

A density functional theory study of the alkylation of isobutane with butene over phosphotungstic acid

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Abstract

The deactivation of solid acid catalysts during the alkylation of isobutane with butene has significantly impeded replacement of the commonly used homogeneous catalysts. The relative rates of alkylation and hydride transfer control the rate of heavy hydrocarbon buildup, leading to blocking of catalyst pores and acid sites. Herein the mechanisms of hydride transfer and alkylation over phosphotungstic acid are examined using *ab initio* density functional theory methods. The transition state of hydride transfer is a carbenium ion, with shared-hydride carbonium ions representing lower energy intermediates. Although the transition state for the alkylation step is also a carbenium ion, it is stabilized by interaction with the alkene reactant. Therefore, the barrier for alkylation is intrinsically lower than that for hydride transfer, thus providing a favorable path to the buildup of heavy hydrocarbons on the acid surface. The implications of these findings on the design of effective catalysts for alkylation are discussed.

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1. Introduction

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, whereas the alkylation of isobutane with butene is carried out using mainly homogeneous HF and H₂SO₄, which are highly corrosive and entail waste disposal and catalyst separation issues. Despite nearly 30 years of research [1–3], the commercialization of solid acid alternatives for alkylation is limited. Catalyst deactivation remains the foremost challenge in finding acceptable solid acid replacements. To advance our efforts toward the design of new solid acid catalysts, a more complete understanding of the fundamental structural and electronic features that control catalyst acidity, selectivity, and potential modes of deactivation is required. Although numerous stud-

ies have been devoted to elucidating the operative mechanisms for solid acid-catalyzed conversion processes, our understanding remains fragmented and rather incomplete. Over the past decade, however, theoretical efforts have helped establish the reaction mechanisms of many hydrocarbon conversion processes over acidic zeolites. Herein we extend that work using quantum mechanical methods to examine the energetics of key reaction steps for alkylation over heteropolyacids (HPAs).

Alkylate produced from the C₄ byproducts of a catalytic cracking unit is used as a high octane (octane number ~95) blending stock for gasoline. The worldwide alkylation production capacity exceeds 1.9 million barrels per day [4]. The alkylation of isobutane with butene occurs via a complex reaction network that produces a broad distribution of products. The desired products are highly branched C₈ alkanes, mainly trimethylpentanes (TMPs). A simplified mechanism for solid acid-catalyzed alkylation is illustrated in Fig. 1 [2,5]. Alkylation is initiated by the adsorption of butene (reaction 1). This is followed by hydride transfer from isobutane to the adsorbed *s*-butyl species to produce an adsorbed *t*-butyl intermediate and an *n*-butane molecule (reaction 2). The adsorbed *t*-butyl in-

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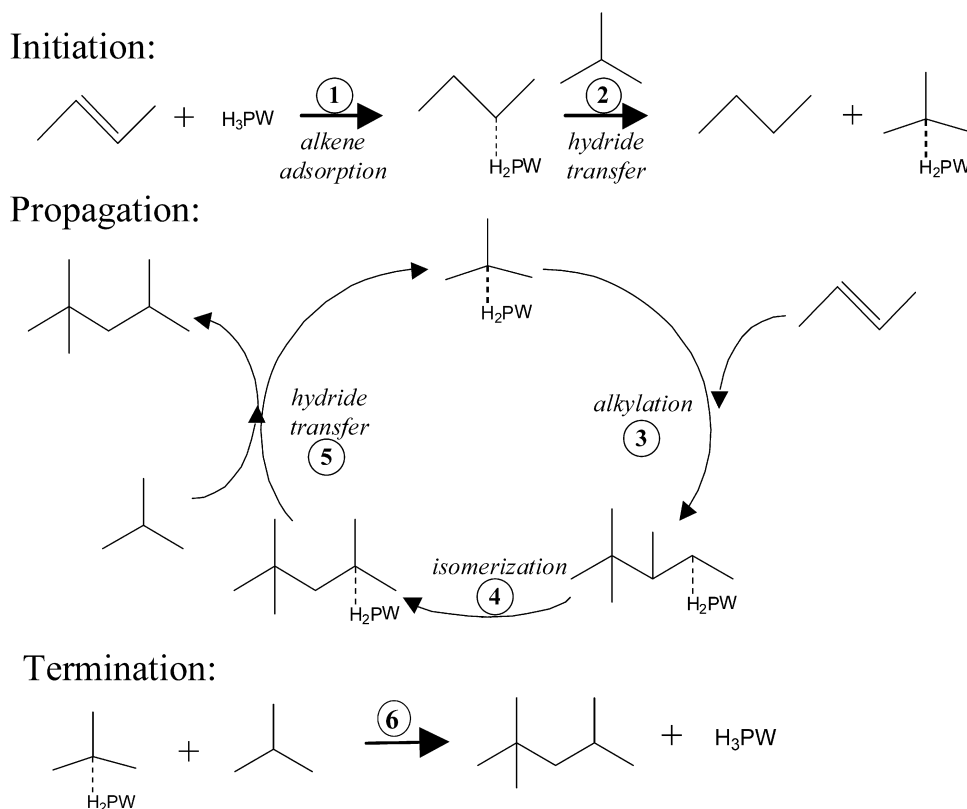


Fig. 1. The mechanism of the alkylation of isobutane and *n*-butene over phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, abbreviated H_xPW). There is no implication as to the nature of the adsorbed alkyl species, and the catalyst is included only to indicate the involvement of the catalytic site.

intermediate initiates the propagation cycle. A butene molecule reacts with the *t*-butyl intermediate to form adsorbed 2,2,3-trimethylpentane (2,2,3-TMP) (reaction 3). The adsorbed 2,2,3-TMP can subsequently isomerize through hydride and methyl shifts (e.g., reaction 4). A fluid-phase isobutane molecule can react with the adsorbed C_8 species via hydride transfer to generate the C_8 alkane product and regenerate the adsorbed *t*-butyl intermediate, which closes the cycle (reaction 5). Termination of the cycle occurs through a sequence typically termed “self-alkylation” (reaction 6) in which an adsorbed *t*-butyl species desorbs as isobutene, which can then alkylate with a second adsorbed *t*-butyl species.

Competing reactions produce undesired side products that ultimately lead to catalyst deactivation. The C_8 species can desorb as an alkene and subsequently alkylate an adsorbed *t*-butyl species rather than undergo hydride transfer. The adsorbed C_8 species can combine with another butene molecule to produce an adsorbed C_{12} species, which can further react. Skeletal isomerization and β -scission reactions lead to a wide distribution of products. Alkene oligomerization can also occur, leading to the production of C_8 alkenes or other heavier hydrocarbons. Heavy hydrocarbons may plug catalyst pores or block active catalyst sites, leading to deactivation. Ideally, hydride transfer from isobutane to the adsorbed C_8 species occurs before further alkylation or alkene desorption, thus terminating the growing chain and preventing heavy hydrocarbon buildup. However, the alkylation step is estimated to occur at a rate two to three orders of magnitude faster than hydride transfer [6,7], and the forma-

tion of multiple alkylates (C_{12} and greater) is directly tied to catalyst deactivation [6]. Deactivated zeolite catalysts contain large amounts of heavy hydrocarbons [8], and only recently has an industrial process, with the catalyst taken off-line and regenerated every 1–3 h, become economical [9,10]. Alkylation is performed industrially in extreme excess of isobutane over butene to maximize the relative hydride transfer rate [1,11].

Zeolites have a high initial activity for alkylation; however, both the activity and the selectivity to C_8 alkanes decrease with time on stream [2,6,7,12,13]. As the olefin conversion decreases, the fraction of higher alkenes in the product stream typically increases, and at long reaction times, only butene oligomerization is catalyzed. This indicates that at long reaction times, the hydride transfer step ceases, and thus the loss of activity and selectivity is assumed to result from a decreased ability to promote the hydride transfer step [2,6,14–16]. 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 [2]. The determination of the reaction mechanism, including the transition state(s) for the hydride transfer step over acid catalysts, will help elucidate the requirements of the active site for hydride transfer. The relative rate of hydride transfer compared with alkylation and isomerization must be considered in the rational design of effective catalytic materials.

Theoretical studies of hydrocarbon conversion has been used to elucidate the important properties of zeolite catalysts for these processes. Whereas the active intermediate for conver-

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