

## Theoretical Insights into Alkylation and Acid Catalysis over Polyoxometalates

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### Introduction

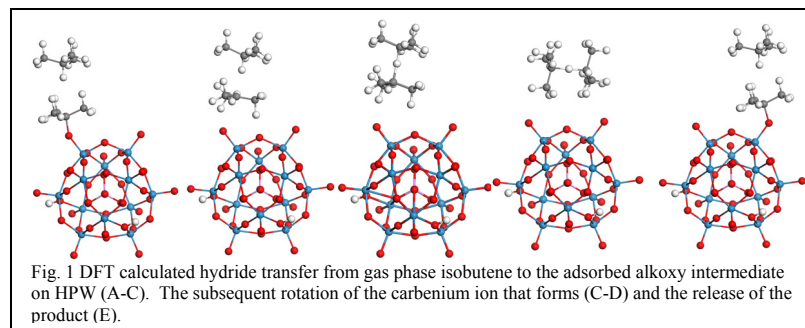
Acid catalysis is at the heart of many hydrocarbon conversion processes including catalytic cracking, isomerization, oligomerization and alkylation. Of these processes, alkylation is predominantly carried out using homogenous HF and H<sub>2</sub>SO<sub>4</sub> which are highly corrosive acids and lead to waste disposal and catalyst separations issues. Heteropolyacids (HPAs) have been shown to be active for the alkylation of isobutane and *n*-butene but suffer from rapid catalyst deactivation.<sup>1</sup> HPAs are proposed to be superacids,<sup>2</sup> and their acid strength has raised hope that their deactivation during alkylation may be surmountable. The titration of acid sites with ammonia shows that the acid sites of HPAs are of uniform strength.<sup>3</sup> As hydride transfer is proposed to require a stronger acid site than the non-selective side reaction, uniformity may increase the reaction selectivity. The diversity of compositions available provides for the tuning of HPA acid strength. Herein, we 1) examine potential mechanisms that control the alkylation of isobutane with *n*-butene and potential deactivation of HPAs by the loss of water and 2) explore how changes in the Keggin composition influence alkylation behavior.

### Results and Discussion

First principles density functional theoretical calculations were used to calculate the proton affinity for different sites and different HPAs in order establish site distributions and their relative acid strengths. The proton affinity of phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or HPW) was found to be 1080 kJ mol<sup>-1</sup>, indicating that it is a substantially stronger acid than typical zeolites, which have proton affinities between 1200-1400 kJ mol<sup>-1</sup>.<sup>4</sup> The activation barrier for anhydrous proton-hopping is slightly lower over phosphotungstic acid than over HZSM-5, indicating the protons may move among oxygen atoms on the exterior of the Keggin unit structure in the reaction environment. The relationship between the measured and calculated acid strength is compared with the calculated reaction energies over HPA. Alkenes were found to initially adsorb through the donation of electron density from the carbon-carbon  $\pi$ -bond to the proton. The transformation of the physisorbed state to the more strongly bound alkoxy state occurs by the donation of the proton and formation of a covalent bond between the alkyl group and an oxygen atom of the catalyst. Both physisorption and chemisorption of propylene are more exothermic on HPW than on the zeolite chabazite<sup>5</sup>. The transition state for alkene adsorption is a carbenium ion in which proton donation is virtually complete before the formation of the alkoxy bond. The activation barrier for this adsorption is lower over HPW than in zeolites. Higher substitution at the alkoxy carbon center leads to a lower activation barrier and stronger adsorption. A tertiary carbenium ion was identified as a stable intermediate during the adsorption of isobutene to HPW.

Hydride transfer proceeds via the transfer of a hydrogen from a weakly interacting isobutane reactant molecule to an adsorbed alkyl intermediate bound to the surface of phosphotungstic acid. The reaction occurs by the initial formation of a surface carbenium ion

and the subsequent complexation of the carbenium ion with isobutane to form a shared-hydride intermediate. The initial hydride transfer from isobutane to the alkoxy intermediate is shown in Fig. 1A-C. The Keggin structure allows only for a perpendicular attack of isobutane. The subsequent transfer of the hydrogen and the release of the product requires a rotation of the carbenium ion complex which is shown in Fig. 1C-E. The overall barrier to hydride transfer is the energy necessary to convert the adsorbed alkyl species to a carbenium-ion. The formation of the carbenium-ion from alkoxide or  $\pi$ -bound adsorbed states occurs without an influence from the nearby isobutane molecule. Hydride transfer to a tertiary carbon atom proceeds with a substantially lower activation barrier than transfer to a secondary carbon. This is due to the greater stability of the more substituted carbenium ion. Alkylation of an adsorbed alkyl species also proceeds through a carbenium-ion transition state. The transition state for alkylation, however, is stabilized by interaction with the alkylating alkene. Alkylation, therefore, proceeds with an intrinsically lower reaction barrier than hydride transfer, thus leading to the



build-up of heavy hydrocarbons and catalyst deactivation. Additionally, the stabilization of the carbenium-ion transition state of concerted alkene dimerization may allow oligomerization to continue over acid sites not active for hydride transfer.

The activation barrier for hydride transfer is controlled by the relative stability of covalently bound alkoxide and carbenium-ion states over the acid catalyst surface. Compared to zeolite structures, the Keggin unit provides greater relative stability for the alkoxide state, therefore hydride transfer barriers are higher over HPAs than over zeolites despite the ranking of HPAs as stronger acids. Over a series of HPAs with varying composition, the relative stability of the ionic transition state is increased with a lower overall anionic charge imparted by the central atom.

### References:

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