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Selective conversion of acetone to isobutene and acetic acid on aluminosilicates: Kinetic coupling between acid-catalyzed and radical-mediated pathways

Stanley Herrmann, Enrique Iglesia *

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, United States

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ABSTRACT

Solid Brønsted acids catalyze aldol condensations that form C—C bonds and remove O-atoms from oxygenate reactants, but sequential β-scission reactions also cleave C—C bonds, leading to isobutene and acetic acid products for acetone reactants. The elementary steps and site requirements that cause these selectivities to depend sensitively on Al content and framework type in aluminosilicate solid acids remain speculative. Acetone reactions on microporous and mesoporous aluminosilicates (FER, TON, MFI, BEA, MCM-41) showed highest β-scission selectivities on MFI and BEA; they increased as the Al content and the intracrystalline density of active protons decreased. The effects of acetone and H_2O pressure on turnover rates and selectivities indicate that an equilibrated pool of reactive C_6 ketols and alkenones are present at pseudo-steady-state concentrations during catalysis and that they act as intermediates in β-scission routes. Two distinct C_6 β-scission pathways contribute to the formation of isobutene and acetic acid: (i) a minor H_2O-mediated route involving β-scission of C_6 ketols on protons and (ii) the predominant anhydrous path, in which H-transfer forms unsaturated C_6 enols at protons and these enols propagate radical chains mediated by transition states stabilized by van der Waals contacts within vicinal microporous voids. This latter route is consistent with coupled-cluster free energy estimates for these unsaturated C_6 enols and their respective free radicals. It accounts for β-scission selectivities that increase with decreasing proton density, a finding that precludes the sole involvement of acid sites and requires instead the kinetic coupling between reactions at protons and propagation steps mediated by transition states confined within proximate voids, even when such voids lack a specific binding site. These mechanistic interpretations also account for the observed effects of residence time, of the loss of active protons by deactivation, of acetone and H_2O pressures, and of aluminosilicate framework structure on selectivity. These mechanistic insights also demonstrate the ability of voids to stabilize transition states that mediate homogeneous reactions by mere confinement, even in the absence of chemical binding onto specific sites, as well as the essential requirement of intimate proximity for the effective kinetic coupling between reactions on protons and in proton-free voids, a process mediated by the diffusion of very reactive and unstable intermediates present at very low local concentrations within microporous frameworks.

1. Introduction

The selective conversion of biomass-derived oxygenates to branched alkenes provides a route to useful chemicals from renewable sources [1–3]. One such pathway converts acetone, often formed from biomass fermentation or pyrolysis processes, to isobutene, a monomer widely used in the synthesis of butyl rubber and polyisobutylene [4,5], and to acetic acid, a co-product that can be converted to alkanones via ketonization [6–8]. This reaction occurs on solid acids, whether based on mesoporous oxides (silica-alumina, silica-tungstenate, silica-phosphoric acid) or on crystalline microporous aluminosilicates (MFI, BEA, ERI, FAU zeolites) [9–15]. Mechanistic details remain unclear because of concurrent and sequential oligomerization, ketonization, and isomerization reactions [16,17], which consume primary products and can form larger deactivating residues at the temperatures required for practical reactivity (550–600 K) [12,18]. Such mechanistic inquiries may allow the more precise tuning of selectivity to increase isobutene and acetic acid yields through more thoughtful choice of solid acids that provide specific confining void or proton densities.

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* Corresponding author.
E-mail address: iglesia@berkeley.edu (E. Iglesia).

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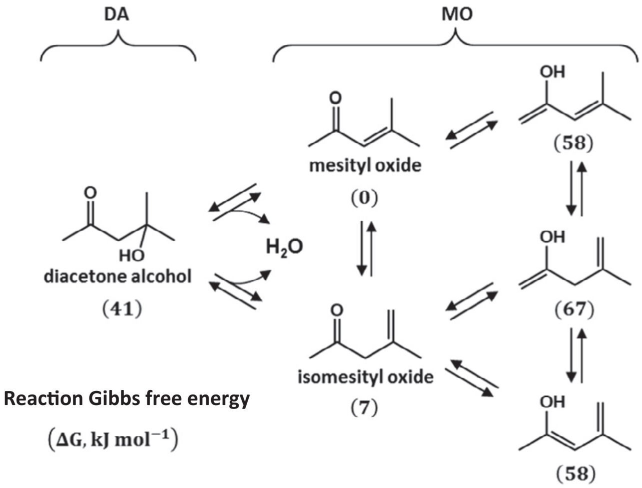
Alkanones form β-ketol dimers via aldol condensation on Brønsted acid sites at near-ambient temperatures [19]. These β-ketol species subsequently dehydrate on such acid sites to form α,β-unsaturated alkanones [20,21]. Alkenes can form via C—C bond cleavage of either the β-ketol species or their α,β-unsaturated alkanone products. The conversion of diacetone alcohol and mesityl oxide, the products of acetone condensation, into isobutene was first reported in 1940 by McAllister, et al. on silica-supported phosphoric acid catalysts [22]. Later studies on zeolitic acids have led to conflicting proposals about (i) the identity of the direct precursor to isobutene and acetic acid (mesityl oxide, diacetone alcohol, trimer oxygenate products, or larger unsaturated residues) [12–15]; (ii) the nature of the active sites (Brønsted or Lewis acid centers) [15,23]; (iii) the mechanistic role of water in determining isobutene selectivity and deactivation rates [12,23]; and (iv) the effect of Si/Al ratio in aluminosilicates on reactivity and isobutene selectivity [12,13,15,24].

These mechanistic and practical issues are addressed here through measurements of condensation turnover rates and isobutene selectivities on aluminosilicates with diverse framework structures (FER, TON, MFI, BEA, MCM-41) and with a range of proton and Al densities. These reactions are shown to occur via elementary steps that combine those involved in the formation of condensation products, previously established through kinetic, isotopic, spectroscopic, and theoretical tools [18], and those that mediate the conversion of an equilibrated pool of C_6 species to isobutene and acetic acid via two distinct routes; these routes involve an acid-catalyzed and a radical-mediated route, with the species that mediate the latter route formed initially on Brønsted acid sites. Condensation is limited by the C—C bond formation step on protons nearly saturated with H-bonded acetone, without detectable involvement of Lewis acid sites. Condensation rates thus reflect the preferential stabilization of the C—C bond formation transition state over H-bonded acetone precursors via van der Waals interactions with the confining framework voids when compared across aluminosilicates of similar acid strength [18]. These steps lead to rates (r_{cond}) that are proportional to acetone pressure (Ac) and to the number of accessible protons:

$$\frac{r_{cond}}{[H^+]} = k_{cond}(\mathrm{Ac}) \qquad (1)$$

with k_{cond} as the first-order condensation rate constant.

This study shows that isobutene and acetic acid form by reactions of an equilibrated pool of β-ketols and α,β-unsaturated alkanones (C_6-pool; Scheme 1), without the involvement of larger chains, as also shown in one previous study, in which isobutene with only one or three ^{13}C-atoms formed from ^{13}C-acetone–^{12}C-acetone mixtures on MFI and BEA [11]. The addition of H_2O on MFI samples with different proton density shows here that isobutene forms via two distinct routes that differ in the involvement of H_2O denoted here as anhydrous and H_2O-mediated β-scission routes. H_2O-mediated routes require only protons and occur at rates strictly proportional to their number for a given void structure and independent of the presence of non-framework Al species that may act as Lewis acids. These H_2O-mediated pathways are likely to involve diacetone alcohol β-scission (β_{DA} pathway), but kinetic data can only ascertain that this is the stoichiometry of the relevant transition state; thus, the hydrolytic cleavage of mesityl oxide may also contribute to such routes. The anhydrous routes, in contrast, involve the β-scission of species with the stoichiometry of mesityl oxide (β_{MO} pathway). These anhydrous pathways are much more prevalent than the H_2O-mediated route and lead to isobutene selectivities that increase, in an unusual and unexpected manner, as the proton density decreases, an observation reported, but not explained, in some previous studies [12,13,24]. These trends reflect pathways that require the presence of small voids acting in concert with protons. Protons isomerize mesityl oxide into unstable reactive intermediates that participate in radical propagation cycles mediated by transition states stabilized by van der Waals contacts with the walls of the confining voids, but without the involvement of specific binding sites.



Scheme 1. Reaction network and Gibbs free energies (relative to mesityl oxide) for all gaseous C_6 species. Gibbs free energy differences between gaseous species and gaseous mesityl oxide molecules are provided in parenthesis (473 K, CCSD, AUG-cc-pVDZ; details in Section 2.3). The value for diacetone alcohol is the free energy difference between diacetone alcohol and the sum of mesityl oxide and H_2O in their gaseous states.

These synergistic effects of protons and small voids for β_{MO} routes cannot be reconciled with elementary steps that involve bifunctional catalysis (two distinct binding sites), or with non-framework Al acting as Lewis acid centers or silanols as weak Brønsted acids. Radical-like pathways enhanced by confinement and requiring nearby protons to replenish unstable compositional isomers of mesityl oxide that propagate radical chains are consistent with all data at hand. These routes resemble those that mediate gas phase decomposition of MO at higher temperatures (685–763 K) [25]; these homogeneous rearrangements are initiated by MO conversion to reactive alkenol isomers, which occurs, in this case, via facile hydride shifts at protons [26]. Confining voids in microporous acids (FER, TON, MFI, BEA) can decrease activation barriers, without the involvement of specific binding sites, as shown previously for other homogeneous reactions, such as NO oxidation [27] and diene cyclodimerization [28]. These previously unrecognized routes for β-scission of acetone-derived C_6 species involve intimate kinetic coupling between proton-catalyzed isomerization and radical-mediated β-scission propagation cycles, a mechanistic conclusion supported by free energy estimates for C_6 intermediates and their respective radicals. These theoretical treatments suggest that these free-radical mediated β-scission pathways, made possible by protons and confining voids within nanometer distances, represent the only plausible mechanism consistent with rate and selectivity data for the anhydrous β-scission routes that prevail at practical conditions for the conversion of acetone to isobutene and acetic acid.

2. Methods

2.1. Catalyst synthesis and characterization protocols

NH_4-MFI (Zeolyst, $Si/Al_{tot} = 16.6$, 29.2, 43.8, and 168.3), NH_4-BEA (Zeolyst, $Si/Al_{tot} = 43.3$), NH_4-FER (Zeolyst, $Si/Al_{tot} = 10.3$), NH_4-TON (BP p.l.c., $Si/Al_{tot} = 40.0$), and NH_4-MCM-41 (Sigma-Aldrich, 643,653, $Si/Al_{tot} = 37.8$) were treated in flowing dry air