elucidate the requirements of the active site for hydride transfer. The relative rate of hydride transfer compared to the alkylation and isomerization steps must be considered in the rational design of effective catalytic materials.

Heteropolyacids (HPAs) are active for the alkylation of isobutane and n-butene but suffer from rapid catalyst deactivation.[2, 3] HPAs are proposed to be superacids, and their acid strength has raised hope that their deactivation during alkylation may be surmountable. The relationship between measurements of acid strength and the energetics of hydrocarbon conversion processes over HPAs will be discussed. The reaction energetics of the individual steps in the alkylation over phosphotungstic acid ($H_3PW_{12}O_{40}$) were determined using DFT methods. The reaction energetics of alkene adsorption and oligomerization, alkylation, and hydride transfer steps are reported to provide molecular scale understanding of the pathways to deactivation due to the buildup of heavy hydrocarbons. The prospects of developing a solid acid catalyst for the alkylation of isobutane and n-butene will be discussed based on the reaction energetics determined for heteropolyacid catalysts. The calculations provide insight into the requirements for an active solid acid.

References:

(1) Weitkamp, J.; Traa, Y. Catal. Today 1999, 49, 193-199.

(2) Blasco, T.; Corma, A.; Martinez, A.; Martinez-Escolano, P. J. Catal. 1998, 177, 306-313.

(3) Gayraud, P. Y.; Stewart, I. H.; Hamid, S. B. D.-A.; Essayem, N.; Derouane, E. G.; Vedrine, J. C. Catal. Today 2000, 63, 223-228.