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Alkene and Alkane Chain Growth on Solid Brønsted Acid Catalysts

By

Michele Lee Sarazen

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

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Summer 2016

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by

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Abstract

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Professor Enrique Iglesia, Chair

An emphasis on clean energy and a more efficient use of current fuel sources is important for an environmentally-conscious future energy landscape. This study aims to elucidate the process of growing low molecular weight alkenes, obtained from both dehydration of renewable oxygenate feedstocks (C_2 - C_4 alcohols) as well as conventional refinery sources, to higher molecular weight hydrocarbons in the transportation fuel range. Light hydrocarbons are converted on solid Brønsted acids via oligomerization, isomerization, β -scission, hydride transfer and cyclization reactions; these reactions are mediated by ion-pair transition states (TS). The relative stability of these ion-pairs, consisting of organic cations derived from reactants and inorganic anions formed by deprotonation of the inorganic catalyst, relative to their relevant precursors determine the rate of each reaction and their prevalence over the others. The anion contributes to TS stability by (i) van der Waals interactions conferred by the geometry of its surroundings (confinement) and (ii) its willingness to accept the negative charge (acid strength) and to interact electrostatically with the organic cation. The cation, in contrast, determines TS stability through its ability to accept the proton and then interact with the anion. These confinement and electrostatic effects can be probed using reactions mediated by TS that differ in size, shape or charge to various extents from each other and from their relevant kinetic precursors; density function theory (DFT) methods that account for the pertinent dispersive interactions further provide detailed information that is inaccessible from experiments alone, such as how the cation and anion conform to each other.

Here, turnover rates (per proton) for C_2 - C_4 alkene oligomerization reactions and for the incorporation of C_4 - C_5 alkanes via hydride transfer on acids of different acid strength and confining environments (TON, MFI, BEA, MOR, FAU zeolites; amorphous silica-alumina (SiAl), Keggin polyoxometalate clusters (POM) clusters on SiO_2) are reported. Along with oligomerization and hydride transfer, product distributions indicate extensive isomerization and β -scission. Rapid methyl and hydride shifts generate equilibrated pools of skeletal and regioisomers, as determined from chemical speciation and isotopic labeling. This conclusion that isomerization is equilibrated during oligomerization is made despite disagreement with tabulated gas-phase thermodynamic distribution because even small inaccuracies in this tabulated data yield significant differences in calculated equilibrium constants. While isomerization is facile on all catalysts, the extent of β -scission is different on different catalysts. It does not trend with confinement, but instead with the micropore connectivity of the acid catalyst, where the presence of voids that are larger than the surrounding channels, created from the intersections of the channel network, increases the

selectivity to secondary β -scission reactions. The product distribution directly correlates with the difference in size between the intersecting void and the subsequent channel, i.e. products made in voids larger than the apertures through which they must diffuse, will first undergo more β -scission to facilitate egression from the crystal as smaller, more mobile species. This thorough molecular view of the product distribution has not previously been investigated for zeolite-catalyzed oligomerization, despite it having commercial relevance.

Turnover rates for C-C bond formation and hydride transfer show that kinetically-relevant steps involve reactions of an alkene or alkane to alkene-derived alkoxides present at saturation coverage, consistent with *in-situ* infrared spectra and DFT estimates of activation free energy barriers and of the stability of alkoxide intermediates. These kinetic data, obtained over a very broad range of reactant pressures, allow a systematic comparison between theory and experiment and also accurate estimates of alkoxide adsorption constants. In doing so, this study provides a quantitative assessment of the effects of surface curvature and of alkene size and structure on alkoxide stabilities.

The rate constants for oligomerization and hydride transfer increase exponentially as acid strength, or the stability of its conjugate anion, increases. Here, the acid strength of a Brønsted acid is defined as the deprotonation energy (DPE) required to heterolytically cleave the O-H bond, which is theoretically accessible for known structures. Effects of acid strength on rate constants reflect DFT-derived transition states that differ in charge from their alkoxide precursors. Rate constants also generally increase with increasing TS size for both oligomerization and hydride transfer on each zeolite framework, because of the combined effects of the greater stability of the larger TS carbenium ions and their more effective contact with the void walls. DFT treatments show that zeolite frameworks distort locally, so as to enhance van der Waals contacts at the expense of a slight distortion of the framework lattice, which ultimately becomes too costly as the TS becomes larger than the size of the confining voids. For example, the lattice of TON (0.57 nm channel) locally moves closer to the TS for smaller TS (ethene dimerization; 0.46 nm diameter) and moves away for larger TS (isobutene dimerization; 0.58 nm diameter); the distortions become too costly, however, when the TS is much larger than the void (isobutane-C₆ hydride transfer; 0.81 nm diameter), consistent with a lower rate constant for TON than for larger pore environments. These energy compromises are also critical in alkoxide formation. DFT-calculated alkoxide energies indicate bulkier alkoxides distort the framework more in smaller, concave environments (TON) than larger pore ones (MOR, HPW).

This array of transition states and their precursors—formed from a range of reactants and catalysts—exploits the diversity in size, shape and charge in solid acid upgrading of alkenes/alkanes and provides unprecedented clarity of the complex relationship between organic moieties and inorganic catalysts when combined with state-of-the-art theoretical methods. The descriptors developed here that relate transition state properties (intrinsic stability of the organic cation, electrostatic interaction with the anion (acid strength) and stabilization via confinement provided by the flexible inorganic framework) to reactivity and selectivity provide a basis for extrapolation to other transition states and acid catalysts than those studied here, which has implications on overall catalyst efficiency.

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CHAPTER ONE

Introduction to Confinement and Acid Strength Effects on the Stability of Transition States and their Precursors for Hydrocarbon Reactions on Solid Acids

Zeolite acids contain microporous voids (< 2 nm) that can form a wide variety of structures, and thus have the potential to produce unique product selectivities due, at least in part, to the shape and size of their confining environments which can either occlude, or preferentially solvate, molecules and transition states based on size [1]. Turnover rates (normalized per proton) for hydrocarbon reactions on zeolites, and on all solid Brønsted acids, depend sensitively on acid strength, because ion-pair transition states and their relevant precursors differ in charge, and transition states preferentially benefit from the more stable conjugate anions provided by stronger acids [2–5]. Turnover rates, as well as selectivities, also depend sensitively on the stabilization by confinement provided by voids of molecular size in zeolitic acids, because transition states of different size benefit to varying extents from their precursors and from other transition states [6–8]. This study investigates how the confinement of protons within microporous and mesoporous acids with different void size and shape and the strength of the acid sites influence the relative stability of precursors and transition states during reactions of light hydrocarbons. In order to provide such molecular detail, a combination characterization of surface species, kinetic and isotopic studies, and computational modeling using state-of-the-art theoretical methods is employed.

Oligomerization of light alkenes first by mineral and, later, by solid zeolitic acids has long been studied as a viable production route of liquid fuel [9–12]. Light alkene conversion on zeolites, however, generates a wide distribution of products, suggesting that many reactions such as C-C bond formation (oligomerization), isomerization, C-C cleavage (β -scission), hydrogen transfer (to form alkanes; alkylation) and aromatization occur concurrently in a complicated reaction mechanism. The effects of zeolite framework on the observed product distribution of propene oligomerization are discussed in Chapter 2. Skeletal and regioisomers equilibrate irrespective of acid strength, void size or framework connectivity, consistent with rapid hydride and methyl shifts. This equilibration was determined using chemical speciation and isotopic scrambling studies because isomer distributions did not vary with conversion or pressure, yet were different than tabulated thermodynamic values, which varied across sources. The framework, or more specifically the connectivity of the framework, influences the selectivity of β -scission to oligomerization. Three-dimensional zeolites contain voids larger than the smallest aperture. As a result, oligomerization forms products that must undergo β -scission to egress through the crystal as smaller species. The relative ratio of the size of these voids to their subsequent channels dictates the product distribution.

The effects of confinement and acid strength on the mechanism of propene oligomerization are explored in Chapter 3. Propene oligomerization turnover rates are proportional to propene pressure (5–450 kPa) on microporous (TON, MFI, BEA, FAU) and mesoporous (amorphous silica-alumina (SiAl) and silica-supported Keggin polyoxometalate clusters (POM)); these rate dependences reflect kinetically-relevant additions of an alkene to a bound propoxide, shown by in situ infrared spectra which indicate saturation coverage, a conclusion also consistent with density functional theory (DFT) estimates of the activation barriers and stability of reactive intermediates. First-order propene oligomerization rate constants increase with decreasing void size because the larger transition states are preferentially stabilized

by van der Waals contacts over smaller alkoxide precursors. These rate constants also increase with increasing acid strength because the more stable conjugate anions in stronger acids stabilize ion-pair transition states more effectively than their less charged alkoxide precursors, as also shown by the DFT-derived charges in their optimized structures. These effects of acid strength are evident in both unsolvated protons (POM clusters with different central atoms and SiAl) and in confined protons (X-MFI where X indicates the isomorphous substitution of Si^{4+} by Al^{3+} , Ga^{3+} or B^{3+}) and are rendered quantitative by assessing acid strength in terms of deprotonation energies (DPE), accessible to DFT treatments because of the known structure of the solid acids used.

In Chapter 4, co-oligomerization reactions of ethene, propene, n-butenes and isobutene on the same series of acid catalysts provide a method to investigate how stabilities of bound species and transition states of different size and shape are affected by proton environment. Rate constants for alkene co-oligomerization increase with increasing transition state size, because of the combined effects of more stable carbenium ions and more effective contact with the void walls, which can become detrimental for transition states too large in size (e.g. isobutene dimerization in H-TON). Mixed alkene oligomerization reactions also give accurate values of relative alkoxide stabilities reflected in ratios of equilibrium constants, information unavailable for single component feeds. Bulkier alkoxides (e.g. tertiary-butoxides) become sterically hindered within smaller, concave environments (TON) as compared to larger pore environments (MOR, HPW), consistent with DFT treatments that rigorously account for van der Waals interactions and accurately capture relative alkoxide stabilities as a function of carbon number as well as substitution (i.e. primary, secondary, tertiary), information that is experimentally inaccessible. The synergy between theory and experiment exposes other mechanistic details, such as the flexibility of zeolites to distort locally to increase van der Waals interactions with the transition state or alkoxide.

The concurrent presence of alkanes, especially isoalkanes, during alkene oligomerization leads to the scavenging of alkene-derived alkoxides via pathways limited by the transfer of a H-atom as discussed in Chapter 5. Hydrogen transfer (HT) rates increase linearly with alkane pressures on all microporous and mesoporous acids, which reflects a reaction of the alkane with alkene-derived alkoxides. HT rate constants increase with increasing void size and then decrease for voids larger than those in BEA zeolite, because van der Waals contacts become less effective for larger voids in FAU and SiAl. Measured rate constants reflect free energy differences between the HT ion-pair transition states and smaller and essentially neutral, bound alkoxides; therefore, stronger acids exhibit larger rate constants. HT rate constants also depend on the identity of the acceptor and vary for bound alkoxides that differ in size and backbone, because their concomitant effects on the delocalization and stability of charge at HT transition states. The equilibrated nature of the bound alkoxide isomers has allowed for the first time an accurate determination of their relative reactivity in HT reactions and a rigorous comparison of their reactivity with different hydrogen donors, where substitution, as well as size, of the hydride donor affects the rate of the hydride transfer step. As a result, theory and experiment combine to probe and to accurately describe the nature and the dynamics of individual chemical events on realistic solid acids at conditions relevant to their industrial practice.

This inquiry into the relative stabilities of the bound species and transition states involved in C-C bond formation, isomerization, β -scission and hydrogen transfer reactions of alkene-alkane mixtures has uncovered unprecedented mechanistic details for the elementary steps most critical in the upgrading of chemical feedstocks. In doing so, it has provided previously

unavailable guidance for designing acids with the most effective strength and location of protons in a way that allows rigorous extrapolations to molecules of size and structure different from those examined here.

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CHAPTER TWO

The Effects of Void Environment and Acid Strength on Alkene Oligomerization Selectivity

Abstract

The effects of channel connectivity, void environment and acid strength on the relative rates of oligomerization, β -scission and isomerization reactions during light alkene (ethene, propene and isobutene) conversion were studied using a series of micro- and mesoporous Brønsted acids. Skeletal and regioisomers equilibrate at all conditions and on catalysts irrespective of acid strength, void size or framework connectivity, consistent with rapid hydride and methyl shifts of alkoxides intermediates and equilibrated communication with their gas-phase alkene analogs (desorption/adsorption). This equilibration was determined using chemical speciation and isotopic scrambling experiments because isomer distributions did not vary with conversion or pressure, yet were different than tabulated thermodynamic values, which varied among sources. While the “shape-selective” nature is inconsequential for the observed skeletal structure or double bond location, it does affect the chain length distribution in oligomerization products. Acids with ordered, one-dimensional pore networks preserve the number of carbons in the chains formed because chains that can form within their channels can egress with unobstructed diffusion regardless of the dimensions of the pores. Amorphous silica alumina and colloidal silica-supported polyoxometalate (POM) clusters have cross-sectional variations in their pore network, but the dimensions are larger than that any of the products formed and allow these products to diffuse intact. This is purely a geometric effect and not one of acid strength, which varies between POM clusters, because the kinetics of oligomerization and β -scission are affected similar by acid strength. Three-dimensional zeolites often have large voids where additional C-C bond formation steps can occur, but are connected by smaller channels or windows. The resulting undulations are of molecular dimension and cause β -scission events to form smaller molecules that can egress more easily through the crystal, while the severity of these undulations affects how many times they undergo oligomerization-cracking events. These conclusions remain consistent irrespective of the reactant alkene (ethene, propene or isobutene), which suggests the robustness of these descriptors for effects of the shape and connectivity of confining voids and of acid strength on selectivity.

2.1. Introduction

The oligomerization of alkenes on solid Brønsted acids provides an effective strategy to form new C-C bonds from small hydrocarbons [1–4]. These processes become attractive as such small molecules are excluded from fuels because of vapor pressure restrictions and as small alkenes become available from biomass-derived oxygenates. Solid acids, such as the acid forms of zeolites, catalyze these reactions [5]. Oligomerization occurs in parallel with its reverse reaction (β -scission in alkenes), albeit at different C-C bond locations in the two directions; thermodynamic trends favor C-C bond formation over cleavage for smaller alkenes and at higher pressures and lower temperatures.

Solid acids also catalyze concurrent hydrogen transfer and cyclization reactions, as well as skeletal and double-bond isomerization reactions that lead to isomers different from those

initially formed in oligomerization events [6–10]. The relative rates of these different reactions are influenced by the channel size in microporous solid acids, which allow selective diffusion of certain reactants and products and the potential preference for some transition states over others based on their size [11]. Previous studies on zeolites (predominantly MFI frameworks) have shown that chain growth selectivity depends sensitively on temperature and residence time, both of which tend to favor secondary reactions of the primary oligomers formed. Here, we address the underpinning descriptors for the effects of the shape, size, and connectivity of the confining voids and of the acid strength and the intracrystalline density of protons on selectivity.

These descriptors are specifically examined for ethene, propene and isobutene (C_n ; $n=2,3,4$) oligomerization reactions in the context of the relative rates of oligomerization and of secondary isomerization and β -scission reactions of the primary alkenes formed. The detailed chemical speciation of the isomers formed and the rate of intramolecular scrambling of ^{13}C atoms within the oligomers derived from 2- ^{13}C -propene show that frequent readsorption and hydride and methyl shifts within primary isomer products lead to skeletal isomers, regioisomers, and stereoisomers at concentrations solely determined by their interconversion thermodynamics, even at very low reactant conversions. Consequently, isomer distributions within chains of a given size are similar on all solid acids, in spite of their large differences in reactivity, void structure, proton density, and acid strength. Such distributions do not depend on conversion or residence time or on reactant pressures for all alkenes. These findings illustrate the preeminence of thermodynamics in determining isomer selectivities in the products formed via alkene oligomerization catalysis.

This study shows that one-dimensional zeolites (TON, MOR) and mesoporous acids, such as Al-MCM-41, amorphous silica-alumina (SiAl) and silica-supported polyoxometalates (POM), preserve the chain length of oligomerization products by allowing the unobstructed diffusion of any chains that can form within their channels and voids. In contrast, three-dimensional zeolites (MFI, BEA, FAU), with void structures that exhibit ubiquitous undulations created by channel intersections (MFI, BEA) or cage-window frameworks (FAU), allow the local formation of oligomers larger than the intervening passages, thus requiring β -scission events for the facile egress of products. The selectivity to true oligomers did not depend on acid strength, irrespective of whether active protons reside within mesoporous voids (POM, MCM-41/SiAl) or in MFI microporous channels (X-MFI, X=Al, Ga, Fe, B). The strength of acid in these solids influences the addition of alkenes to alkoxide oligomers and the β -scission of the larger alkoxides to the same extent, because these reactions involve ion-pair transition states with similar charges at their cationic organic moiety and its conjugate anion. In fact, these reactions merely represent two opposite directions of the same elementary step, albeit with the possibility that different C-C are formed and cleaved in the two directions.

These findings indicate that oligomerization selectivities depend on the size, shape and connectivity of the framework because of how such structural features influence the diffusion of the largest products that can form within the local confining environment. The design of such features into the local environment around protons thus becomes pertinent for the chain length distribution in oligomerization product, but are inconsequential for their skeletal structure or the location of their double bonds; these molecular features are set by the equilibration of the gaseous alkene isomers, a conclusion that required the systematic reconsideration of previously reported formation Gibbs free energies for hexene isomers.

2.2. Experimental Methods

2.1. Measurements of alkene chain growth selectivity

MFI, TON, MOR, BEA, FAU, MCM-41 and amorphous silica-alumina (SiAl) samples were obtained from commercial sources (as described in Table 1). All zeolites were exchanged with NH_4 cations using procedures described elsewhere [12,13]. The number of protons in each sample was measured from the amount of NH_3 evolved upon heating NH_4 -exchanged samples. Transmission electron microscope (TEM) images were taken on Philips/FEI Tecnai 12 microscope operated at 120 kV for crystal size estimates by suspending the samples were in ethanol and dispersing them onto ultrathin carbon/holey carbon films supported on 400 mesh Cu grids (Ted Pella Inc.). Keggin POM clusters were dispersed onto amorphous silica (Cab-O-Sil HS-5; $310 \text{ m}^2 \text{ g}^{-1}$; $1.5 \text{ cm}^3 \text{ g}^{-1}$ pore volume). The number of protons in Keggin POM clusters and mesoporous aluminosilicates (MCM-41, SiAl) was determined from the amount of a non-coordinating titrant (2,6-di-*tert*-butylpyridine) required to fully suppress rates during 2-methyl pentane isomerization [14] and propene oligomerization reactions, respectively; the proton densities in all samples are listed in Table 1. Solid acid powders were pelleted, crushed and sieved to retain 180-250 μm aggregates before used in catalytic experiments.

Table 1. Framework structure, source, Si/Al ratio and proton counts for the solid acids used in this study

Acid	Source	Si/Al Ratio ¹	H ⁺ /Al (H ⁺ /u.c.) Ratio
BEA	Zeolyst	11.8	0.40 (2.0) ²
MFI	Zeolyst	16.6	0.65 (3.6) ²
MFI	Zeolyst	29.2	0.78 (2.5) ²
MFI	Zeolyst	43.8	1.0 (2.1) ²
MFI	Zeolyst	173	0.64 (0.36) ²
MFI	Sud-Chemie	14	0.71 (4.3) ²
MFI	Tri-Cat	25	0.35 (1.3) ²
MOR	Zeolyst	10	0.86 (2.9) ²
TON	BP	39	0.55 (0.36) ²
TON	BP	49	0.50 (0.26) ²
TON	BP	24	0.38 (0.40) ²
FAU	Engelhard	7.5	0.37 (8.5) ²
Silica-Alumina	Sigma-Aldrich	5.5	0.25 ³
MCM-41	Sigma-Aldrich	39	0.3 ³
		Si/T Ratio ¹	H ⁺ /T Ratio ²
Ga-MFI	BP	45	0.86 (1.8)
B-MFI	BP	43	0.77 (1.7)
Fe-MFI	[13]	61	0.85 (1.3)
POM content on Silica (wt. %)		POM surface density (POM nm ⁻²)	Protons (H ⁺ /POM) ³
H ₃ PW ₁₂ O ₄₀		5	0.03
H ₄ SiW ₁₂ O ₄₀		5	0.03

¹from elemental analysis (ICP-OES; Galbraith Laboratories).

²from decomposition of NH_4^+ exchanged sample.

³from 2,6-di-*tert*-butylpyridine titration.

Oligomerization rates and selectivities were measured in a tubular reactor (316 stainless-steel, 12 mm I.D.) with plug-flow hydrodynamics. Temperatures were controlled using a resistively-heated furnace and the system pressure set by a backpressure regulator (Tempresco). NH₄-zeolites and mesoporous aluminosilicates were treated in 5% O₂ in He (83.3 cm³ g⁻¹ s⁻¹, Praxair) by heating to 818 K (at 0.025 K s⁻¹) and holding for 3 h to convert NH₄⁺ cations to H⁺ and then cooled to reaction temperature. Supported Keggin POM clusters in their H-form were treated in flowing He (50 cm³ g⁻¹ s⁻¹; 99.999%, Praxair) by heating to reaction temperature (503 K; at 0.083 K s⁻¹).

Ethene (99.9%, Praxair), propene (99.9%, Praxair) and isobutene (99.9%, Praxair) were introduced into a He stream (99.999%, Praxair) using electronic mass flow controllers at the molar rates required to achieve the desired pressures. The reactor effluent was transferred through heated lines (>373 K) to a gas chromatograph (Agilent 6890). Reactant and product concentrations were measured by flame ionization detection after chromatographic separation (methyl silicone Agilent HP-1 column, 50 m x 0.32 mm x 1.05 μm); the elution order of products was determined from injections to a gas chromatograph fitted with the same column type, but with flame ionization and mass spectrometric detectors (Agilent 7890 A/Agilent 5975C) and compared to known retention times of hydrocarbon mixtures on similar columns [15,16]. Oligomerization rates were normalized by the number of protons in each sample; selectivities were calculated on a per carbon basis.

2.2.2. Calculating the selectivity to true oligomers from measured product distributions

The chain length of the products formed from an alkene with n carbons reflects the relative contribution of C-C bond formation (oligomerization) and cleavage (β-scission). Product distributions become increasingly binomial after many sequential β-scission and oligomerization events. An underlying binomial distribution was used to describe those molecules with chain lengths different from those of true oligomers (C_n, C_{2n}...) and then used to predict the molar concentration of products made from β-scission with chain lengths the same as true oligomers (Eq. 1):

$$[C_{m \bullet n}] = [C_{m \bullet n, t}] - [C_{m \bullet n, b}] \quad (1)$$

where $[C_{m \bullet n, t}]$ is the total molar concentration of product with $m \bullet n$ carbons formed from a reactant with n carbons and $[C_{m \bullet n, b}]$ is the molar concentration of species with $m \bullet n$ carbons predicted from an underlying binomial distribution fit to products of intermediate length (i.e. not C_n, C_{2n}...). The molar concentrations of oligomers with $m \bullet n$ carbons that have not undergone β-scission ($[C_{m \bullet n}]$), were used to calculate a true oligomer selectivity parameter defined by:

$$\chi_n = \frac{\sum_{m=1} [C_{m \bullet n}]}{\sum_{l=1} [C_{l, t}]} \quad (2)$$

2.2.3. Mechanistic provenance of oligomerization products and their intramolecular ^{13}C scrambling in oligomerization products of 2- ^{13}C -propene

Kinetic and isotopic tracer experiments were carried out in a glass batch reactor [17], the contents of which were recirculated using a an oil-free graphite gear micropump (GA V23, Micropump). Gas samples were extracted from the recirculating stream using a sampling valve and transferred through heated lines ($>373\text{ K}$) into a gas chromatograph equipped with flame ionization and mass spectrometric detectors (Agilent 7890 A/Agilent 5975C) each connected to a capillary column (HP-1, methyl silicone, 50 m x 0.32 mm x 1.05 μm film) to determine the chemical and isotopic composition of the reactor contents.

^{13}C -labeled propene (2- ^{13}C -propene, 99 % atom ^{13}C , Sigma-Aldrich) was used as the reactant with He as balance (99.999 %, Praxair). Catalysts (TON, MFI, SiAl and HSiW) were treated as described in Section 2.1 before exposure to 2- ^{13}C -propene. Isotopologue distributions of the products were determined using previously reported matrix deconvolution methods [18]. The labeled reactant was used to determine the origins of the products formed (oligomerization vs. subsequent β -scission) and, more specifically, the number of times a product has traversed an oligomerization-cracking cycle [17]. These distributions consist of a unimodal component superimposed with a component that approaches a binomial distribution; the products were separated into the carbon fraction of molecules that contribute to either the binomial or unimodal distribution, which were attributed to contributions from β -scission and oligomerization, respectively. The fraction of a given isotopologue in species j with l carbon atoms that has i ^{13}C atoms was described by:

$$\left[I^{13}\text{C}_i \right]_j = \left[\chi_j U_j + (1 - \chi_j) \left(\frac{I!}{(l-i)!i!} \left(\langle f_{^{13}\text{C}} \rangle \right)^i \left(1 - \langle f_{^{13}\text{C}} \rangle \right)^{l-i} \right) \right] \quad (3)$$

where the first term of the sum ($\chi_j U_j$) corresponds to the unimodal contribution with carbon fraction χ_j and the second term reflects the contribution from the part of the distribution that becomes increasingly binomial with increasing $(1 - \chi_j)$ values. Here, U_i is a unimodal component at the expected number of ^{13}C in the species j (e.g. 2 labels for any C_6 isomer) and $\langle f_{^{13}\text{C}} \rangle$ is the mean ^{13}C fraction in species j as calculated by Equation 4.

$$\langle f_{^{13}\text{C}} \rangle_j = \frac{\left[I^{13}\text{C}_i \right]_j}{I} \quad (4)$$

The value of χ_j was determined by regressing the measured isotopologue distribution to the functional form of Equation 3. The calculated χ_j value is numerically the same as the true oligomer selectivity parameter (Eq. 2), but it is specific to each distinct chemical species j instead of averaging over the entire product slate.

The labeled reactant was also used to determine the extent of isomerization within products with the same number of C-atoms. Isomerization causes intramolecular scrambling of ^{13}C because cyclopropyl carbenium ion transition states mediate methyl shifts that result in both isomerization and intramolecular exchange among C-atoms. The amount of ^{13}C label at each C position in a given chemical isomer molecule was determined from the isotopic content of its

mass fragments after chromatographic separation of the isomers. Rapid intramolecular scrambling would give the same ^{13}C fraction at each C-position, as prescribed by Equation 4. An isotopic scrambling conversion (σ) is defined here in Equation 5 residual sum of squares:

$$\sigma = 1 - \frac{\sum_{k=1}^{k=l} (f_k - \langle f_{^{13}\text{C}} \rangle)^2}{\sum_{l=1}^{k=l} (f_{\text{expected}} - \langle f_{^{13}\text{C}} \rangle)^2} \quad (5)$$

where f_k is the measured ^{13}C fraction at position k , f_{expected} is the ^{13}C fraction at each position expected without intramolecular scrambling for each distinct chemical isomer and $\langle f_{^{13}\text{C}} \rangle$ is the ^{13}C fraction of a fully scrambled molecule, which is equal at all positions. This expected location is used to normalize the residual sum of squares. For example, a hexene isomer formed via 2- ^{13}C -propene oligomerization would lead to ^{13}C -atoms at the 2 and 4 positions and ^{12}C atoms at the other four positions. Values of σ of 0 and 1 correspond to unscrambled and fully scrambled molecules, respectively.

The absence of significant intramolecular scrambling during ionization and detection in the mass spectrometer chamber was determined by introducing 1- ^{13}C -hexane and its alkene analogs, formed via dehydrogenation of 1- ^{13}C -hexane on Pt/Al₂O₃ into the spectrometer chamber. The Pt/Al₂O₃ sample (1.5% wt.) [14] was used in the recirculating reactor to dehydrogenate 1- ^{13}C -hexane into an equilibrated mixture of alkene regioisomers at 573 K (0.4 kPa 1- ^{13}C -hexane).

2.2.4. Thermodynamics of hexene isomer interconversions

The approach to equilibrium (η) for the formation of each C₆ chemical isomers (j) from 2-methyl-2-pentene (2M2P), chosen here as reference, is given by:

$$\eta = \frac{\left(\frac{C_j}{C_{2M2P}} \right)}{K_{2M2P \leftrightarrow j}} \quad (6)$$

Here, $K_{2M2P \leftrightarrow j}$ is the equilibrium constant for 2-methyl-2-pentene conversion to the j hexene isomer, present at a concentration C_j . The values of the equilibrium constants were calculated from high conversion data obtained from the recirculating batch reactor (described in Section 3.1). These values were compared with literature values [19,20] and with values obtained using corrected group additivity methods [21]. Previously tabulated Gibbs free energies for isomer formation varied among these sources, by as much as 15 kJ/mol (at 503 K) in some cases, leading to widely different η values depending on the source used. All equilibrated isomers of a given length (η values near unity at all conversions) were treated as a kinetic lump in all subsequent kinetic analyses, in accordance with the chemical speciation and isotopic scrambling data shown here.

2.3. Results and Discussion

2.3.1. Hydride and methyl shifts reactions in alkoxides formed via C_3H_6 oligomerization

Hydride and methyl shifts in bound alkoxides lead to a mixture of skeletal and regioisomers within each chemical species of a given carbon number derived from these alkoxides. The observed isomers are grouped here according to their backbone skeletons: 2-methylpentenes (2-MP), 3-methylpentenes (3-MP), linear hexenes (n-H) and 2,3-dimethylbutenes (23-DMB). 2,2-Dimethylbutenes were not detected because quaternary C-atoms form via skeletal isomerization through unstable carbenium-ion transition states with significant primary character [14]. The concentrations of each chemical isomer (relative to 2M2P) did not vary with C_3H_6 conversion as it changed with residence time (Supplemental Information, Fig. S1; SI), except for 2,3-DMB, one of the slowest diffusing skeletal isomers in TON, the catalyst with the smallest channels; these concentration ratios also did not vary with changes reactant pressure (25-400 kPa C_3H_6 in Fig. S2; SI). These invariant approach to equilibrium parameters (η , Eq. 1) for all isomers, however, were neither 0 nor 1 (Fig. S3; SI) when estimated using reported thermodynamic data [19,20] and the deviation from one did not improve systematically with temperature (using data from [20]; Fig. S4 473-533 K; SI). Such data varied broadly among literature sources that used group additivity corrections, in some cases by as much as 15 kJ/mol (at 503 K; K_{eq} values tabulated from such data in Appendix; ΔG_{eq} in Fig. S5; SI).

Intermediate values of η that do not vary with residence time or reactant pressure must reflect either (i) a specific kinetic preference for a given isomer distribution formed directly from the oligomerization transition state (TS) and the absence of secondary readsorption and isomerization reactions or (ii) full equilibration among isomers but inaccurate thermodynamic data. The first possibility seems implausible in view of the equilibrated nature of adsorption-desorption process of alkene reactants and the facile nature of hydride and methyl shifts on solid acids [12,14]; this explanation is also at odds with the similar distributions observed on solid acids with very different acid strength and confining environments (Fig. S6; SI).

These arguments, taken together with the aforementioned inconsistencies among reported thermodynamic data, led us to reconsider the accuracy of tabulated free energies and to use instead the isomer distributions measured on a mesoporous sample (SiAl) at high fractional propene conversions (0.30) as the basis for the isomer equilibrium calculations on all other solid acids. The equilibrated nature of all regioisomers within each 2-MP, 3-MP and n-H skeletal group on TON, MFI and SiAl is evident from their η values obtained in this manner (Fig. 1); these η values are near unity even at propene fractional conversions below 0.05 and all temperatures, pressures, and conversions. We conclude from these data that hydride and methyl shifts are fast in C_6 oligomers and that the concentration of all isomers with a given carbon number depends only on their thermodynamics properties as gaseous species, even at very low conversions and modest temperatures (Fig. 1: 503 K). These η values were near unity for 2-MP, 3-MP and n-H backbones on all solid acids examined here (BEA and HSiW shown in Fig. S7; SI) at all propene fractional conversions (0.02-0.8; Fig. S8; SI) and all alkene pressures (2-500 kPa C_3H_6); similar conclusions are reached for C_4 and C_5 chains, indicative of their significant isomerization after they form via secondary β -scission of primary (C_6) or secondary (C_9 , C_{12} , ...) oligomerization products (Figs. S9 and S10 for C_5 ; SI).

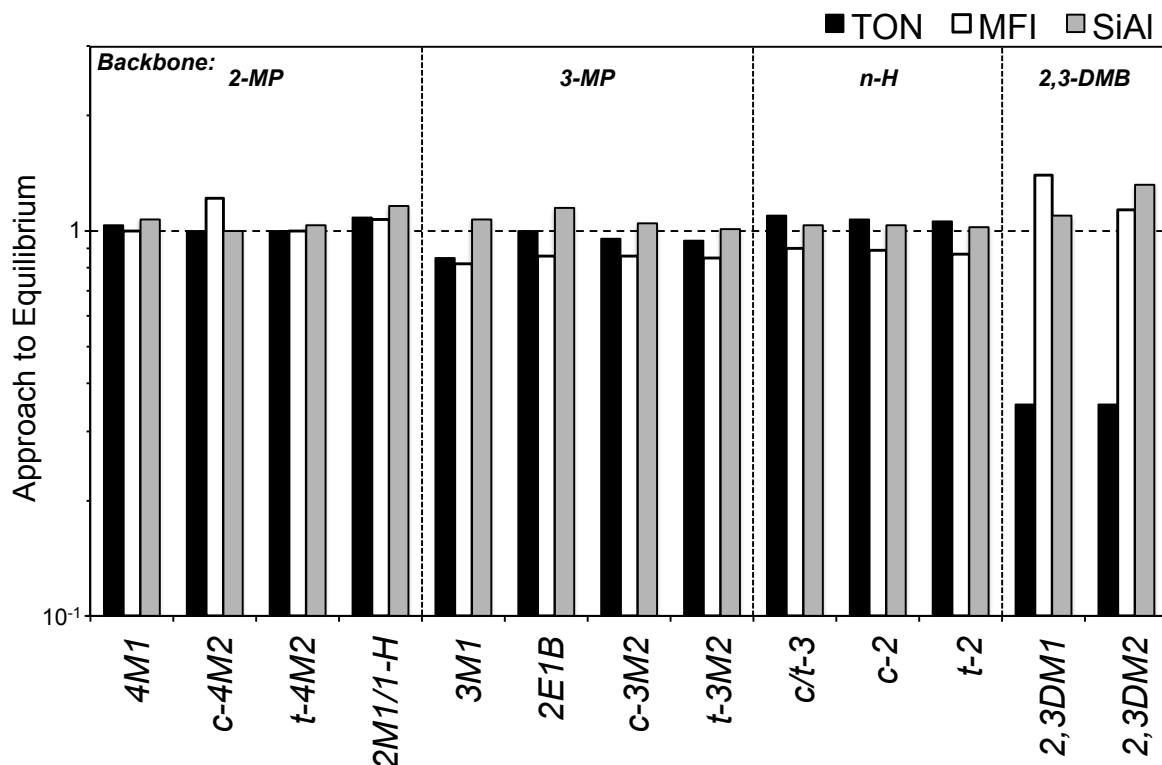


Figure 1. Approach to equilibrium for the formation of hexene isomers from 2-methyl-2-pentene on TON (black), MFI (white) and SiAl (gray) [503 K, < 0.05 C₃H₆ conversion, 60 kPa]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB). Data for BEA and HSiW are found in Figure S2 (SI).

Isomers with 2,3-DMB backbones are also present at near equilibrium levels on all solid acids, except TON; this appears to reflect the small one-dimensional 10-MR channels in TON (0.46 nm x 0.57 nm [22]), which can inhibit the formation or the diffusion of molecules with “bulkier” backbones. Indeed, molecular dynamics simulations show that n-heptane diffuses much faster than 2-methylhexane or 3-methylhexane (10-fold larger diffusivities at 600 K)[23]. On TON, these 2,3-DMB isomers approach their equilibrium concentrations as H⁺ densities increase (0.1 and 0.32 η values for 2,3-DM1B for 0.26 H⁺/u.c. (1.7 % conversion) and 0.36 H⁺/u.c. (1.1 % conversion), respectively) and as conversion increases with increasing residence time (0.22 to 0.93 for 0.1 % and 42 % conversion on 0.36 H⁺/u.c. TON) (details in Figs. S8 and S11; SI). These site density and conversion effects for 2,3-DMB isomers suggest that their lower on η values are likely to reflect their local equilibration within TON crystals but the slower diffusion of these bulkier isomers through such crystals. These diffusional hurdles are consistent with fast isotopic scrambling within 2,3 DMB isomers (Section 3.2), which indicates that chemical equilibrium is indeed locally attained during propene oligomerization

3.2. Isotopic evidence for fast methyl shifts in oligomers formed from 2-¹³C-propene

Methyl shifts cause intramolecular exchange of C-atoms among backbone locations; their rates can be inferred from the extent of which the locations of the two ¹³C-atoms in C₆ oligomers

formed from 2-¹³C-propene have shifted from their expected positions. An oligomerization event that forms 2MP backbones, for instance, would place these two ¹³C-atoms at positions 2 and 4 along the backbone, but the cyclopropyl carbenium ions that mediate methyl shifts (and the required concerted H-shifts) would cause to intramolecular scrambling [14,24]. Ultimately, very fast intramolecular methyl and hydride shifts would form isotopologues with the same ¹³C content at all locations throughout each chemical species.

Figure 2 shows the isotopologue distributions and ¹³C contents (total and per carbon) in the parent ion and in the pentyl, butyl and propyl fragment ions derived from the 2M2P isomer formed via C₃H₆ oligomerization on TON (8 % conversion, 2 kPa 2-¹³C-propene, 0.36 H⁺/u.c., 503 K). The two ¹³C atoms in 2M2P are distributed uniformly among all six C-atoms (0.29-0.37 ¹³C fraction; Fig. 3 center) within experimental accuracy. Uniform intramolecular ¹³C distributions were also evident in representative isomers examined from each skeletal backbone: t-4M2P (formed from 2M2P via H-shift), t-2H (via chain lengthening), t-3M2P (via methyl shift), and 23DM2B (via branching) (Fig. 3). The ¹³C-content in each C-atom cannot be individually determined for some groupings of C-atoms (denoted by the ovals in Fig. 3), but the combined isotopic content in each grouping is consistent with fast intramolecular scrambling. Isotopic scrambling conversions (σ , Eq. 5) are near unity at all conversions for all the skeletal isomers and regioisomers formed from 2-¹³C-propene on TON, MFI, SiAl and HSiW (0.02-0.8 fractional conversion, 2 kPa 503 K; Fig. 4), consistent with fast skeletal and double-bond isomerization on all solid acids. These isotopic data demonstrate the local attainment of chemical equilibrium at acid sites; they also indicate that the observed deviations from chemical equilibrium for the bulkier 23DMB isomers on TON (Figs. 1, S3 and S4) must reflect diffusional constraints instead of intrinsic kinetic hurdles.

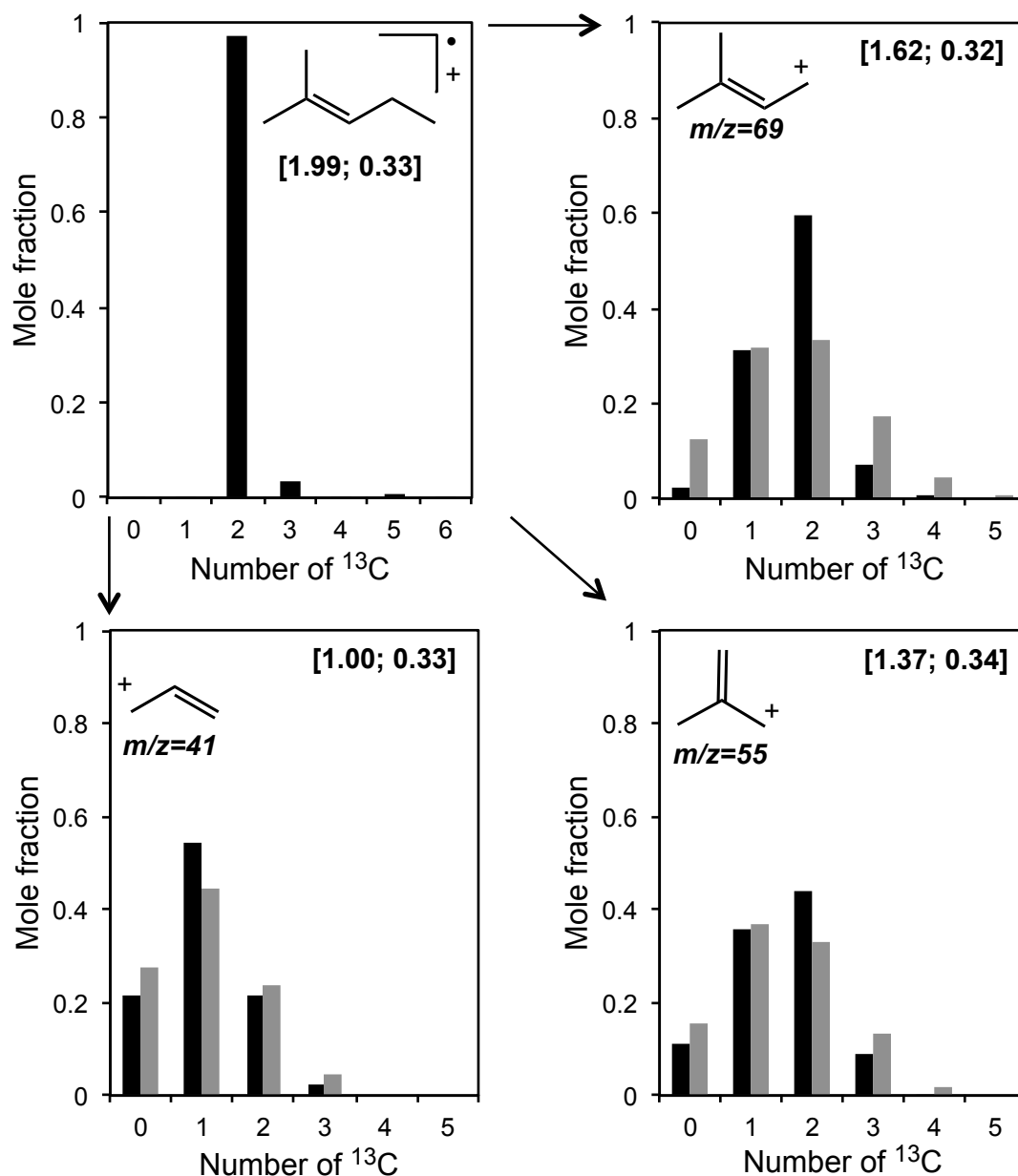


Figure 2. ^{13}C isotopologue distributions for the parent and the pentyl, butyl and propyl fragment ions of 2M2P was formed on TON [8 % C_3H_6 conversion, 2 kPa 2- ^{13}C -propene, 503 K]. Average number of ^{13}C -atoms and fractional amount per carbon are shown in the brackets, respectively for each ion. The expected binomial distribution for the total ^{13}C content of each ion is indicated by light gray bars.

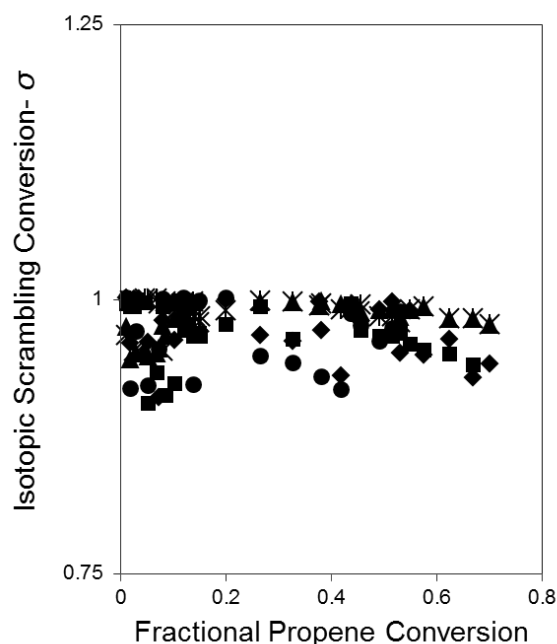
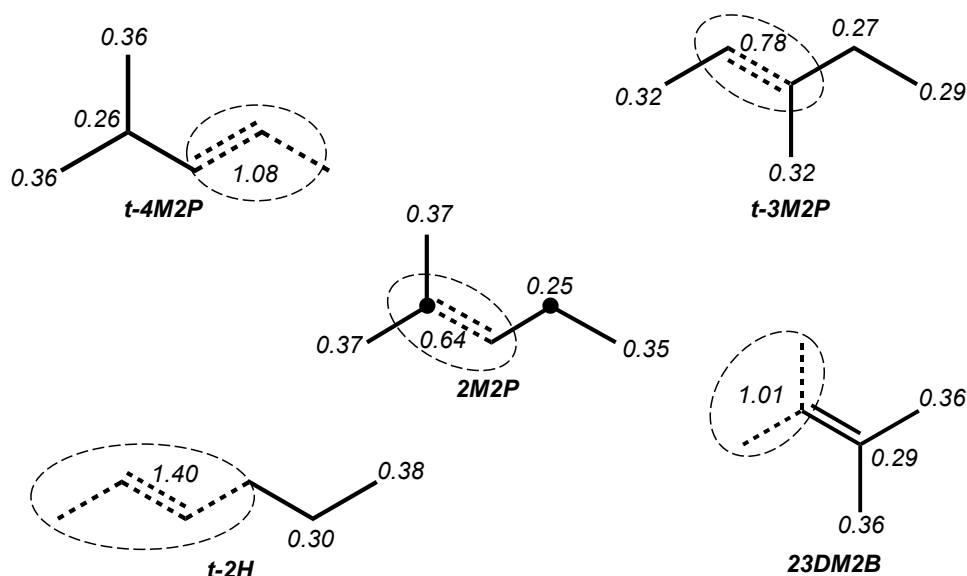


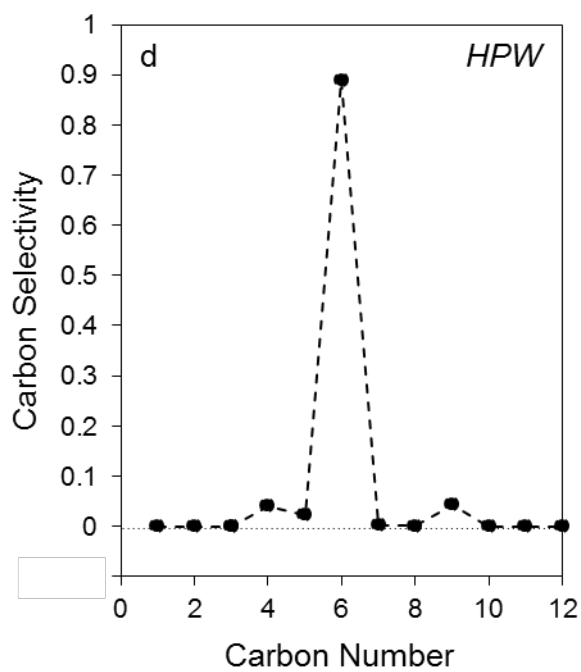
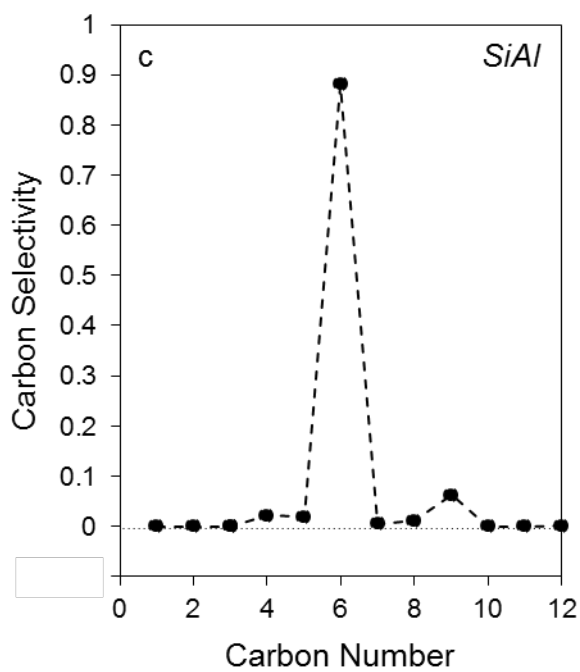
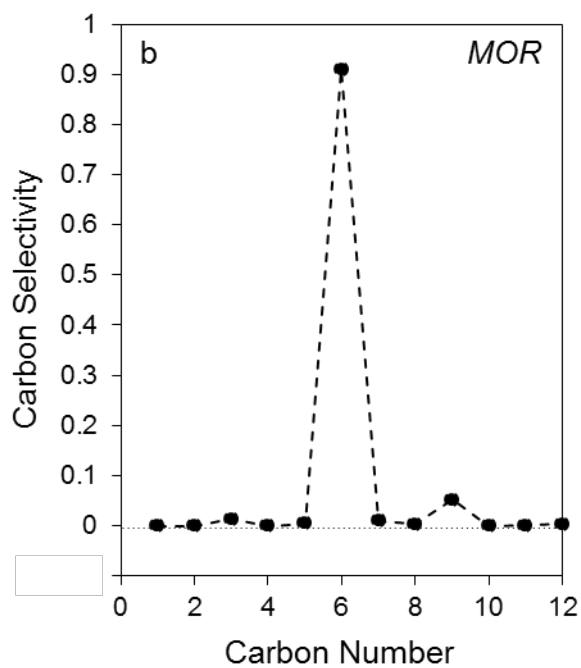
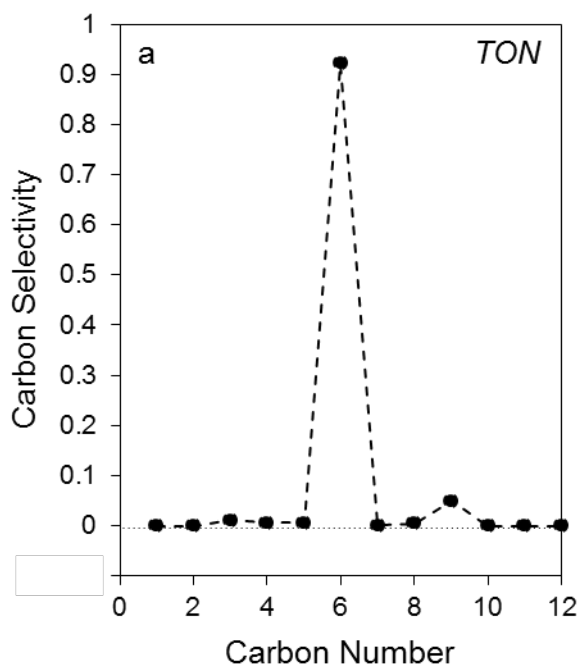
Figure 4. Isotopic scrambling conversion (σ ; Eq. 6) for hexene isomers 2M2P(◆), trans-4M2P(*), trans-2-H(●), trans-3M2P(■) and 23DM2B(▲) on TON, SiAl, MFI and HSiW [2 kPa 2- ^{13}C -propene, 503 K].

The observed rapid intramolecular scrambling did not occur within the mass spectrometer chamber during ionization and detection. The introduction of 1-¹³C-hexane or its alkene analogs (formed via dehydrogenation of 1-¹³C-hexane on Pt/Al₂O₃; 35% conversion; 0.4 kPa 1-¹³C-hexane; 573 K) led to pentyl and butyl fragments with isotopic contents consistent with unscrambled 1-¹³C-hexane and 1-¹³C-t-3-hexene molecules (0.51-0.56; Table S1; SI), indicating that neither alkanes nor alkenes isomerize during ionization. The very small deviations from the expected values (0.50) are in agreement with the slow rates of such intramolecular rearrangements reported for linear octenes during ionization and detection in mass spectrometers [25]. The intramolecular scrambling occurring in the reactor is also evident from the fact that products that can only be made from β -scission exhibit a binomial number of carbons, which reflects they were formed from intramolecularly scrambled larger molecules (Fig. S13; SI).

These data, taken together with the equilibrium isomer distributions derived from chemical speciation, are consistent with fast interconversions among isomers at all conditions of propene oligomerization. Such equilibration reflects the thermodynamics of gaseous alkene isomers; it provides evidence for the very rapid communication between alkenes and surface protons via adsorption-desorption steps, even at the very short residence times that lead to differential propene conversions. Such equilibrated adsorption-desorption processes for products as well as propene reactants also show that neither reactant adsorption nor product desorption can be the kinetically-relevant steps in oligomerization catalytic sequences. This rapid intramolecular equilibration among skeletal and double-bond alkene isomers, even for the 2,3-DMB isomer backbones that did not attain full chemical equilibrium on TON, (Figs. 3 and 4), precludes any determination of individual rates of formation of each isomer from oligomerization transition states. The prevalence and previous use of inaccurate thermodynamic data may have lead to equivocal claims of kinetic and even shape selectivities in previous studies [2,26]. Any deviations from the thermodynamic distribution of gaseous alkene isomers in oligomerization reflect instead diffusional constraints for specific isomers. The equilibrated nature of all isomers of chains with a given number of C-atoms allows their rigorous lumping as a single chemical species in all rate and selectivity expressions.

2.3.3. Discerning origins and fate of products formed via oligomerization and secondary β -scission events

Propene oligomerization forms “true isomers” with l number of C-atoms ($l=m \cdot n$; C₆[−], C₉[−], C₁₂[−], ... for $n=3$); these isomers can undergo secondary β -scission to form chains of intermediate chain length ($l \neq m \cdot n$; C₄[−], C₅[−], C₇[−], C₈[−], ... for $n=3$) (Scheme 1). Figure 5 shows the fraction of the C-atoms in the converted propene that appear as chains with l C-atoms (503 K, 60 kPa C₃H₆) at low reactant fractional conversions (< 0.05) on TON, MOR, SiAl, and SiO₂-supported H₃PW₁₂O₄₀ (HPW) (Figs. 1a-1d) and on BEA, MFI and FAU (Figs. 1e-1g). The products formed are predominantly alkenes, with only trace concentrations of small alkanes ($n \leq 6$; < 2.5 % C-atoms), which form via H-transfer from larger alkenes to alkoxides (Scheme 1) together with dienes and cycloalkenes co-products that become detectable only at higher propene conversions (Fig. S13; SI; < 0.2 % C-atoms of products).



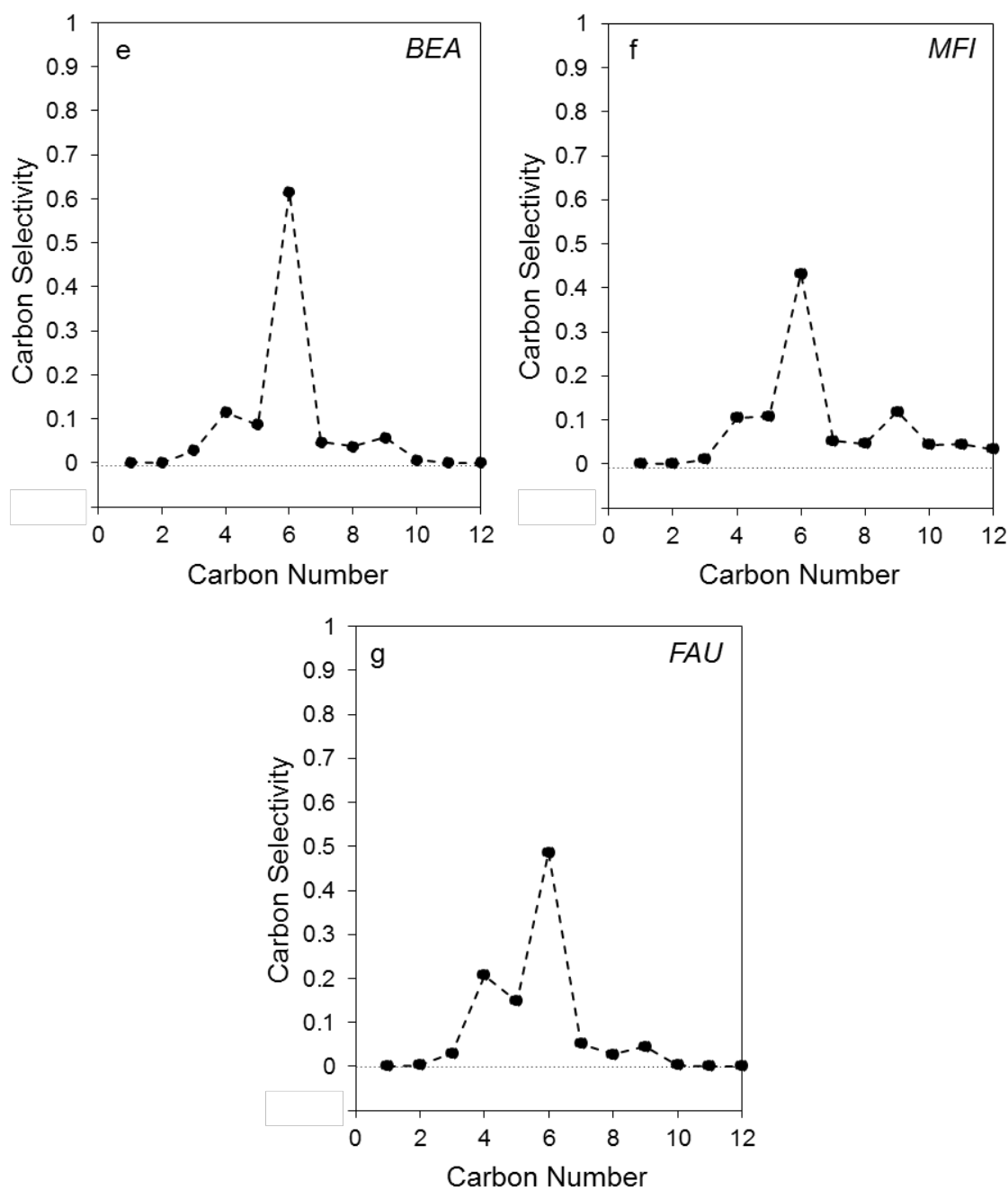
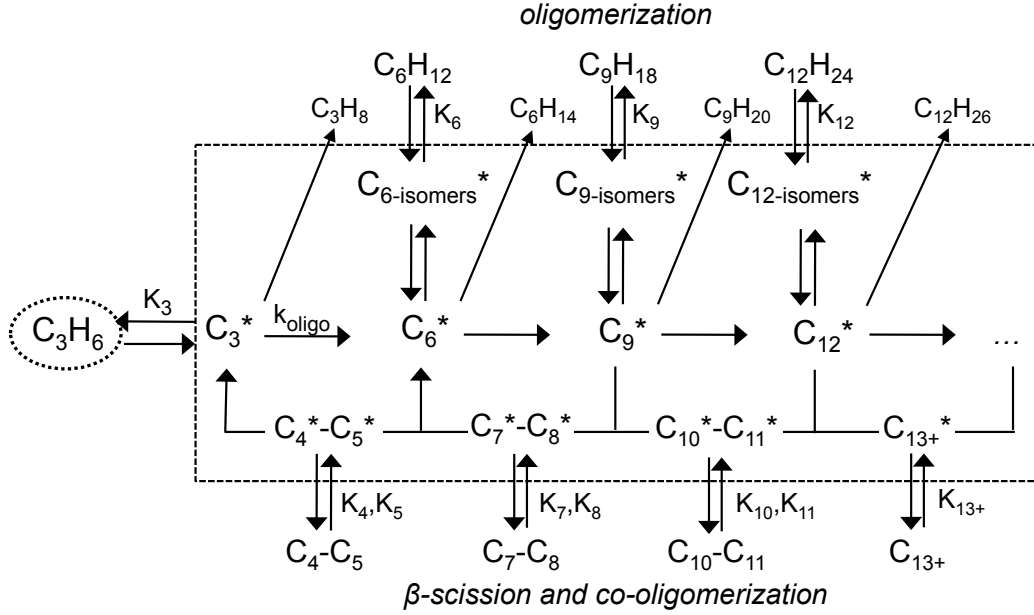


Figure 5. Carbon selectivities for chains in l number of carbon atoms formed in C_3H_6 oligomerization reactions with propene fractional conversions given in parentheses: (a) TON (0.005), (b) MOR (0.009), (c) SiAl (0.005), (d) HPW (0.003), (e) BEA (0.004), (f) MFI (0.009) and (g) FAU (0.003) [503 K, 60 kPa].



Scheme 1. C_3H_6 oligomerization-cracking reaction network on solid acids. C_l^* represents alkoxides of l carbons that are equilibrated with their gas-phase concentrations by K_l and k_{oligo} is the rate constant for oligomerization.

The different carbon number distributions observed on different solid acids (Fig. 5) can be expressed in terms of the relative rates of C-C bond formation and cleavage events. β -Scission can occur for an alkene with l C-atoms with a rate constant $k_{\beta,l}$; chains with fewer than six C-atoms do not undergo β -scission because of the unstable carbenium ions involved, consistent with the absence of ethene or methane in products (Fig. 5) and [27].

Oligomerization steps that form true oligomers include the addition of propene to any alkoxide derived from an alkene of a length corresponding to those of true oligomer ($l=m \cdot n$). For example, the ratio of these rates for C_6 alkenes is given by:

$$\frac{r_{\beta,6}}{r_{oligo,6}} = \frac{k_{\beta,6} K_6 P_6}{k_{oligo,3} K_3 (P_3)^2} \quad (7)$$

where K_l is the equilibrium constant for alkoxide formation with l C-atoms, $k_{oligo,3}$ is the rate constant for formation of C_6 oligomers and P_l is the pressure of an alkene with l C-atoms. In order to account for all products, Equation 7 must be summed over all carbon numbers (Eq. 8):

$$\frac{r_{\beta}}{r_{oligo}} = \frac{\sum_{l=6} k_{\beta,l} K_l P_l}{\sum_{m=1} k_{oligo,m} K_{3m} P_{3m}^2} \quad (8)$$

where $k_{oligo,m}$ is the rate constant for oligomerization step m with propene and oligomer with $3m$ C-atoms. The true oligomer selectivity parameter (χ) (Eq. 2) is related to the ratio of rates in Equation 8 by:

$$\chi = 1 - \frac{r_{\beta}}{r_{oligo}} \quad (9)$$

This χ parameter gives the fraction of all C-atoms in the converted reactants that remain as true oligomers by exiting the catalyst bed before a β -scission event (Section 2.2). The secondary nature of β -scission events leads to χ values that decrease with increasing propene conversion (Fig. 6). The χ values increase, however, with increasing propene pressure for samples that do not have χ values of unity, consistent with Equations 7 and 9 (conversion range 0.02-0.04; Fig. S14; SI).

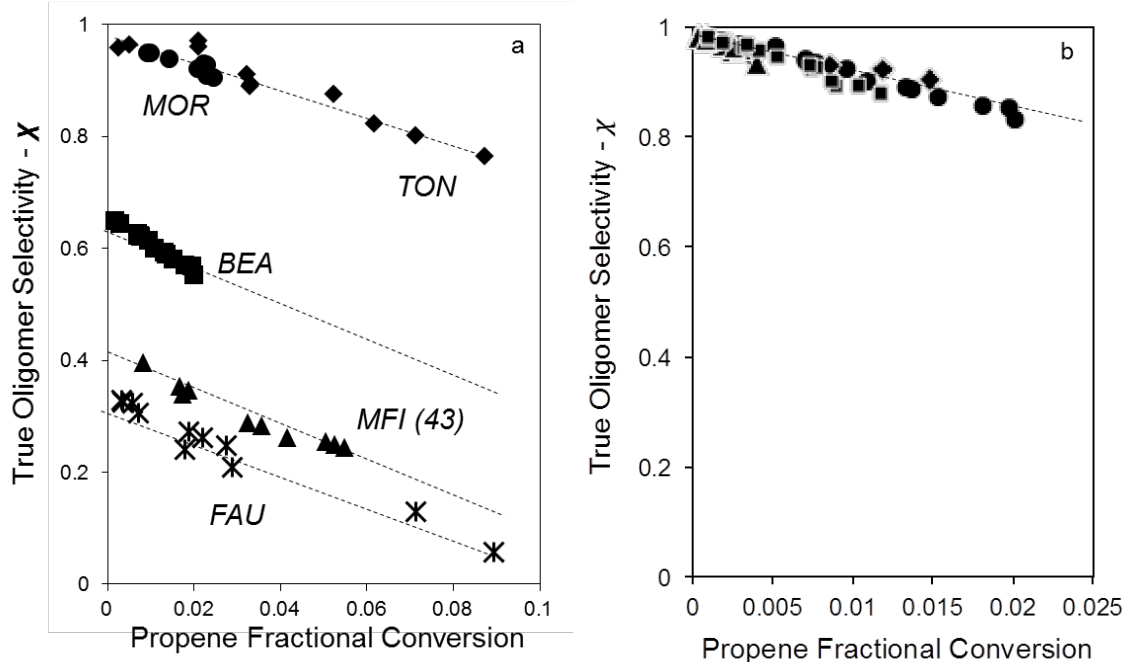


Figure 6. True oligomer selectivity (χ ; Eq. 2) for C_3H_6 oligomerization as a function of propene fractional conversion for zeolites (a) TON (◆), MOR (●), BEA (■), MFI (▲) and FAU (✱) and mesoporous acids (b) MCM-41 (■), SiAl (●), HPW (◆) and HSiW (▲) at [60 kPa, 503 K, dashed lines are trendlines to guide the eye].

The formation of C_4 and C_5 products from propene (and others with $l \neq m \cdot 3$ C-atoms) provide direct evidence of the occurrence of β -scission events. β -Scission in larger species, however, can also form products of the same length as oligomers, an occurrence for which we account by fitting a binomial distribution to the intermediate C-length products and then subtracting it (Section 2.2; Fig. 7). The contribution from this distribution is much greater in 3-D zeolites (MFI, BEA, FAU) than other acids (Figs. 5 and 7) and it becomes increasingly binomial with increasing conversion, indicating fewer of the observed oligomers are in fact “true oligomers”. The use of $2\text{-}^{13}\text{C}$ -propene can also rigorously quantify the fraction of “true oligomers” in the products. The intervening intramolecular ^{13}C scrambling that occurs with oligomerization- β -scission events (Section 3.2) leads to a binomial distribution in the number of

^{13}C -atoms in a product formed from cleaving of a fully intramolecularly scrambled species. For example, each C_6 formed from 2- ^{13}C -propene dimerization contains two ^{13}C -atoms (Fig. 8a; e.g., 2M2P on TON at low conversions (dark grey)). Isotopologues of C_6 isomers with more and less than two ^{13}C -atoms start to appear as conversion increases (Fig. 8a and b; light gray for both TON and MFI). The shift from a unimodal to a binomial distribution suggest that fewer “true oligomers” leave the catalyst bed intact, while an increasing number form via β -scission of larger oligomers as conversion increases with increasing residence time. This is consistent with the observed binomial isotopologue distributions of products that can be made only via β -scission ($\text{C}_4^=$ and $\text{C}_5^=$; Fig. S13; SI).

The isotopologue distributions shown in Figure 8 indicate that the fraction of 2M2P isomers that leave before β -scission ($\chi_{2\text{M2P}}$; Eq. 3) is smaller on MFI than TON. In fact, both chemical speciation and isotopic labeling experiments show that MFI samples give smaller χ values and more binomial-like chain length distributions (Figs. 5-8) than TON samples at all propene conversions and pressures. The sections that follow address the mechanistic underpinnings for these differences and also extend the effects of void structure to other reactants and zeolite frameworks, while also addressing the role of acid strength in determining oligomerization selectivity.

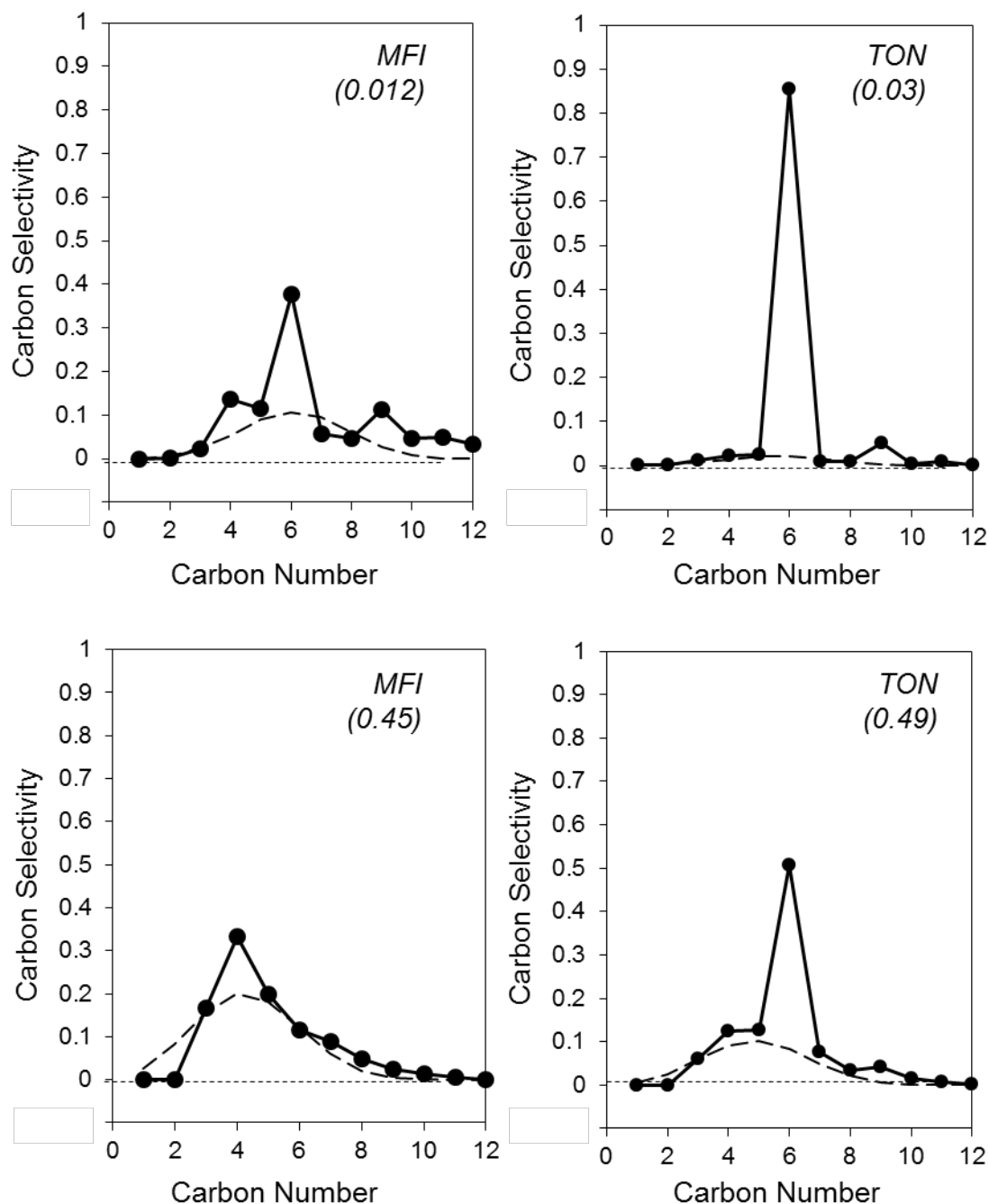


Figure 7. Carbon selectivity for C_3H_6 oligomerization on MFI and TON at either low (0.012 and 0.03, respectively; top) or high C_3H_6 fractional conversion (0.45 and 0.49, respectively; bottom) with non-oligomer products fit to a binomial distribution (--) [503 K, 60 kPa]. The amount of reactant C_3H_6 shown is calculated from the binomial distribution.

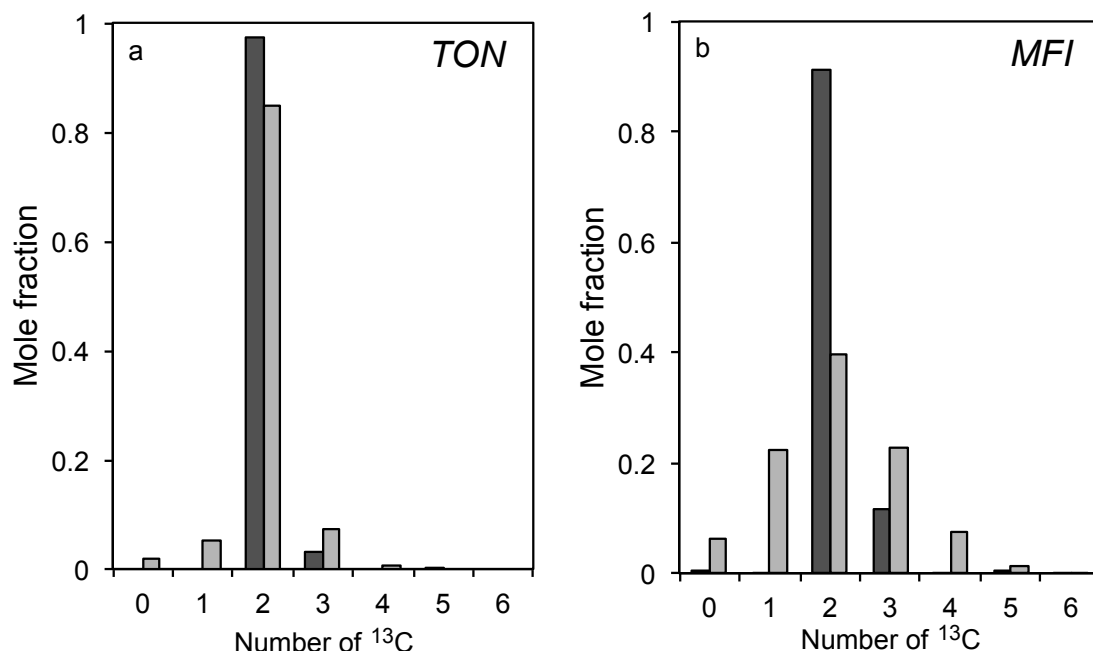


Figure 8. Comparing isotopologue distribution for 2-methyl-2-pentene on TON (a) at low (0.03; dark gray) and high fractional conversion (0.49; light gray) and on MFI (b) at low (0.01; dark gray) and high fractional conversion (0.45; light gray) [2 kPa 2- ^{13}C -propene, 503 K].

2.3.4. Relative rates of oligomerization and β -scission on solid acids with different frameworks

The effects of framework structure on the relative rates of oligomerization and β -scission, described by the χ values for each solid acid, were examined for a broad range of aluminosilicates frameworks. The data in Figure 6 suggest that one-dimensional zeolites, with channels of uniform cross section, and mesoporous solids, with channels significantly larger than the oligomers formed, lead to higher χ values than three-dimensional zeolites at all conversions; three dimensional zeolites exhibit fluctuations in cross sectional channel areas that molecules must traverse as they form and diffuse through the void structure.

We examine the effects of such undulations in a more systematic manner by using the ratio of the pore limiting diameter (PLD) to the largest cavity diameter (LCD) for each zeolite framework [28] as a suitable and quantitative descriptor. We turn to this undulation parameter (Ω) as a metric because channel size, by itself, cannot account for the much greater contribution of β -scission on MFI and FAU than on TON and MOR despite the fact that TON and MFI (10-MR zeolites) and FAU and MOR (12-MR zeolites) share similar connecting apertures. Zeolites with voids larger than the channels connecting such voids give PLD/LCD (Ω) ratios smaller than unity (MFI (3-D 10-MR channels), FAU (3-D cages with 12-MR windows) and BEA (3-D, 12-MR channels); Fig. 9). One-dimensional zeolites, here TON (10-MR) and MOR (12-MR with 8-MR side pockets), and mesoporous MCM-41 give Ω values of unity, because they lack undulations in their channels. SiAl and the SiO_2 silica support for the POM clusters consist of colloidal aggregates with evident cross-sectional changes in their voids, but their dimensions (2.4 nm) are larger than those of the largest chains that are likely to form in oligomerization reactions.

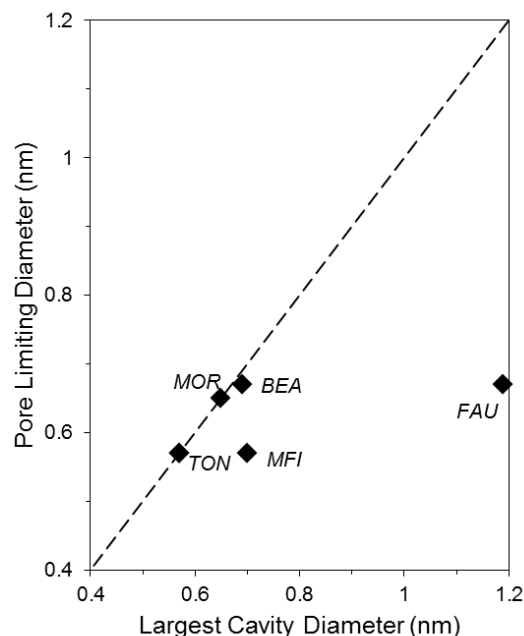


Figure 9. Largest cavity diameter plotted against pore limiting diameter for various zeolites. The dashed line represents a unity ratio.

MFI contains intersecting sinusoidal and straight channels (0.51-0.56 nm) that create a large void (0.7 nm; [22,28,29]). Such large voids can accommodate larger transition states, such as those required for subsequent addition of alkenes to C_6 alkoxides, than their intervening connecting channels and apertures. The larger oligomers thus formed must egress the void structure through these smaller intervening channels. The concomitant diffusional hurdles cause the retention of these oligomers within MFI crystals (and the other 3-D zeolites), until smaller molecules form via β -scission events. The cylindrical channels in TON, in contrast, cannot grow chains larger than those able to egress from the void structure. The absence of intersections, and of the larger voids or cage-like structures that such intersections form, leads to χ values near unity, as observed previously without a definite mechanistic interpretation [30]. Thus, the Ω parameter, defined here as the PLD/LCD ratio, represents a more appropriate description than the specific respective dimensions of the apertures or cages in these porous solids.

High χ values were also observed on one-dimensional MOR zeolites (Fig. 10) and on all mesoporous samples (Fig. 6), in spite of their much larger channels and voids. These similar selectivities indicate that the size of the voids do not directly influence the extent of β -scission. Instead, β -scission is only required to occur when a restriction along the diffusional path selectively blocks the diffusion of larger oligomers, which can form only in voids large enough to accommodate the transition states of subsequent C-C bond formations. True oligomer selectivity parameters (χ) decrease as Ω values decrease and become much smaller than unity for all three-dimensional zeolites (MFI, BEA, FAU; Fig. 10). Such trends reflect the ability of larger voids to form larger oligomers that must undergo β -scission to allow their facile egress as smaller chains through the smaller channels that connect such larger voids. These trends become much stronger as the difference in size between the void and the subsequent channel, which causes fewer oligomers to egress intact.

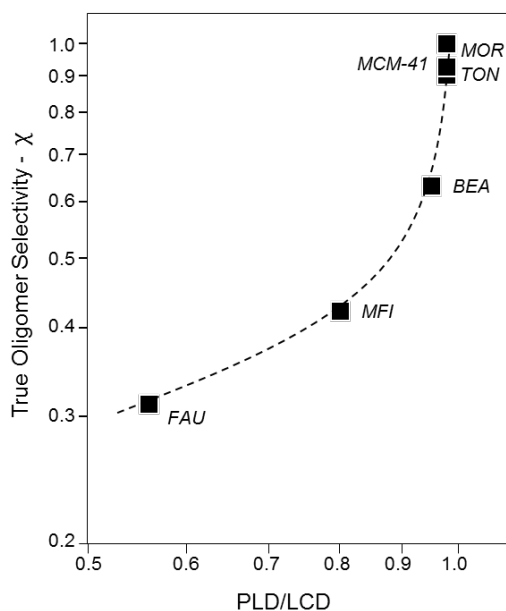


Figure 10. True oligomer selectivity parameter (χ) for C_3H_6 oligomerization as a function of pore limiting diameter/largest cavity diameter (PLD/LCD) TON (0.005 fractional conversion), MOR (0.009), MCM-41 (0.005), BEA (0.004), MFI (0.009) and FAU (0.003) [503 K, 60 kPa, dashed lines are trendlines to guide the eye].

The lower selectivity to β -scission over oligomerization on 1-D zeolites and mesoporous samples compared with that on 3-D zeolites, irrespective of channel size, is consistent with the different extent to which the number of ^{13}C -atoms in oligomers formed from 2- ^{13}C -propene approaches binomial in these samples (Fig. 8). The randomization of the number of ^{13}C -atoms acts as a descriptor of the number of times the C-atoms in such chains have traverse an oligomerization-cracking sequence. Figure 11 shows that χ_{2M2P} values decrease with increasing conversion, but are higher on 1-D TON and mesoporous acids than on MFI. The higher χ_{2M2P} value and than the macroscopic χ for the entire distribution value (Fig. 10) on MFI at low conversions (0.87 versus 0.42, respectively), indicate that the products have not gone through the cycle several times and the majority of β -scission results in C_4 and C_5 products, consistent with Figure 7.

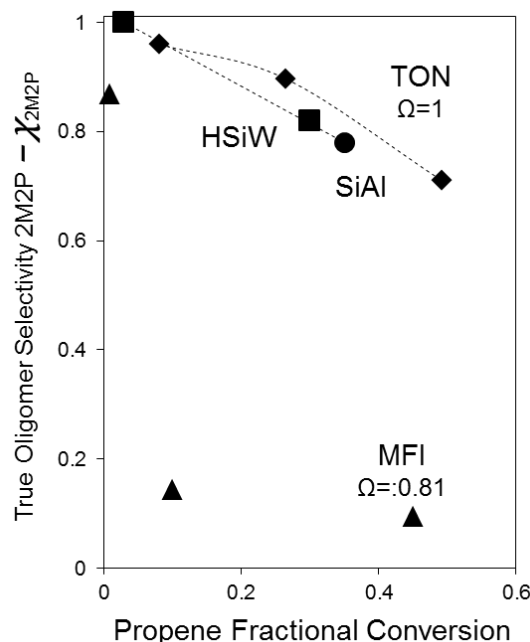


Figure 11. True oligomer selectivity parameter for 2M2P (χ_{2M2P} ; Eq. 3) as a function of propene fractional conversion on TON (◆), MFI (▲), SiAl (●) and HSiW (■) [2 kPa 2-¹³C-propene, 503 K, dashed lines are trendlines to guide the eye]. The ratio of pore limiting diameter/largest cavity diameter (Ω ; PLD/LCD) is given for zeolite samples.

2.3.5. Effects of acid strength and site density on the selectivity of β -scission to oligomerization

Microporous and mesoporous aluminosilicates provide diverse void environments but acid sites of similar strength [31]. Keggin POM clusters, in contrast, are solid acids of greater strength than aluminosilicates (1085 vs. 1190-1222 kJ mol⁻¹ deprotonation energies (DPE) for H₃PW₁₂O₄₀ and aluminosilicates) [13,32]. Figures 6b and 12 show that χ values are unaffected by acid strength on all solid acids with mesoporous voids (H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀, MCM-41, SiAl). Acid strength influences the rate of addition of alkenes to alkoxide oligomers and that of β -scission events in larger alkoxides to the same extent. Both reactions involve full ion-pairs at their respective transition states [12,33]; their similar charge causes the stability of the two transition states to benefit similarly from the more stable conjugate anions in stronger acids. This similarity renders χ values independent of acid strength because it represents a ratio of the rate constants that describe these reactions, which are equally affected by acids of different strength (Eq. 7-9).

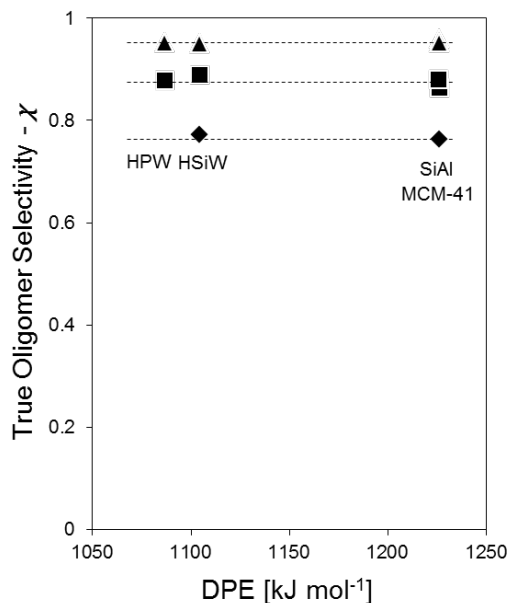


Figure 12. True oligomer selectivity, χ , for C_3H_6 oligomerization as a function of deprotonation energy [DPE [32]; $kJ\ mol^{-1}$] for mesoporous samples: HPW, HSiW, MCM-41 and SiAl at different fractional conversion; 0.002-0.004 (◆), 0.009-0.01 (■) and 0.04-0.05 (▲) [503 K, 58 kPa C_3H_6].

Such effects can also be probed using X-MFI zeolites with different isomorphously substituted heteroatoms ($X=Al^{3+}$, Ga^{3+} , Fe^{3+} , B^{3+}). These samples provide a very diverse range of acid strength within a zeolite framework that imposes diffusional constraints through the undulations that enhance contributions from β -scission. The number of protons per crystal volume also enhances contributions of these secondary reactions. The combined effects are described by the Thiele modulus:

$$\Phi^2 \propto \frac{k}{D_e} \psi \quad (10)$$

$$\psi = [H^+]L^2 \quad (11)$$

which is proportional to the site reactivity (k), the volumetric proton density $[H^+]$, the square of the characteristic diffusion distance, in this case the zeolite crystal radius (L); it also depends inversely on the diffusivity of the precursor molecule that undergoes β -scission (D_e). The values of true oligomer selectivities for Al-MFI with a large range of proton densities (0.36-4.5 H^+ /unit cell) are plotted against Ψ in Figure 13, where L is the crystal size estimated from TEM (Ψ values are given in Table 2). The monotonic trend in Figure 13 confirms that, for a given acid strength (Al-MFI), Ψ provides an adequate surrogate for the Thiele modulus and increasing this value increases the selectivity to diffusion-enhanced secondary reactions (decreases χ). Acid strength affects the rate constants in Equation 10 and also should affect the selectivity to the extent that stronger acids impose a larger diffusive barrier [34]. The muddled effects in Figure 14 are, therefore, indicative of the use of an incomplete descriptor of the catalyst properties that account for the magnitude of χ .

Table 2. Values of the diffusion parameters for MFI and TON zeolites.

Framework	H ⁺ /u.c.	Ψ [mol H ⁺ nm ⁻¹]
MFI	4.5	7484
	3.6	9595
	2.5	4593
	2.1	3721
	1.1	5431
	0.36	808
TON	0.4	416
	0.36	622
	0.26	121

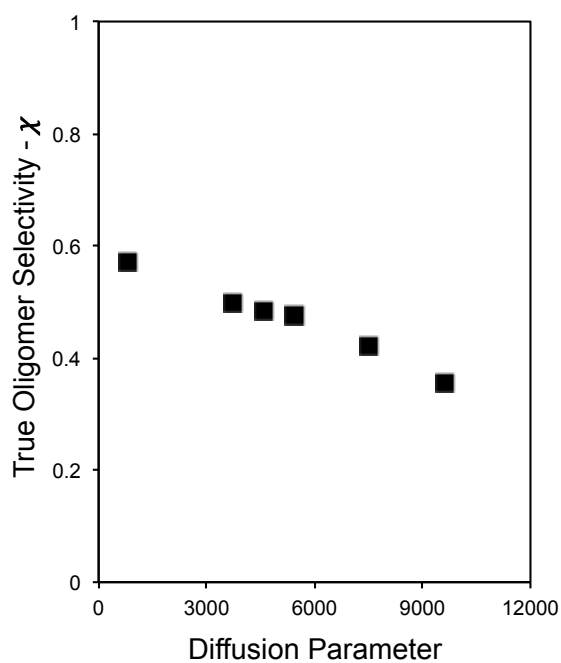


Figure 13. True oligomer selectivity parameter, χ , for C₃H₆ oligomerization as a function of diffusion parameter on Al-MFI zeolites [503 K, 58 kPa C₃H₆, 0.005-0.015 fractional conversion].

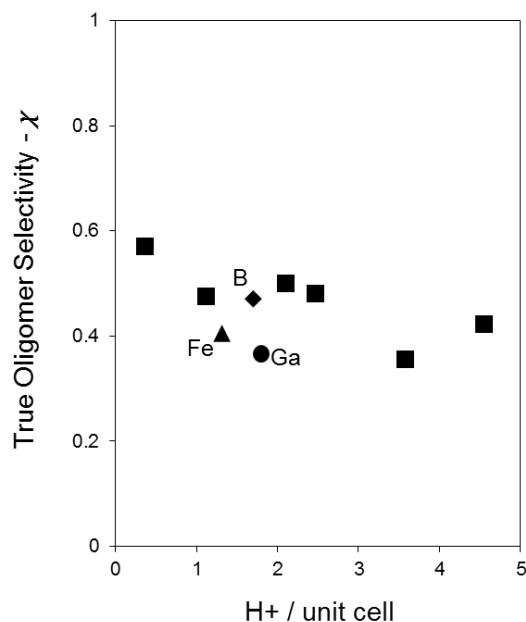


Figure 14. True oligomer selectivity parameter, χ , for C_3H_6 oligomerization as a function of proton density $[H^+/\text{unit cell}]$ for MFI samples with different heteroatoms: Al (■), Fe(▲), Ga (●) and B(◆) [503 K, 58 kPa C_3H_6 , 0.005-0.015 fractional conversion].

Such diffusional enhancements of secondary reactions of primary oligomerization products in MFI can also be inferred from the effects of the diffusion parameter (Ψ) on the relative abundance of dimers (C_6) and trimers (C_9) formed from propene. These selectivities indicate that the larger oligomers do not form as much in the small channels of TON compared to intersection void in MFI (Fig. 15). The trimers that are formed, however, experience transport limitations egressing from the MFI crystal where the undulation of channel structure induces β -scission such that smaller alkenes can egress without restriction.

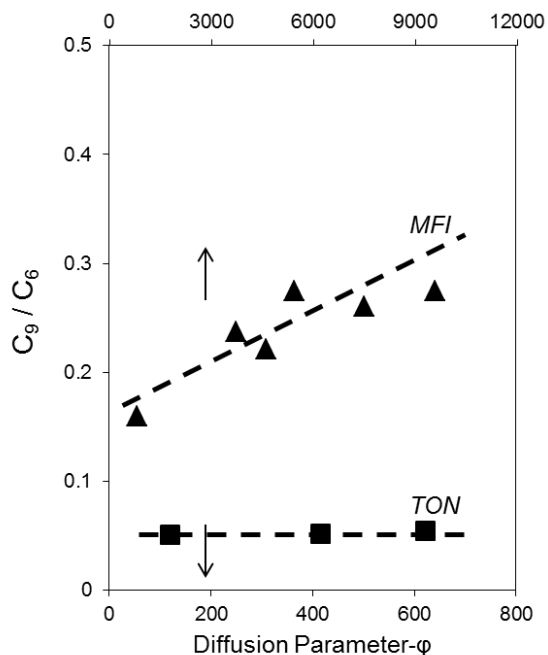


Figure 15. Larger oligomer selectivity (C_9/C_6) during C_3H_6 oligomerization for MFI (▲) and TON (■) as a function of diffusion parameter [503 K, 58 kPa C_3H_6 , 0.01 fractional conversion]. The diffusion parameters for the two zeolites are different due to a large difference in zeolite crystal size of the samples.

2.3.6. Effects of reactant alkene chain length on oligomerization selectivity

The chain length and substituents in the reactant alkenes influence the turnover rates for both oligomerization and the β -scission reactions of oligomerization products and consequently the distribution of chain lengths in products (Eq. 7-8). Figure 16 shows that these distributions in the products formed from C_2H_4 (a-b) and $i-C_4H_8$ (c-d) reactants differ markedly on TON and MFI, as in the case of propene reactants (Fig. 5). The one-dimensional TON framework allows true oligomer products (C_4 , C_6 and C_8 for C_2H_4 ; C_8 for $i-C_4H_8$) to egress without significant β -scission, thus leading to χ values near unity for both reactants (Fig. 17 a and b). In contrast, such χ values are much smaller for C_2H_4 reactions on MFI than TON at all conversions. The chain length distribution is nearly binomial (Fig. 16b) for C_2H_4 , as in the case of C_3H_6 reactants (Figs. 5 and 7). These binomial distribution of chain lengths are reminiscent of those reported at higher alkene conversions for C_2 - C_{10} alkenes on MFI [1,35].

Isobutene reactions also gave lower χ values on MFI than TON at all conversions (Fig. 17c), but χ values were larger than for C_2H_4 (Fig. 17a) or C_3H_6 reactants on MFI (Fig. 17b). This is due to the fact that C_8 formation from $i-C_4H_8$ is more facile than C_6 formation from C_3H_6 (turnover rates: $0.10 \text{ mol (H}^+\text{-s)}^{-1}$ versus $0.02 \text{ mol (H}^+\text{-s)}^{-1}$ at 60 kPa, respectively [12]) because it involves a more substituted carbenium ion in the C-C bond formation transition state, which is kinetically-relevant for both alkenes [12]. This higher reactivity appears in the denominator of the expression for χ (Eq. 8-9), increasing the value of the parameter. β -scission of the initial C_8 product would also be faster than that for the C_6 product, however, this step is far from equilibrium; rapid isomerization of the product skeletal backbone (Section 3.1-3.2) results in C_8

isomers that would have to return via less stable carbenium ions. In this case, isomerization saves the chain length from undergoing β -scission. These results show that the conclusions about the effects of undulations in the void space remain valid for other light alkenes; such effects weaken for alkene reactant backbones that form particularly stable carbenium ions at the oligomerization TS, because the rapid skeletal isomerization of the primary oligomers form leads to molecular structures that undergo C-C cleavage through less stable transition states than those involved in the formation of the primary oligomers. Such equilibration of oligomer backbones thus protects chains from extensive β -scission during oligomerization of alkene reactants, such as isobutene.

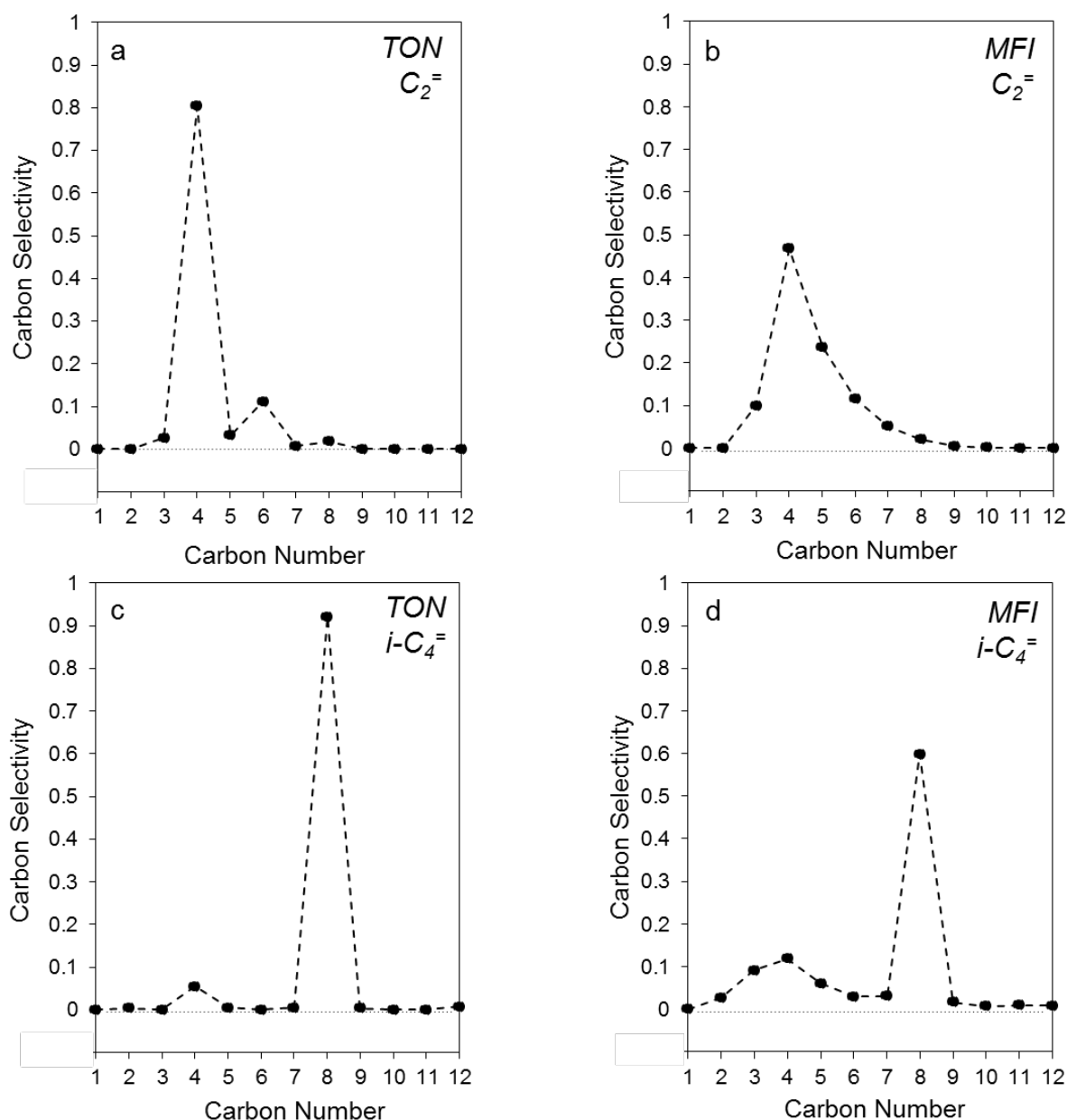


Figure 16. Carbon selectivity for C_2H_4 oligomerization on TON (a; 0.002 fractional conversion) and MFI (b; 0.002) and for $i-C_4H_8$ oligomerization on TON (c; 0.01) and MFI (d; 0.01) [503 K, 60 kPa < 0.05 conversion].

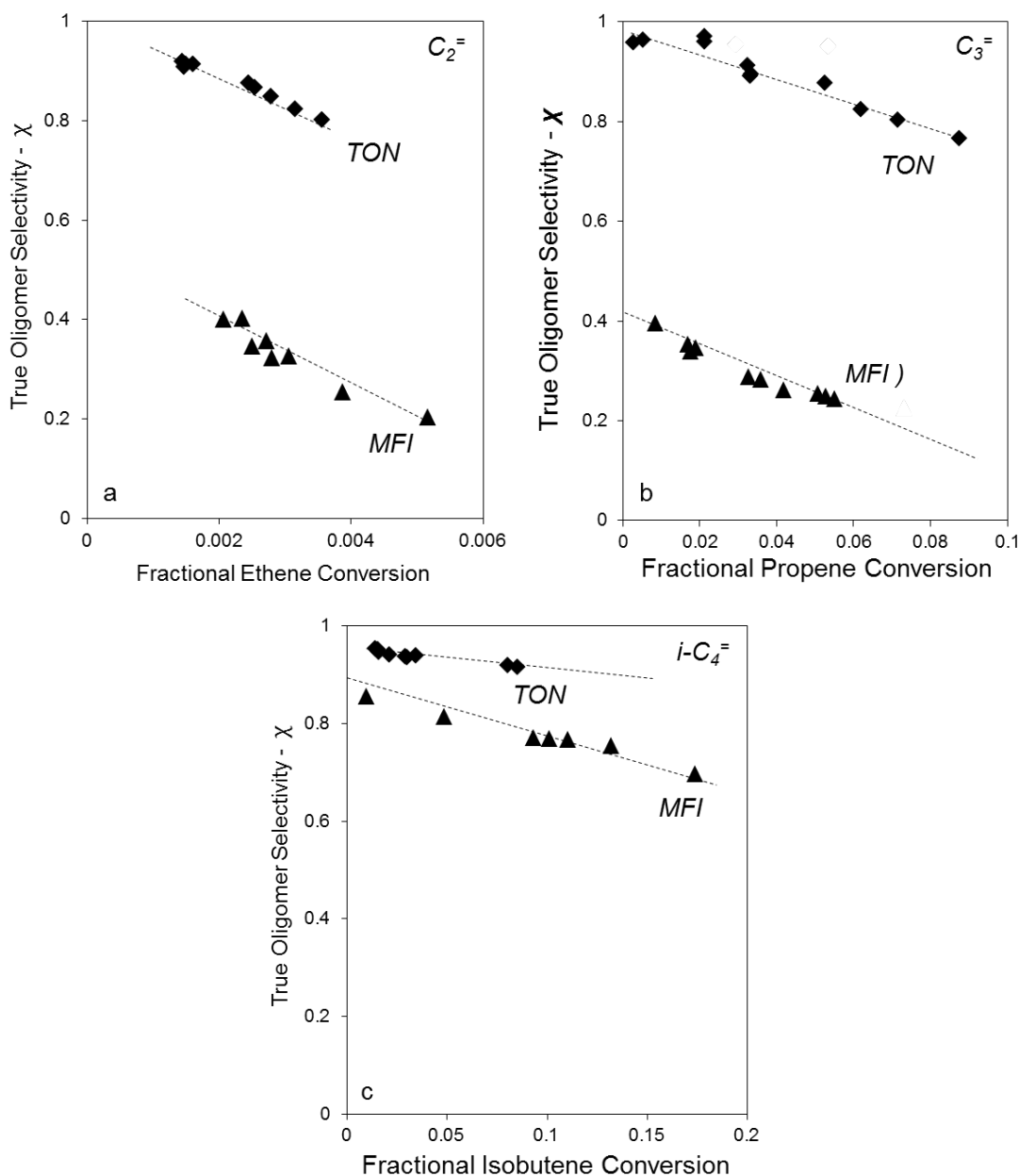


Figure 17. True oligomer selectivity (χ ; Eq. 2) for C_2H_4 (a) and $i-C_4H_8$ (b) oligomerization as a function of alkene fractional conversion for zeolites TON ($\blacklozenge$) and MFI ($\blacktriangle$) [60 kPa, 503 K].

2.4. Conclusions

The relative rates of oligomerization, β -scission and isomerization reactions during light alkene conversion on Brønsted acidic zeolites and mesoporous solid acids were compared for a variety of frameworks and acid strengths. Chemical speciation and isotopic scrambling experiments show rapid hydride and methyl shifts and frequent readsorption lead to equilibrated mixtures of skeletal and regioisomers for chains of any given length at all conditions and on all solid acids. While the channel network does not influence the skeletal structure of the products, it does affect ability for product to diffuse intact. A true oligomer selectivity parameter (χ) was developed to

describe the fraction of products that egress without β -scission, which varies among catalysts of different channel connectivity and void environment. One-dimensional zeolites and mesoporous acids (both ordered 1-D and colloidal 3-D) generated χ values close to unity, indicating the products that can egress via unobstructed diffusion, irrespective of channel size or acid strength. Three-dimensional zeolites, which exhibit larger voids connected by smaller apertures, generated χ values closer to zero. These larger voids allow subsequent C-C bond formation, but the cross-sectional undulations prevent egress of larger oligomers and require smaller, more mobile species to form via β -scission. These results and mechanistic interpretations demonstrate an understanding of how micro- and mesoporous framework (i.e. confinement and connectivity) influence selectivity during reactions, specifically light alkene oligomerization to useful, higher molecular products, in order to provide predictive guidance for other alkene reactants and void structures.

2.5 Appendix

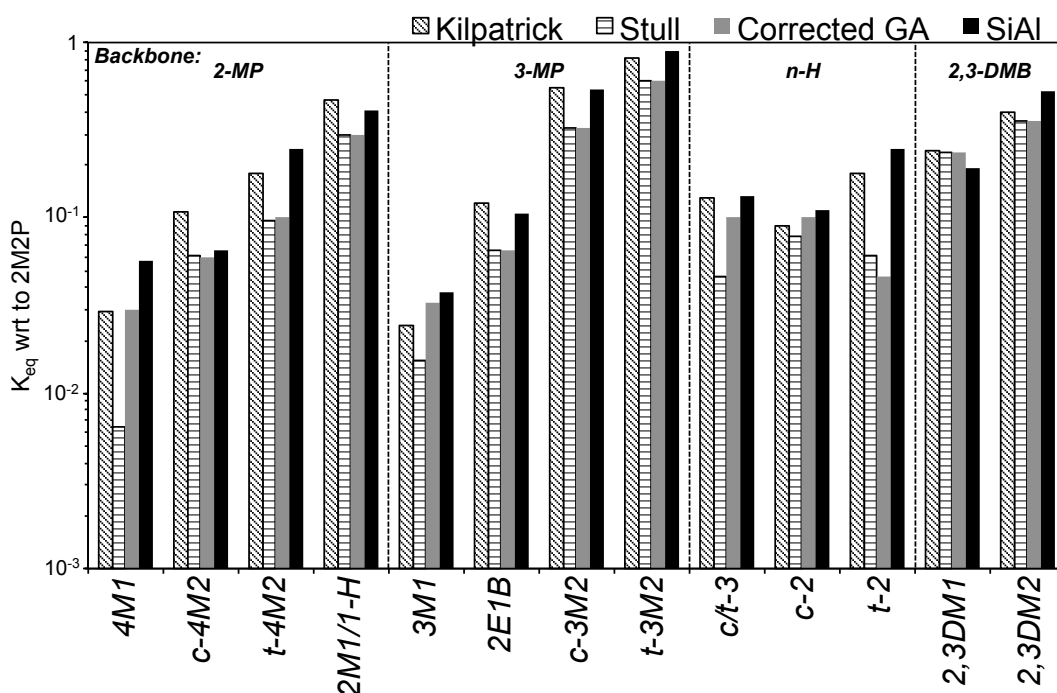


Figure A1. Equilibrium constants for the isomerization of 2-methyl-2-pentene to other hexene isomers at 503 K from Kilpatrick, et al [20] (diagonal stripe), Stull, et al [19] (horizontal stripe), correct group additivity methods and data collected from SiAl (14 % C_3H_6 conversion, 503 K, black). Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

2.6. Supplemental Information

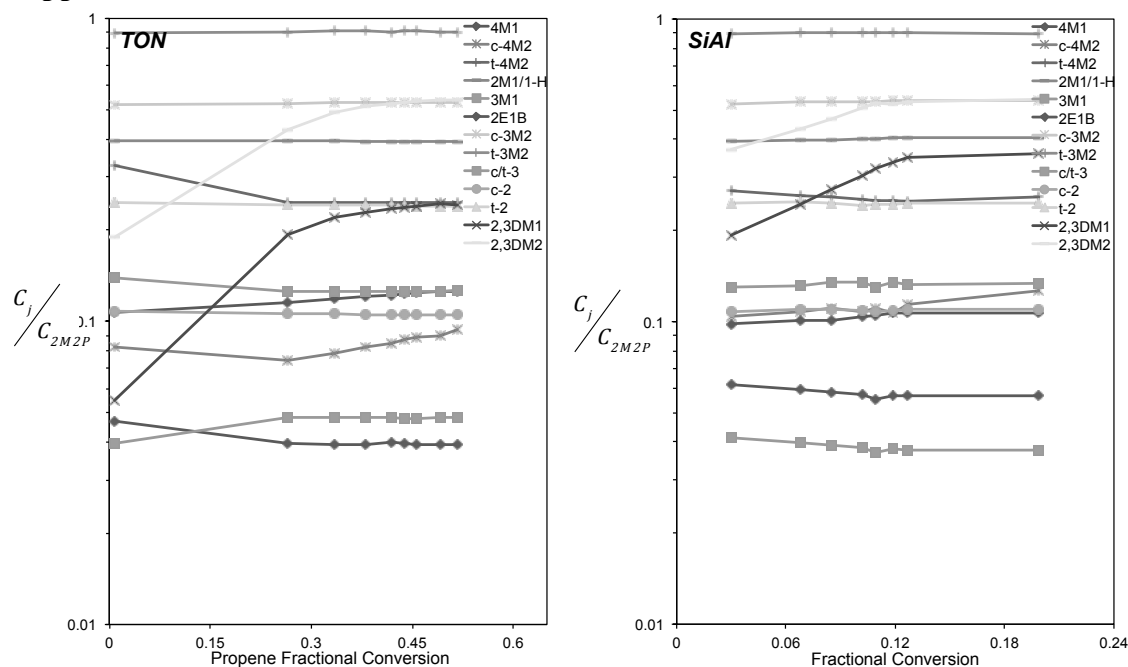


Figure S1. Concentration ratios, or calculated equilibrium constants, for hexene isomers with respect to 2-methyl-2-pentene on TON and SiAl at 503 K, 60 kPa C_3H_6 as a function of fractional conversion.

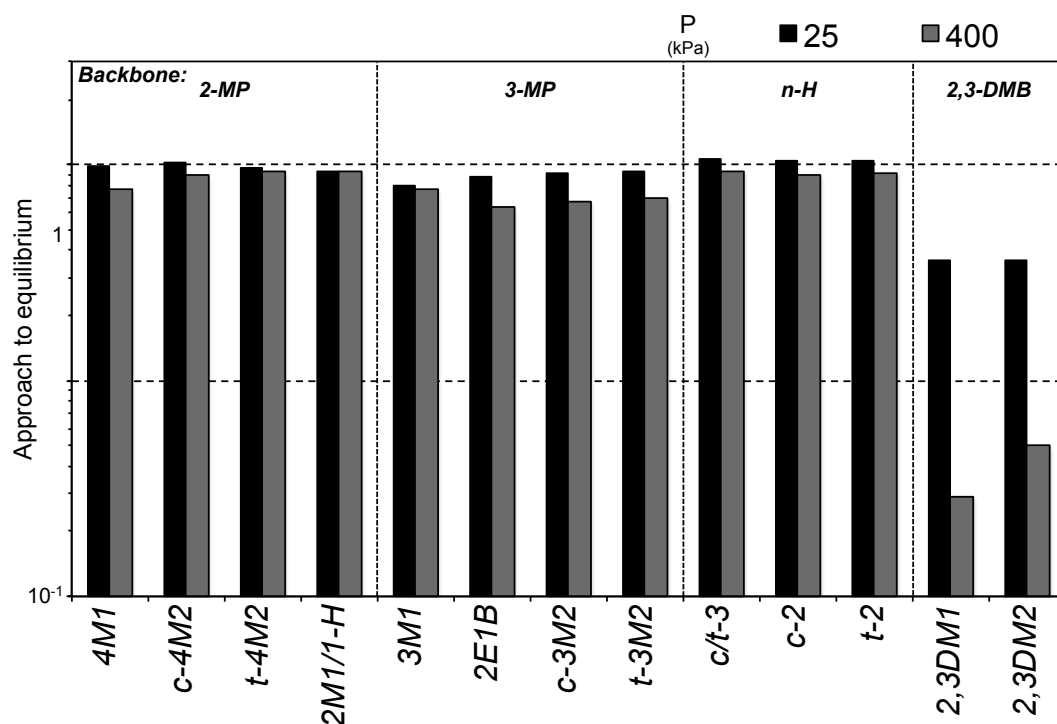


Figure S2. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on TON at 25 kPa (black) and 400 kPa (black) C_3H_6 [503 K, <5 % C_3H_6 conversion]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

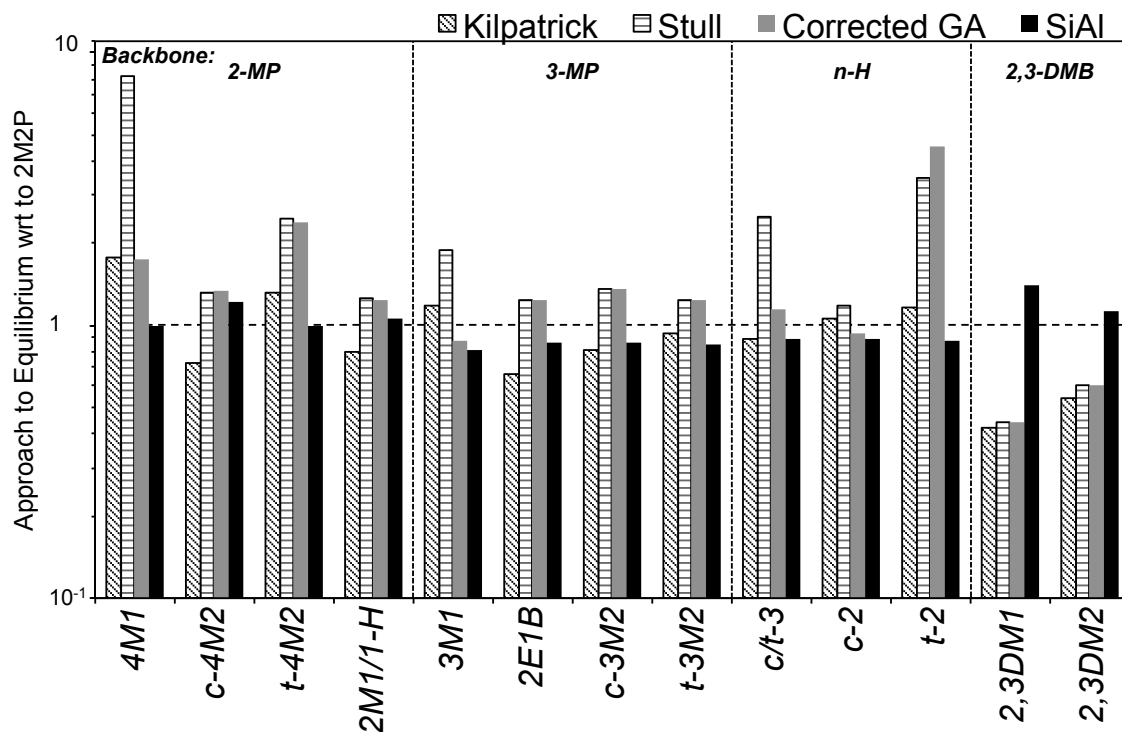


Figure S3. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on SiAl [503 K, 60 kPa C_3H_6 1% conversion] using calculated equilibrium constants for SiAl at a fractional conversion of 0.14 and tabulated equilibrium constants.

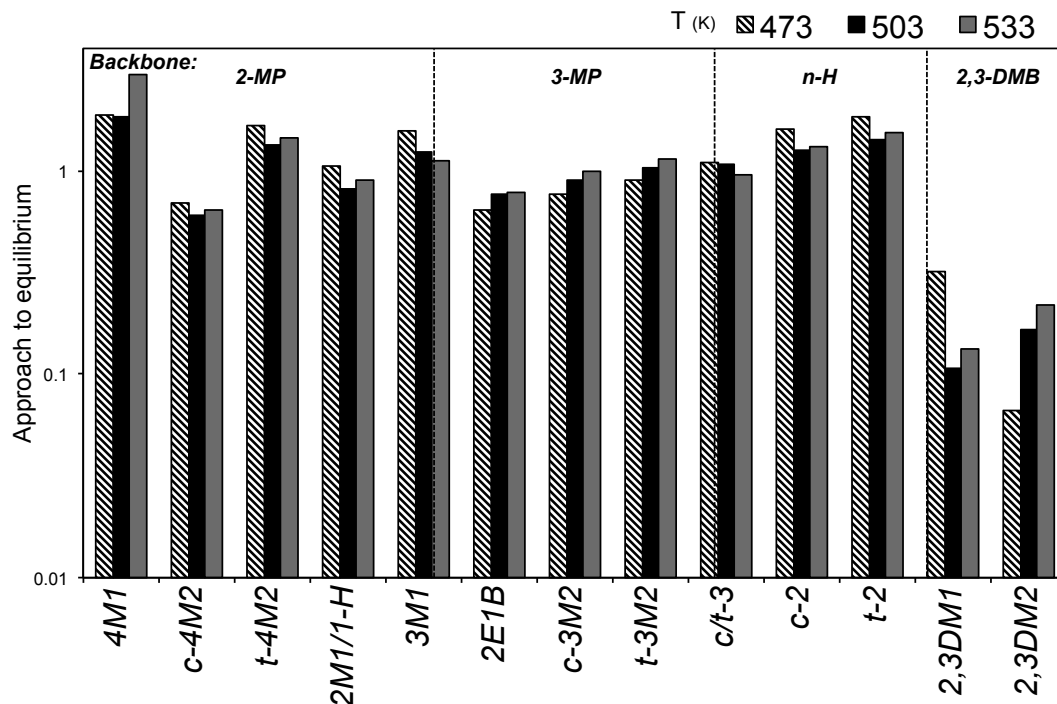


Figure S4. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on TON at 473 K (striped), 503 K (black) and 533 K (gray) C_3H_6 using tabulated data from Kilpatrick et al [20] [25 kPa, <5 % C_3H_6 conversion]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

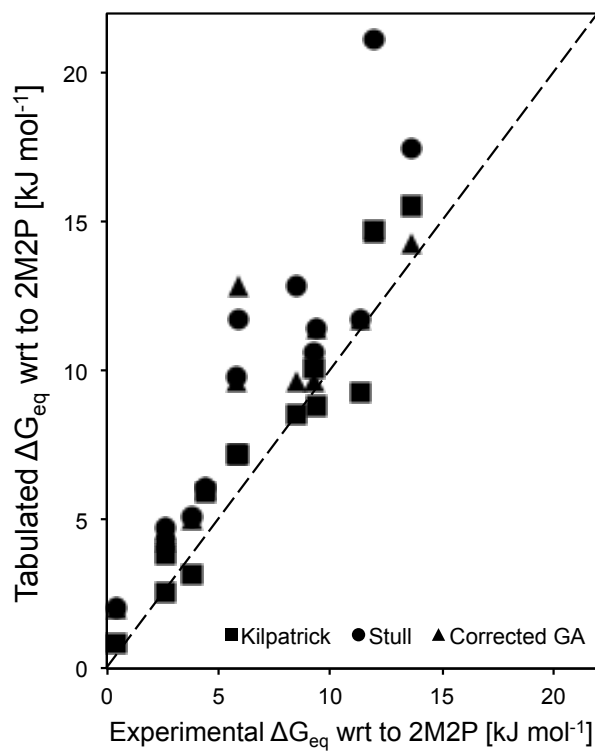


Figure S5. Parity plot of experimental ΔG_{eq} for the isomerization of 2-methyl-2-pentene to other hexene isomers at 503 K, 60 kPa C_3H_6 on SiAl (14% C_3H_6 conversion) versus tabulated values; both are in kJ mol^{-1} .

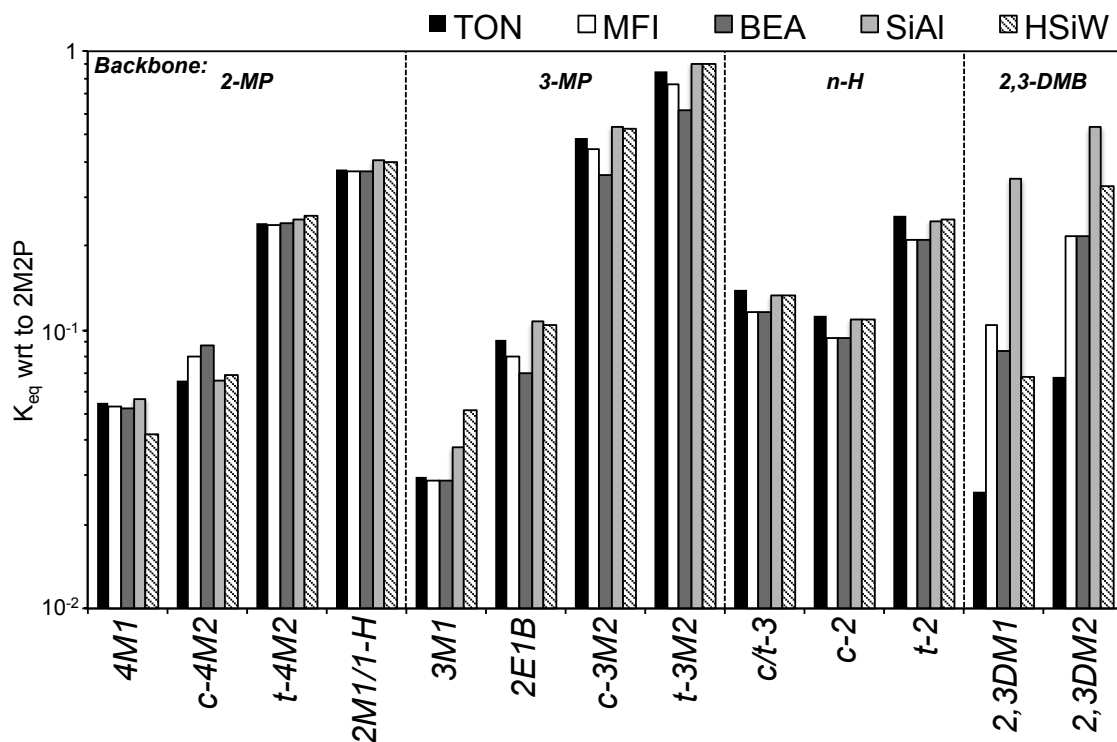


Figure S6. Calculated equilibrium constants for the isomerization of 2-methyl-2-pentene to other hexene isomers at 503 K, 60 kPa C_3H_6 on TON (44% C_3H_6 conversion, black), MFI (15% C_3H_6 conversion, white), BEA (15% C_3H_6 conversion, dark gray), SiAl (14% C_3H_6 conversion, light gray) and HSiW (10% C_3H_6 conversion, diagonal stripe). Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

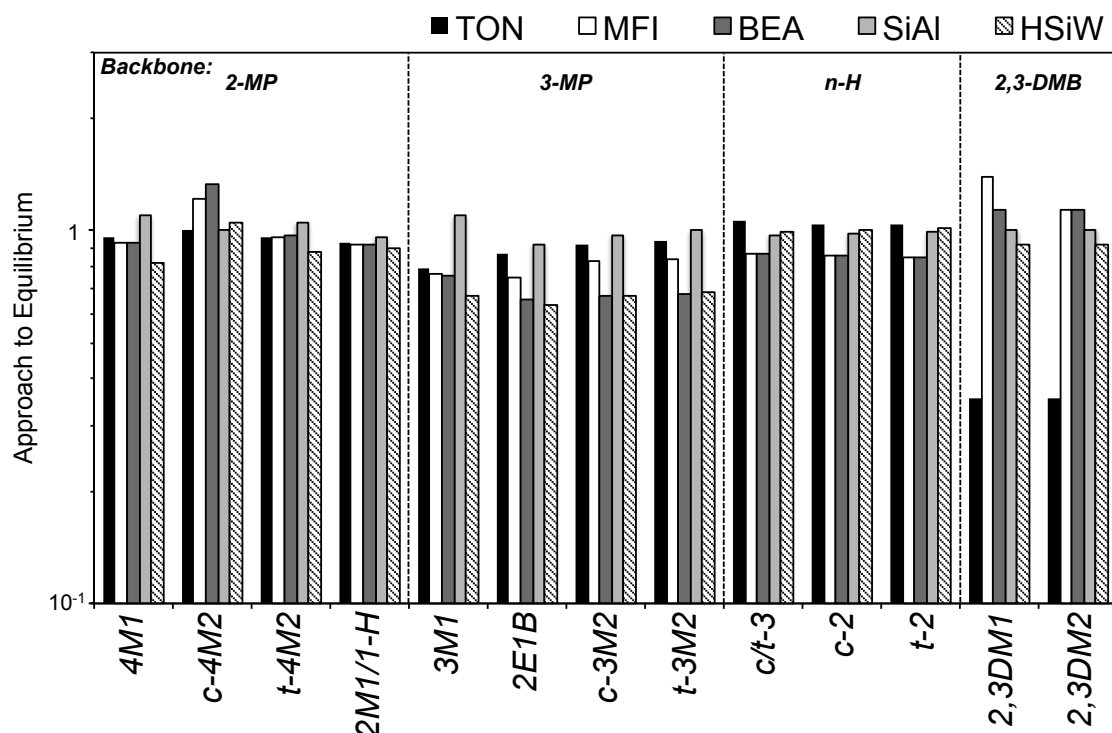


Figure S7. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on the samples tested with their fractional conversions given: TON (0.005), MFI (0.009), BEA (0.004), SiAl (0.005) and HSiW (0.003) using calculated equilibrium constants for SiAl at a fractional conversion of 0.14. [503 K, 60 kPa]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

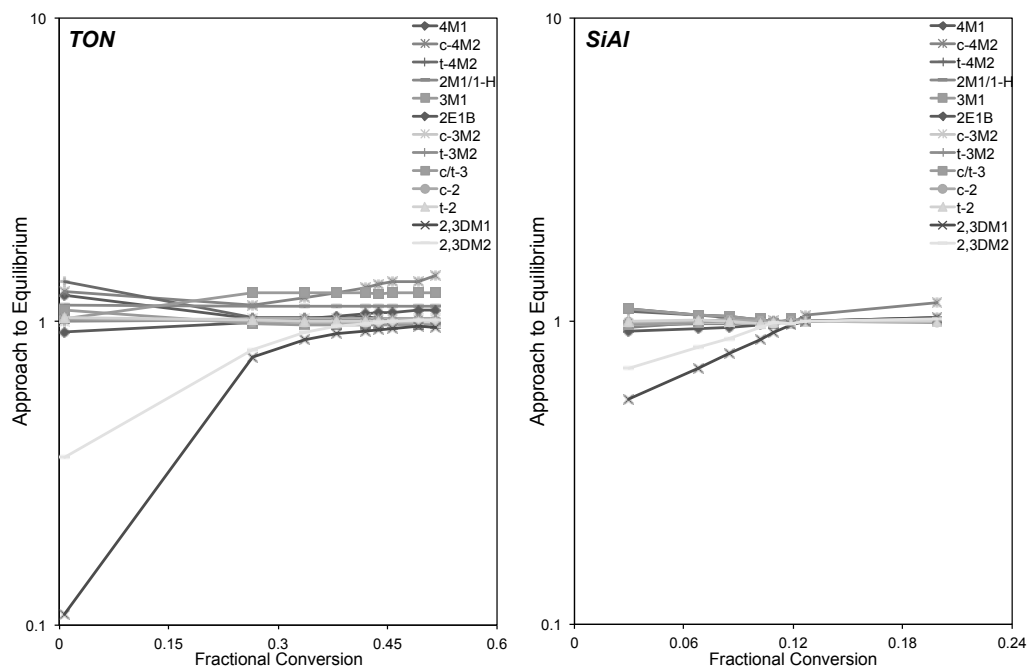


Figure S8. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on TON and SiAl at 503 K, 60 kPa C_3H_6 as a function of fractional conversion using calculated equilibrium constants for SiAl at a fractional conversion of 0.14.

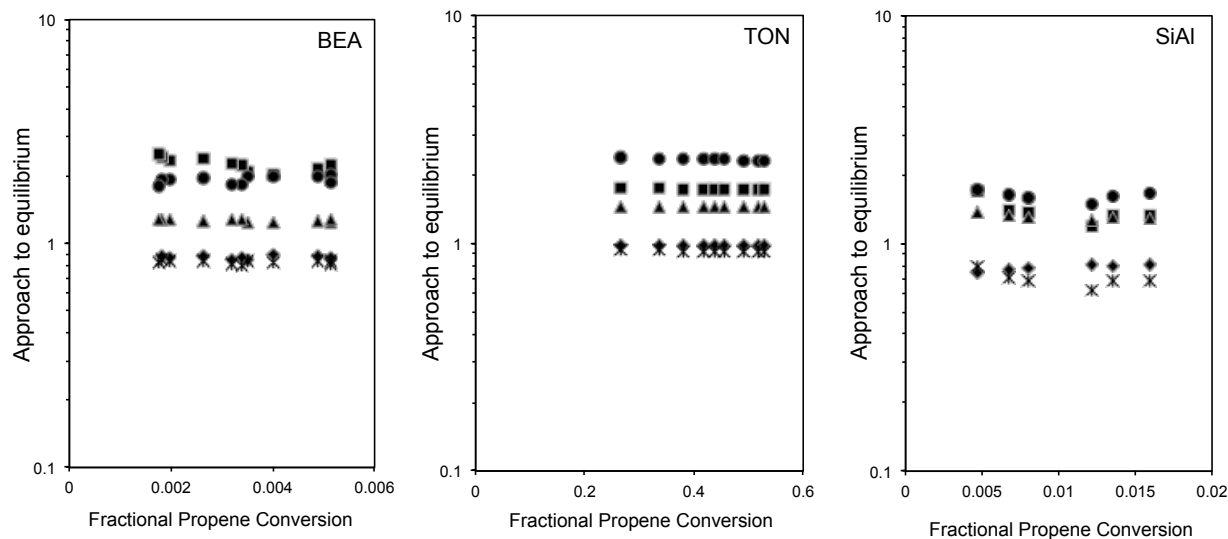


Figure S9. Approach to equilibrium for the formation of pentene isomers with respect to 2-methyl-2-butene on BEA, TON and SiAl using tabulated data from Kilpatrick et al [20] [503 K, 60 kPa]. Values are not unity but are independent of conversion.

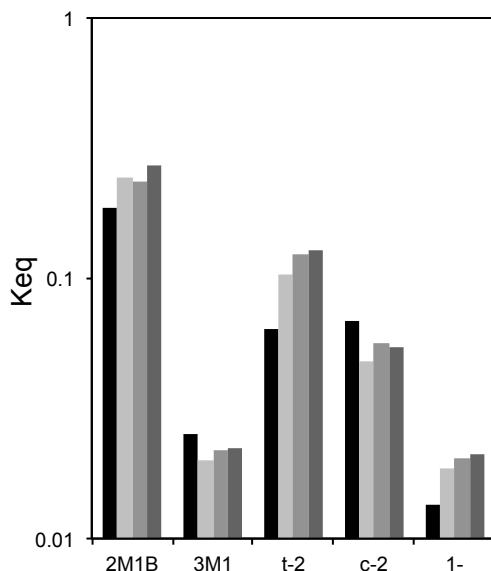


Figure S10. Calculated equilibrium constants for the isomerization of 2-methyl-2-butene to other pentene isomers (2-methyl-1-butene, 3-methyl-1-butene, t-2-pentene, c-2-pentene, 1-pentene) at 503 K, 60 kPa C_3H_6 on SiAl, BEA and TON (with increasing gray darkness, respectively). Tabulated values from [20] are shown in black.

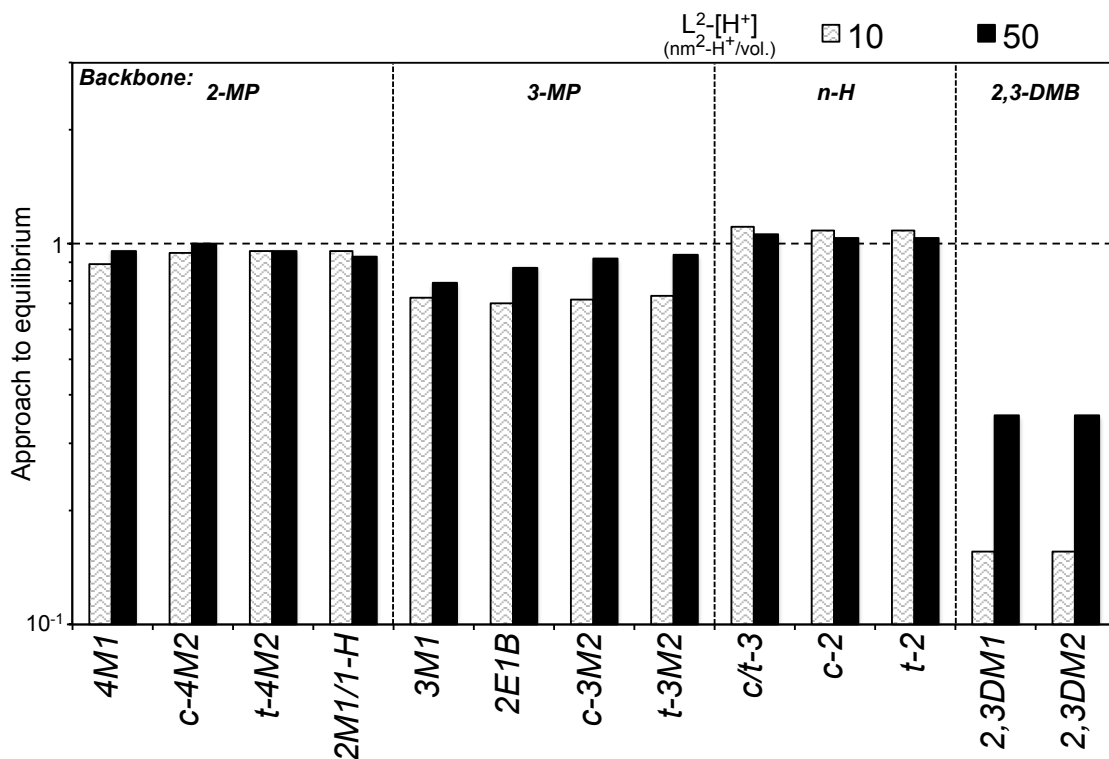


Figure S11. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on TON with different site density ($L^2-[H^+]$; $nm^2-H^+/vol.$): 10 (white chevron) and 50 (black) [503 K, <5 % C_3H_6 conversion, 60 kPa]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

Table S1. Isotopic content of 1-¹³C-hexane and 1-¹³C-t-3-hexene.

ion	1- ¹³ C-hexane	1- ¹³ C-t-3-hexene
Parent	0.99	0.99
Pentyl	0.55	0.56
Butyl	0.51	0.53

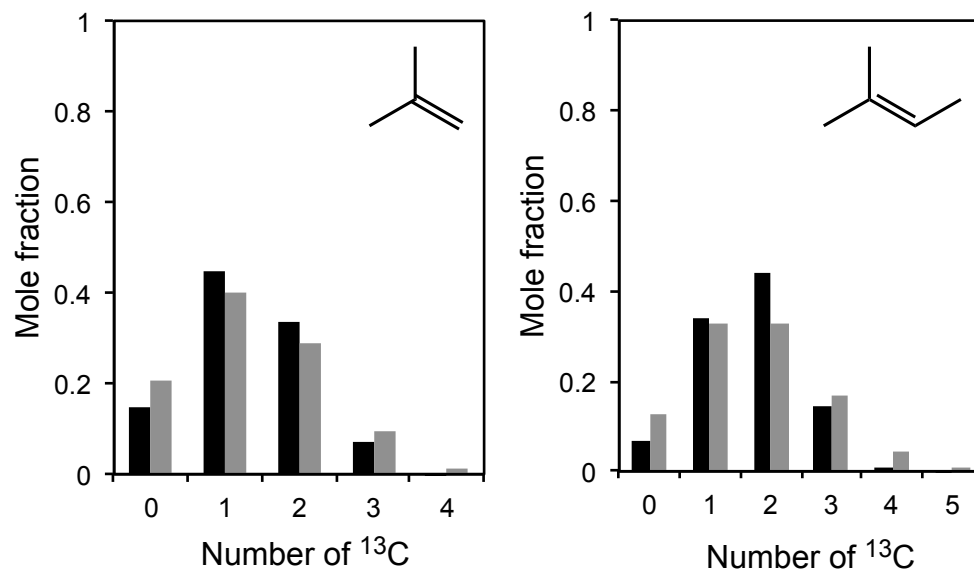


Figure S13. Isotopologue distribution for isobutene (parent ion: 56, left) and 2-methyl-2-butene (parent ion: 70, right) on TON [8% C₃H₆ conversion, 2 kPa 2-¹³C-propene, 503 K]. The expected binomial distribution is indicated by hashed bars.

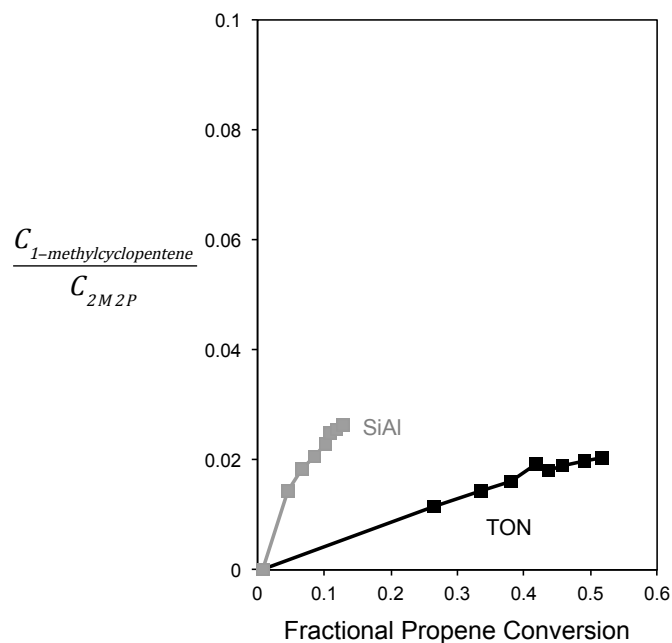


Figure S14. Concentration ratio of 1-methylcyclopentene relative to 2-methyl-2-pentene on TON and SiAl as a function of fractional conversion [503 K, 60 kPa C_3H_6].

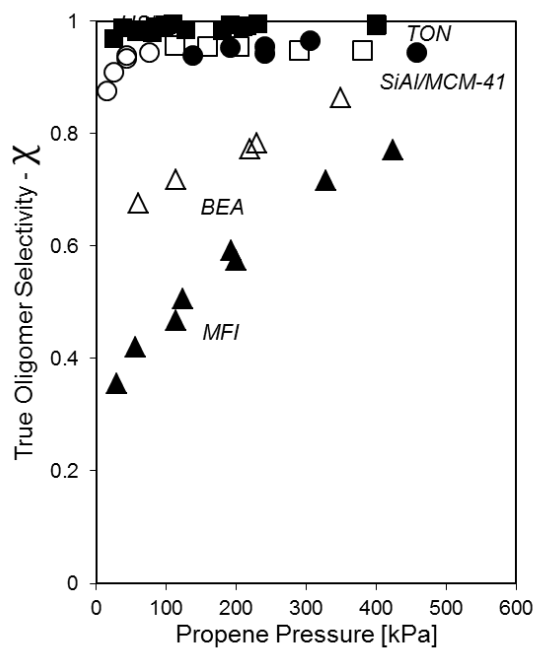


Figure S15. True oligomers selectivity, χ , as a function of C_3H_6 pressure for TON (■), SiAl (□), MCM-41 (●), HSiW (○), BEA (△) and MFI (▲) [503 K; <5 % C_3H_6 conversion].

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CHAPTER THREE

Catalysis on Solid Acids: Mechanism and Catalyst and Molecular Descriptors in Oligomerization of Light Alkenes

Abstract

This study addresses fundamental descriptions of confinement and acid strength effects on stability for transition states and intermediates involved in alkene oligomerization on solid acids. Kinetic and infrared data and theoretical treatments that account for dispersive interactions show that turnover rates (per H^+) on aluminosilicates and heterosilicates with microporous voids (TON, MFI, BEA, FAU) and on mesoporous acids (amorphous silica-alumina, dispersed polyoxometalates) reflect the free energy of C-C bond formation transition states referenced to gaseous alkenes and to bound alkoxides present at equilibrated configurations and saturation coverages. These free energy barriers decrease as the size of confining voids decrease in aluminosilicates containing acid sites of similar acid and approach bimolecular transition state (TS) sizes derived from density functional theory (DFT) for propene and isobutene reactants. Such TS structures are preferentially stabilized over smaller bound alkoxides via contacts with the confining framework. These effects of size, typically based on heuristic geometric analogies, are described here instead by the dispersive component of DFT-derived energies for TS and intermediates, which bring together the effects of size and the shape, for different framework voids and TS and alkoxide structures derived from alkenes of different size; these organic moieties differ in “fit” within voids but also in their proton affinity, as a result of the ion-pair character of TS structures. The larger charge in TS structures relative to their alkoxide precursors cause free energy barriers to decrease as conjugate anions become more stable in stronger acids. Consequently, oligomerization rate constants decrease exponentially with increasing deprotonation energy on unconfined acid sites in polyoxometalates and silica-alumina and on confined sites within MFI frameworks with Al, Ga, Fe, or B heteroatoms. Reactivity descriptions based on geometry or acid strength are replaced by their more relevant energetic descriptors—van der Waals confinement energies, proton affinities of organic molecules, and deprotonation energies—to account for reactivity, here for different reactants on diverse solid acids, but in general for acid catalysis.

3.1. Introduction

Light alkene oligomerization on solid Brønsted acids is an attractive route for the synthesis of chemical feedstocks and transportation fuels from undervalued precursors [1–4]. Turnover rates (per proton) for reactions of hydrocarbons and oxygenates on solid acids depend sensitively on the size and shape of the molecular-sized voids that contain the active protons in microporous aluminosilicates [5–7]. The strength of the Brønsted acid sites also influences reactivity when ion-pair transition states differ in charge from their adsorbed precursor species [8–11]. Acid forms of zeolites and mesoporous aluminosilicates contain acid sites of similar strength [12], but which reside within confining voids of very different size and connectivity, thus creating diverse reactivities and selectivities in spite of their similar acid strength [6]. Such

effects reflect the preferential solvation of specific molecules or transition states through van der Waals interactions, as a consequence of their different ability to contact the surrounding framework.

The isomorphous substitution of different heteroatoms (Al, Ga, Fe, B) into a given silicate framework preserves a similar confining environment, while varying acid strength [11]; SiO₂-supported Keggin polyoxometalates (POM) clusters with W-addenda atoms and different central atoms contain sites of diverse acid strength; these acid sites are significantly stronger than those in aluminosilicates [13], but lack the molecular confinement properties of microporous solids. These materials allow a rigorous assessment of how the stability of the conjugate anion, the pre-eminent feature of the deprotonation energies that determine acid strength, influences the free energy of the relevant transition states and adsorbed precursors. Extensive studies of alkene oligomerization catalysis have broadly explored the reactive and selective properties of acid catalysts [1–3,14–19], but without the broad range of materials or the systematic and purposeful variations in void environment and acid strength, the detailed measurements and mechanistic interpretation of turnover rates, or the theoretical treatments that we combine in the present study.

We find that the addition of alkenes to alkene-derived alkoxides is the sole kinetically-relevant step in propene and isobutene oligomerization turnovers and that the adsorption-desorption steps of alkene reactants and products are quasi-equilibrated. Such conclusions, as well as the saturation alkoxide coverages prevalent during catalysis, are consistent with measured rate dependences on alkene pressure, with the vibrational spectra of bound alkoxides, and with density functional theory (DFT) treatments of the stability of the transition states and bound intermediates that mediate oligomerization reactions.

First-order rate constants (per H⁺) were independent of Al content or proton density for a given framework structure on zeolites and mesoporous aluminosilicates; therefore, measured rates are unaffected by any diffusional artifacts and proton locations must remain the same at all Al contents. Rate constants increased monotonically as the aluminosilicate voids became smaller (FAU, MFI, BEA, TON). Such trends reflect the preferential stabilization of bimolecular transition states that are larger than their alkoxide precursors and contact the confining framework more effectively, as also observed for other reactions [5,20,21]. These trends are quantified here by the dispersive component of DFT-derived energies [22,23], an energy descriptor that we use here to replace heuristic geometric arguments for confinement effects. Rate constants also increased on a given catalyst as the reactant, and thus the transition state, increased in size from propene to isobutene reactants. Such effects reflect a combination of the more stable nature of the larger carbenium ions and their more effective van der Waals contacts with frameworks for larger transition states. The effectiveness of such contacts is enhanced, especially for larger transition states, by local distortions of the zeolite framework, which compensate the energetic penalty from such crystal distortions with stronger van der Waals interactions between transition states and their confining voids.

Oligomerization rate constants decreased exponentially with increasing deprotonation energies (DPE), a rigorous descriptor of acid strength, for acid sites present within mesoporous silicas (POM (H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀); silica-alumina (SiAl)) or microporous heterosilicates (X-MFI; X=Al³⁺, Ga³⁺, Fe³⁺, B³⁺). These effects of acid strength on transition state stability, combined with the additive effects of confinement, provide predictive guidance for the design of solid acids with the appropriate strength and proton location, in a way that allows accurate

extrapolation to molecules that differ in size and structure from propene and isobutene, the reactants used here to illustrate these concepts.

3.2. Experimental Methods

3.2.1 Materials used and assessment of the number of accessible protons

BEA, MFI (all X-MFI), TON, FAU and mesoporous silica-alumina (provenance, Si/Al ratio in Table 1) were obtained from commercial sources and received with protons, ammonium, or structure-directing agents (used in their synthesis) as balancing cations. Si and Al (Table 1a) contents were measured by inductively-coupled plasma optical emission spectroscopy. All samples were treated in flowing dry air ($2.5 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, zero grade, Praxair) by heating to 818 K (at 0.0167 K s^{-1}) and holding for 3 h to remove any synthetic residues, to decompose NH_4^+ cations, to remove ambient moisture, and to convert all samples to their H-form. These samples were then exchanged with NH_4^+ using aqueous solutions of 0.1 M NH_4NO_3 ($300 \text{ cm}^3 \text{ g-zeolite}^{-1}$, 98 % ACS Reagent, Sigma-Aldrich) at 353 K for 2 h and the solids obtained isolated by centrifugation. This procedure was carried out thrice and samples were finally rinsed with deionized water ($500 \text{ cm}^3 \text{ g}^{-1}$) and isolated by filtration. These protocols led to starting materials in a common NH_4 -form, which is more stable for storage and allows the number of protons to be determined using the procedure described next.

The number of protons was measured from the amount of NH_3 evolved by placing the NH_4 -form of zeolites (0.05–0.13 g) on a quartz frit held within a quartz tube and heating to 923 K (at 0.833 K s^{-1}) in a flowing mixture of Ar ($0.83 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, 99.999%) in He. A Si-coated stainless steel capillary held at 420 K (0.254 mm i.d., 183 cm length) was placed immediately below the samples and connected to a mass spectrometer (MKS Spectra Minilab) to measure NH_3 (17, 16 amu), H_2O (18, 17 amu) and Ar (40 amu) concentrations in the effluent stream.

Keggin POM clusters were dispersed onto mesoporous colloidal silica (Cab-O-Sil HS-5; $310 \text{ m}^2 \text{ g}^{-1}$; $1.5 \text{ cm}^3 \text{ g}^{-1}$ pore volume) [8]. The number of protons in Keggin POM clusters and amorphous silica-alumina (SiAl) was measured by titration with a non-coordinating amine (2,6-di-*tert*-butylpyridine) during 2-methyl pentane isomerization [8] and propene oligomerization reactions, respectively (Table 1b). Turnover rates for both reactions were fully suppressed by the addition of the hindered titrant, indicating that both reactions occur only on Brønsted acids sites. Agreement between both methods of proton enumeration has been previously described for methanol dehydration [5].

Table 1. Source, Si/Al ratio and proton counts for solid acids used in this study

	Sample	Source	Si/T* Ratio ¹	H ⁺ /T* Ratio
			(*T=Al unless otherwise noted)	
a	BEA	Zeolyst	11.8	0.39 ²
	BEA	Zeolyst	43	1.0 ²
	MFI	Zeolyst	16.6	0.65 ²
	MFI	Zeolyst	29.2	0.78 ²
	MFI	Zeolyst	43.8	1.0 ²
	MFI	Zeolyst	173	0.64 ²
	MFI	Sud-Chemie	14	0.71 ²
	MFI	Tri-Cat	25	0.35 ²
	MFI	BP	26	0.80 ²

	Ga-MFI	BP; [24]	45	0.86 ²
	Fe-MFI	[11]	61	0.86 ²
	B-MFI	BP; [25]	43	0.77 ²
	TON	BP	24	0.40 ²
	TON	BP	39	0.55 ²
	TON	BP	49	0.50 ²
	LZ-210	Engelhard	7.5	0.37 ²
	Silica-Alumina	Sigma-Aldrich	5.5	0.25 ³
b	Sample	POM content on Silica (wt %)	POM surface density (POM nm⁻²)	Protons (H⁺/POM)³
	H ₃ PW ₁₂ O ₄₀	5	0.04	0.72
	H ₄ SiW ₁₂ O ₄₀	5	0.04	1.6

¹from elemental analysis (ICP-OES).

²from decomposition of NH₄⁺ exchanged sample.

³from 2,6-di-tert-butylpyridine titration.

3.2.2 Alkene oligomerization turnover rates

All samples (Table 1) were pelleted, crushed, and sieved to retain 180-250 μm aggregates. Alkene conversion turnover rates were measured on samples (15-100 mg) placed within a tubular reactor with plug-flow hydrodynamics (316 stainless steel; 12 mm I.D.). The temperature was set using a three-zone resistively-heated furnace (Applied Test Systems Series 3210; Watlow controllers; 96 Series) and measured with a K-type thermocouple held within an internal concentric thermowell placed with its tip in the axial center point of the packed bed. Microporous aluminosilicates and other heterosilicates in their NH₄-form were treated before catalytic rate measurements in a 5 % O₂ in He stream (83.3 cm³ g⁻¹ s⁻¹, Praxair) by heating to 818 K (at 0.025 K s⁻¹) and holding for 3 h to convert the NH₄⁺ to H⁺, and then cooled to 503 K. Keggin POM clusters (H-form) were treated in flowing He (50 cm³ g⁻¹ s⁻¹; 99.999 %, Praxair) by heating to 503 K (at 0.083 K s⁻¹) to remove adsorbed moisture. Propene (99.9 %, Praxair) or isobutene (99.9 %, Praxair) were introduced into a He stream (99.999 %, Praxair) at the molar rates required to achieve the desired alkene pressure; the total system pressure was maintained using a dome-loaded regulator (Tempresco). The effluent was transferred through lines held above 373 K into a gas chromatograph (Agilent 6890) to measure reactant and product concentrations using flame ionization detection after chromatographic separation with a methyl silicone capillary column (Agilent HP-1 column, 50 m x 0.32 mm x 1.05 μm film) where known retention times of hydrocarbon mixtures on similar columns were used for molecular speciation [26,27].

3.2.3 Infrared assessment of hydroxyl groups and adsorbed species during catalysis

Infrared spectra were collected using a Nicolet NEXUS 670 infrared spectrometer equipped with a Hg-Cd-Te (MCT) detector cooled with liquid N₂. Self-supported wafers (~20-40 mg) were sealed within a quartz vacuum infrared cell fitted with NaCl windows and treated in flowing dry air (20.8 cm³ g⁻¹ s⁻¹, zero grade, Praxair) by heating to 818 K (at 0.033 K s⁻¹), holding for 3 h, and cooling to reaction temperature in flowing He. Propene (99.9 %, Praxair) or isobutene (99.9 %, Praxair) were then introduced into the He flow (99.999 %, Praxair) at rates

designed to give desired alkene pressures. Spectra were collected with 2 cm⁻¹ resolution and 4000-400 cm⁻¹ by averaging 64 scans.

3.2.4 Density functional theory methods

Periodic density functional theory in the Vienna ab initio Simulation Package (VASP) [28–31], was used to determine optimized structures and energies for stable intermediate and transition states. Wavefunctions were represented by a periodic plane-wave basis set expansion (to a cut-off energy of 396 eV) and projector-augmented wave (PAW) pseudopotentials were used to describe electron-core interactions [32,33]. Exchange and correlation energies for zeolites were calculated within the generalized gradient approximation using revised Perdew–Burke–Ernzerhof (RPBE) functionals [34–36] with dispersive energies and forces calculated by DFT-D3 during each energy minimization [22,23]. Calculations for Keggin POM clusters were done with revised Perdew–Wang (PW91; [37]) functional in order to be consistent with previous studies [8–10,13,38]. A 1 x 1 x 1 Monkhorst–Pack k-point mesh was used to sample the first Brillouin zone in both cases [39].

Minimum energy reaction paths were calculated using nudged elastic band (NEB) methods [40] with structures converged to energies within 1×10^{-4} eV and forces to within 0.3 eV Å⁻¹ to identify starting structures for TS structures, which were further refined using Dimer methods [41]. Energies were converged self-consistently to $<1 \times 10^{-6}$ eV for each optimization step and structures were converged until forces on all of the atoms were < 0.05 eV Å⁻¹. Reactant, product and transition state energies include contributions from electronic energies (E_0), zero-point vibrational energies (ZPVE), vibrational free energies (G_{vib}) and translational and rotational free energies (G_{trans} and G_{rot}) for gaseous molecules. ZPVE and G_{vib} values were determined from the frequencies in optimized structures. Low-frequency modes of weakly bound adsorbates were excluded because of significant inaccuracies in their contributions to free energies. Instead, these modes were incorporated as a fraction (0.7) of the translational and rotational gas phase entropies of alkene analogs from statistical mechanics, a method shown to accurately estimate adsorption entropies of adsorbed molecules on oxide surfaces [42].

Keggin POM clusters were described by placing full clusters (1.1 nm diameter) at the center of 3 x 3 x 3 nm³ unit cells to prevent electronic interactions among neighboring cells. Deprotonation energies (DPE) values are defined as the energy required to remove a proton (H^+ , with energy E_{H^+}) from an acid (AH , with energy E_{AH}) to non-interacting distances leaving the isolated conjugate base (A^- , with energy E_{A^-}).

$$DPE = E_{\text{H}^+} + E_{\text{A}^-} - E_{\text{HA}} \quad (1)$$

The DPE values for POM clusters were calculated with secondary alkoxides bound at all but the bridging proton being removed (Fig. 1; HPW) to account for the saturation coverages inferred from kinetic data. On clusters of semiconducting oxides, such bound species influence intracluster binding properties, including DPE values. The isolated nature of the protons in aluminosilicates and their insulating properties as solids causes their properties to be insensitive to coverages at remote sites. DPE values are therefore reported on bare surfaces for zeolites averaged over all oxygen and T-site locations [11].

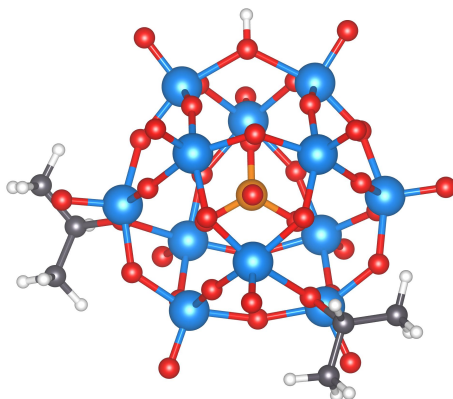


Figure 1. DFT-optimized HPW structure with secondary propoxides at the two nonreacting proton locations [PW-91].

TON, MFI and FAU zeolites were described using five, one and one unit cells (unit cells defined in [43]), respectively, because they contained large and similar numbers of atoms and fully captured the details of the relevant voids, while providing a vacuum region that prevents electronic interactions among chemical species present in periodic images. The following proton locations (as per site numbering convention [43]) were used for catalysis: Al1-O1(H) in FAU, which is located in the supercage; Al12-O20(H) in MFI, which is located in the intersection void of the sinusoid and straight channels; Al3-O4(H) in TON, which is in the one-dimensional channel, the location of 3 of the 4 unique T-sites in the framework.

3.3. Results and Discussion

3.3.1 Kinetic and spectroscopic assessment of alkene dimerization mechanism

Alkenes with i carbon atoms react on acid catalysts to form dimers (C_{2i}) and larger oligomers (C_{3i} , C_{4i} , etc.), via subsequent addition of alkenes. The rate of the initial dimerization step equals the rate of propene consumption when propene is predominantly converted to C_6 oligomers, as typically observed at lower conversion and pressure. These propene dimerization turnover rates (normalized by H^+) are proportional to the pressure of the propene reactant (10–450 kPa, 503 K) on TON, BEA, MFI and FAU zeolites (Fig. 2a) and on silica-supported polyoxometalate (POM) clusters ($H_3PW_{12}O_{40}$, herein forth denoted as HPW) and amorphous silica-alumina (SiAl) mesoporous acids (Fig. 2b). A similar first-order kinetic dependence was observed on Ga-MFI, Fe-MFI, B-MFI and on Al-TON and Al-MFI samples with other Si/Al ratios and these data are included in the Supplementary Information (SI; Fig. S1). The insensitivity of turnover rates to Si/Al ratios (site density) is discussed in Section 3.2. The effects of framework substitution in heterosilicates with MFI structure are discussed in terms of acid strength and deprotonation energies in Section 3.3.

Regressed first-order rate constants (per H^+) vary by a factor of ~ 100 among these catalysts (Fig. 2c); such large differences in reactivity are even evident among microporous aluminosilicates samples that differ solely in their ability to confine transition states and precursors, but contain acid sites of similar strength [12]. The semi-logarithmic scale in Figure 2c highlights these large effects of confining structure and acid strength and the expected exponential dependence of rate constants on free energies of activation. The underlying chemical

meaning of these effects requires a mechanistic interpretation of these rate constants in the context of the formalism of transition state theory. It also requires a systematic and rigorous description, first in terms of geometries but ultimately in terms of energies, of how van der Waals interactions and the stability of the conjugate anions influence transition state (TS) structures and the precursors to such structures, as discussed below.

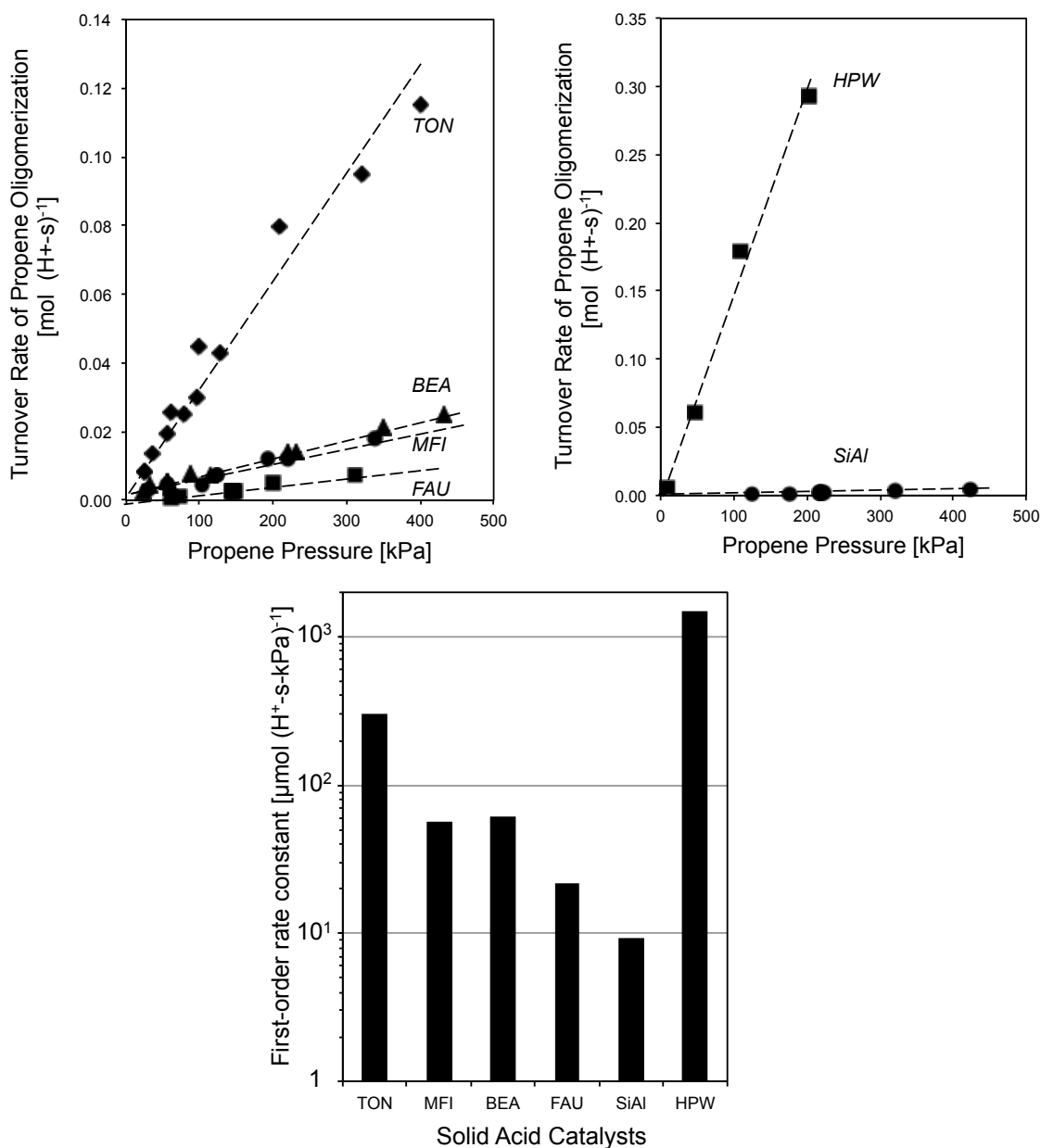


Figure 2. Propene oligomerization turnover rates on zeolites (a) (TON: ◆, BEA: ▲, MFI: ●, FAU: ■) and mesoporous samples (b) (HPW: ■, SiAl: ●) as a function of propene pressure [503 K; <5 % propene conversion; dashed lines represent linear regression fits]. (c) Fitted first order rate constants on all solid acids.

The effects of reactant pressure on turnover rates is consistent with the formation of dimers via kinetically-relevant steps in which a gaseous or confined alkene reacts with an alkene-derived adsorbed species at saturation coverages on protons; such adsorbed species may consist of π -bonded, H-bonded, or protonated alkenes, the latter, in turn, with surface attachments at various points along the alkene (e.g., primary and secondary alkoxides from propene). The observed first-order kinetic behavior may also reflect the kinetically-relevant formation of an activated form of the alkene on essentially uncovered proton sites. Previous studies have concluded that alkene protonation is quasi-equilibrated (for which alkenes and on which catalysts and from what evidence) and that the bimolecular step that forms the C-C bond limits oligomerization rates [17,44]. Such a proposal is confirmed here by the alkoxide-saturated surfaces detected by infrared spectroscopy during reaction and by the equilibration among the isomers formed in oligomerization events, which requires their adsorption-desorption equilibration.

The *in-situ* infrared spectra during alkene oligomerization on MFI and TON lack any detectable bands for unperturbed protons, evident in both samples before contact with propene. The Brønsted $\nu(\text{O-H})$ band, evident in MFI and TON at $\sim 3600\text{ cm}^{-1}$ [45] (Fig. 3 left, Spectrum A (MFI); Fig. 3 right, Spectrum A (TON); 503 K) disappears upon exposure to propene (10 kPa; Fig. 3 left, Spectrum B (MFI); Fig. 3 right, Spectrum B (TON); 503 K) even at the lowest pressures used in kinetic measurements (10 kPa). Infrared bands characteristic of $-\text{O}-\text{C}_n\text{H}_{2n+1}$ species with saturated C-H bonds appear at $1500\text{--}1450\text{ cm}^{-1}$ [46–48]. Stretches observed at $1360\text{--}1365\text{ cm}^{-1}$ are consistent with a $\nu(\text{O-C})$ band as they correlate with DFT treatments, which indicate that secondary and primary propoxide species at the T-12 location in MFI or T-3 location in TON would exhibit similar stretches (Table S1; SI). Further evidence for covalently bound species is the complete disappearance of the OH band without the appearance of a broad shifter band characteristic of a perturbed wavenumber, which would have indicated π -bonding or H-bonding.

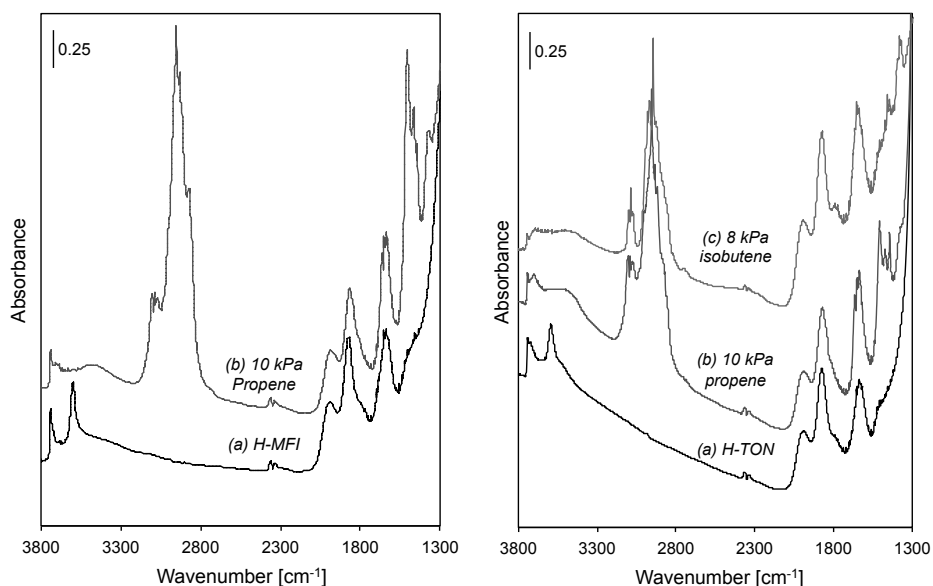


Figure 3. Left: Infrared spectra of MFI (Si/Al=43) at 503 K before contact with propene (a) and 10 kPa propene (after 0.18 ks; b). Right: Infrared spectra of TON (Si/Al=39) at 503 K in H-form (a), in 10 kPa propene (after 0.18 ks; b) and in 8 kPa isobutene (after 0.18 ks, c).

The hexene dimers formed from propene consist of skeletal and regioisomers in proportions set by their gaseous thermodynamic properties on all solid acids (TON, MFI, BEA, SiAl, HSiW; 0.01-0.5 fractional propene conversion; 10-400 kPa, 503 K) [49]. Such equilibration requires facile hydride and methyl shifts in their respective bound alkoxides, but also fast and quasi-equilibrated adsorption-desorption events. These hexenes consist of equilibrated regioisomers for all skeletal backbones (2-methylpentenes (2-MP), 3-methylpentenes (3-MP), linear hexenes (n-H) and 2,3-dimethylbutenes (23-DMB)); all the skeletal backbones that are also present in thermodynamic proportions. These conclusions are consistent with the observed full intramolecular scrambling in all products formed from 2-¹³C-propene on TON, MFI, SiAl and HSiW (503 K, 2 kPa; [49]).

These isomer distributions lead us to conclude that all alkoxides are in equilibrium with the respective reactant and product alkenes and that fast hydride shifts lead to alkoxides with surface attachments also prescribed by thermodynamics. As a result, all kinetic and thermodynamic constants represent ensemble averages over all equilibrated species, as derived in detail in Section 3.3. The formation of individual isomers via dimerization is, therefore, neither set by any kinetic hurdles nor indicative of any specific dimerization pathways or C-C bond formation TS structures. Such isomers solely reflect their thermodynamic properties as gaseous species. The pool of alkoxides formed from reactant or product alkenes and the combined product molecules containing a given number of C-atoms can each be rigorously treated as single lumped chemical species in all kinetic and thermodynamic treatments of reactivity or selectivity. Along with C-C bond formation and isomerization, β -scission also occurs, which leads to products of intermediate chain lengths that are able to subsequently react with the reactant alkene to form chains differing in size from dimers or trimers. The relative contribution of these reactions is discussed in Section 3.3.

3.3.2. Effects of Brønsted acid site density on propene dimerization turnover rates

Previous studies have shown that turnover rates (per H⁺) for hexane cracking [50], monomolecular cracking and dehydrogenation of isobutane [20] and methanol dehydration [11] do not vary with Al content in MFI or FAU. Theoretical treatments confirmed that isolated Al sites have similar acid strength in all zeolite frameworks and among all T-sites within a given framework [12]. Here, we address the effects of Al content and of the concomitant changes in proton density (H⁺/u.c., per unit cell) on dimerization turnover rates on TON, MFI and BEA. Turnover rates on TON samples with 25, 39, and 49 Si/Al ratios were the same within experimental uncertainties ($1.74\text{--}1.76 \times 10^{-2} \text{ mol (H}^+\text{-s)}^{-1}$ at 58 kPa; Fig. 4). Thus, the strength of the acid sites in TON did not vary with Al content. TON is a one-dimensional 10-MR zeolite (0.46 nm x 0.57 nm [43]; 0.57 nm pore-limiting diameter [51]; Fig. 5) with four crystallographically distinct T-sites (three are accessible to molecules from the connecting channels). In TON, the confining environments around each of its three accessible T-sites are similar; thus differences in the Al distribution with Si/Al ratio would not have significantly influenced reactivity. The proton density can also influence reactivity when diffusional restrictions create intracrystalline gradients of the reactant alkene, because such gradients become more severe at higher proton concentrations as a result of higher reactant depletion rates. Consequently, the similar turnover rates on TON samples with 25-49 Si/Al ratios provide clear evidence for the absence of diffusional corruptions in measured rates. These conclusions are confirmed by estimates using the Weisz-Prater criterion [52] or effectiveness factor [53] for

propene reactants at 503 K on TON and MFI (Tables S2 and S3; SI) using TEM estimates of crystal sizes [49] and reported diffusivities [54,55].

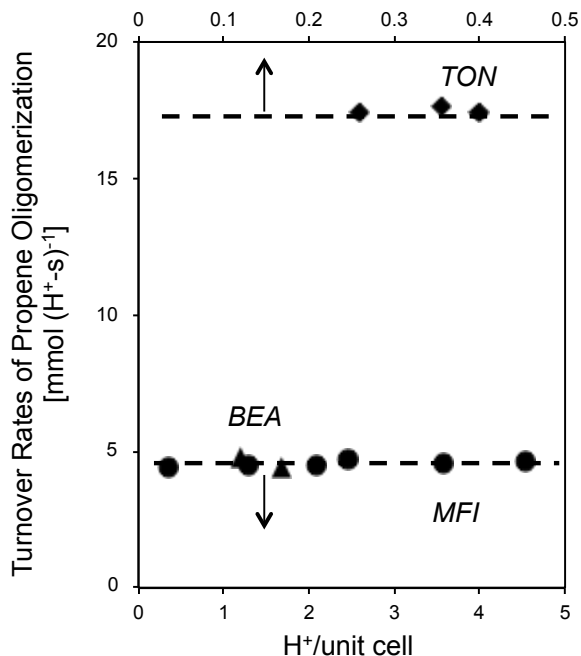


Figure 4. Propene oligomerization rates (per H⁺) as a function H⁺ per unit cell on TON (◆; 58 kPa), BEA (▲; 80 kPa) and MFI (●; 75 kPa) [503 K; <5 % propene conversion].

Propene dimerization turnover rates were also independent of Si/Al ratio (14-173) and proton density (0.4-4.5 H⁺/u.c.) on MFI zeolites (Fig. 4; <5 % conversion). MFI structures contain 12 crystallographically distinct T-sites residing within in three general types of confining environments: (i) 10-MR straight channels (0.53 x 0.56 nm [43]); (ii) 10-MR sinusoidal channels (0.51 x 0.55 nm [43]); and (iii) the cage-like voids created by their intersections (0.70 nm [51]) (Fig. 5). The strength and location of the acid sites in these MFI samples must therefore be similar and measured rates must reflect intracrystalline propene concentrations in equilibrium with the extracrystalline fluid, thus leading to measured rates that are not corrupted by diffusional effects. The similar turnover rates observed on MFI and BEA (12-MR; 3-D; 0.66 nm x 0.67 nm [43]; 0.67 nm pore-limiting diameter [51]; Fig. 5) suggest that the relevant transition states are stabilized by van der Waals interactions within voids of similar size, indicative of protons located at the intersection regions in the case of MFI frameworks. A similar conclusion is evident from turnover rates that are about four-fold lower on MFI than in TON, suggesting that the TON channels, similar in size to those in the MFI channels, preferentially stabilize the TS over the alkoxide precursors. Consequently, the preferential or Al-dependent location of protons within the channels of MFI would lead to turnover rates higher than on BEA and closer to those measured on TON, in contrast with experiments (Fig. 4). We conclude that the Al atoms and the associated protons are located at channel intersection in these MFI samples. Similar conclusions were inferred from methanol dehydration rates, for which protons in MFI samples with Si/Al ratios larger than ~15 were shown to reside only at channel intersections [11].

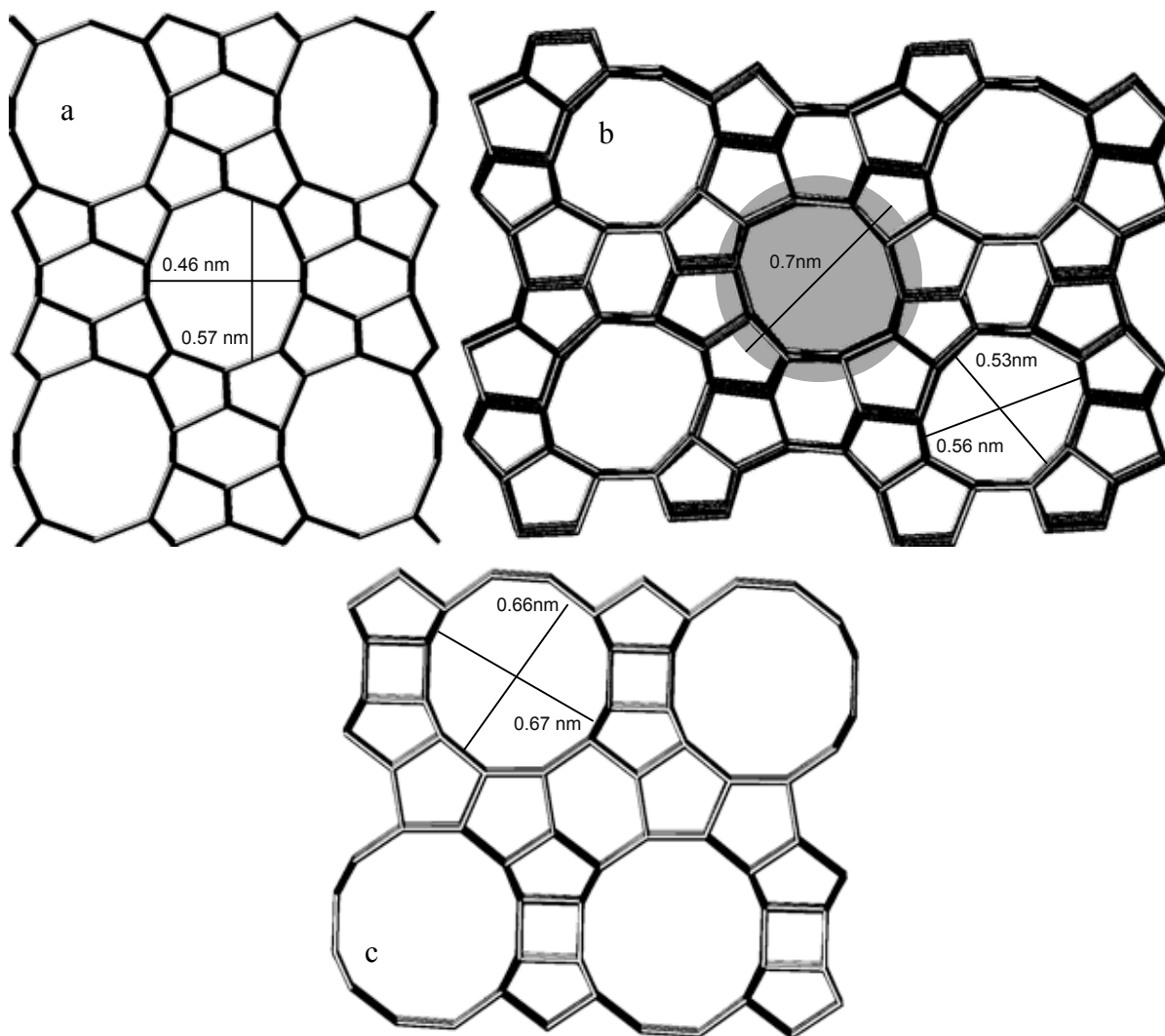


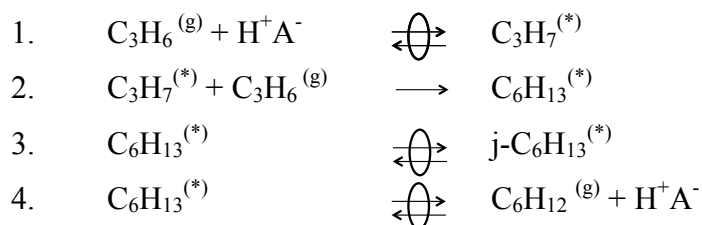
Figure 5. Pore geometry of TON (a) down the [001] 1-D 10-MR channel, and MFI (b) down the [010] 10-MR straight channel with the size of the intersection with the 10-MR sinusoidal channel shown by the dark circle and BEA (c) down the [100] 12-MR straight channel [43].

3.3.3 Assessment of alkene oligomerization mechanism using density functional theory

The elementary steps proposed in Scheme 1 combine evidence from the effects of pressure on dimerization rates, the saturated alkoxide coverages detected in the infrared spectra, and DFT treatments that support the involvement and kinetic relevance of specific elementary steps, intermediates, and transition states. Scheme 1 illustrates the proposed sequence of elementary steps for propene reactants, but the conclusions remain unchanged for isobutene (Section 3.5) and for other alkenes and their mixtures, as we describe in a later report.

Quasi-equilibrated formation of propoxides occurs via protonation (Scheme 1, Steps 1). These propoxides are present as equilibrated primary ($C_{3,1}^{(*)}$) and secondary ($C_{3,2}^{(*)}$) propoxides, depending on the C-atom attached to the framework, as a consequence of fast intramolecular hydride shifts and of their respective fast adsorption-desorption steps [49,56]. The preferential formation of propoxides over π -bonded propene molecules is consistent with DFT-derived free energies and with calculated vibrational frequencies (Table S1; SI) that correspond to the

infrared bands detected (and to the disappearance of O-H bands) in the infrared spectra of MFI during propene reactions (503 K, 10 kPa; Fig. 3). The equilibrated nature of propoxide isomers precludes any possible kinetic evidence for their relative coverages on saturated surfaces because all kinetic consequences reflect only their lumped surface concentrations. DFT-calculated structures of primary and secondary propoxides on TON (Fig. 6) have similar free energies of formation (ΔG_{3j} at 503 K and 1 bar = $-21.8 \text{ kJ mol}^{-1}$ and $-23.2 \text{ kJ mol}^{-1}$, respectively), indicating that they co-exist at comparable coverages; their negative formation free energies indicate that unoccupied protons are present at trace concentrations at typical propene pressures (10-500 kPa).



Scheme 1. Sequence of elementary steps for dimerization of propene on Brønsted acid sites (H^+A^-) where (g) and (*) indicates a gas-phase or surface bound species, respectively and *j*- indicates a particular hexene isomer. Ovals over double arrows denote quasi-equilibrated steps.

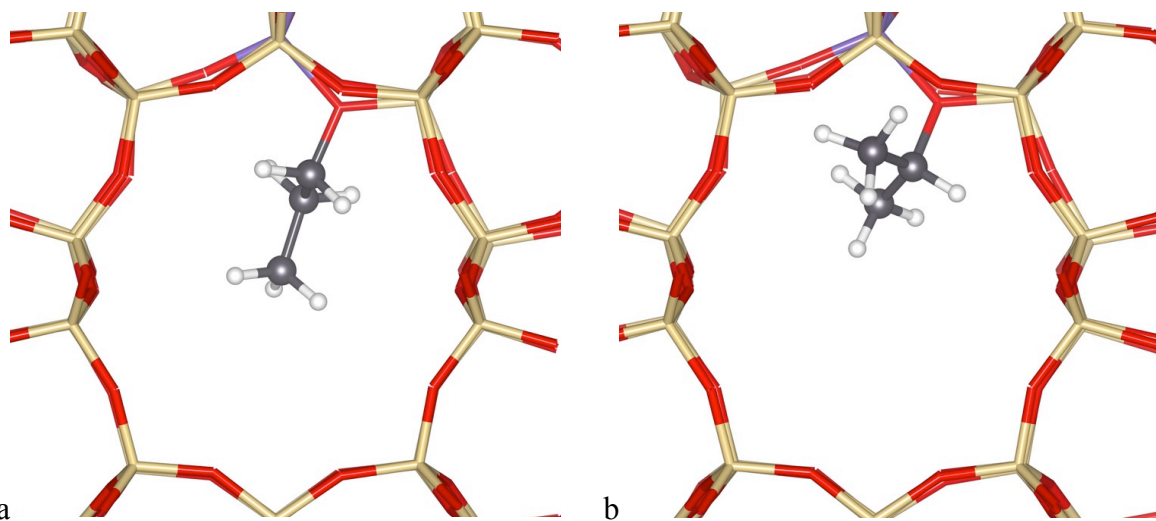
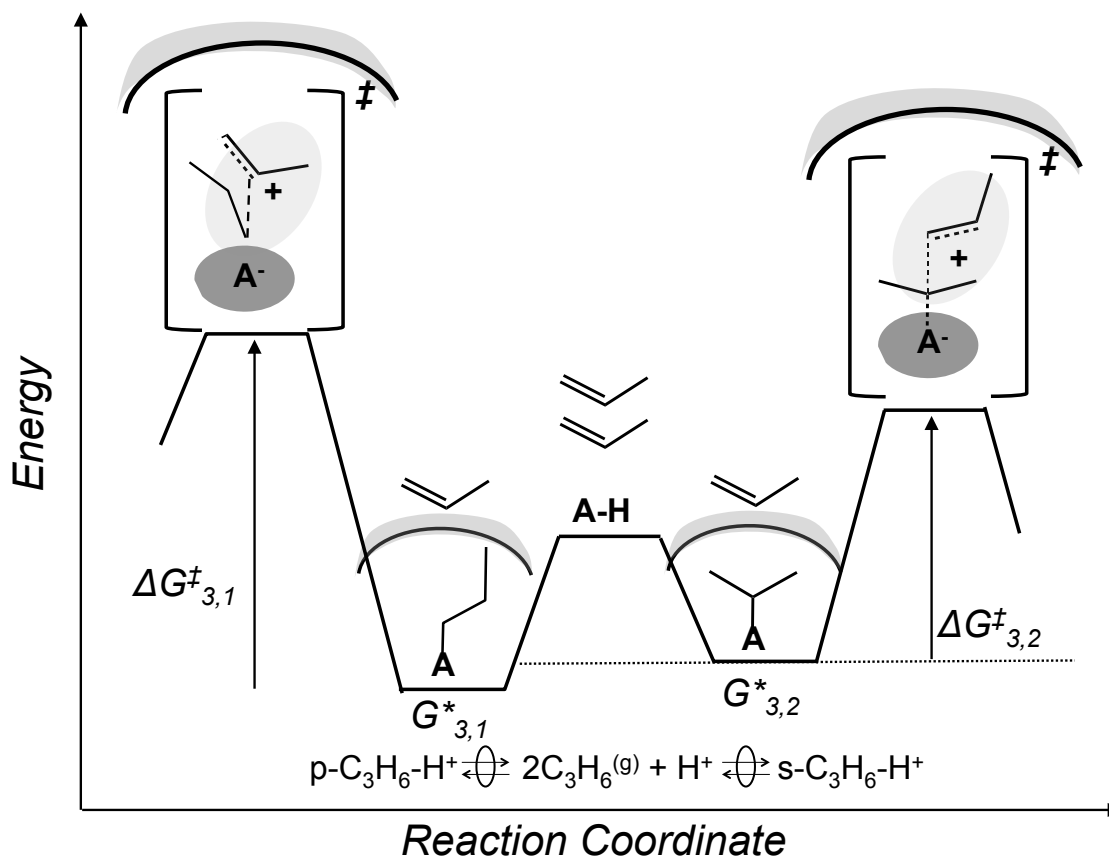


Figure 6. DFT-derived structures of primary ($\text{C}_{3,1}^{(*)}$; a) and secondary ($\text{C}_{3,2}^{(*)}$; b) bound propoxides on TON (Al3-O4; RPBE+D3BJ).



Scheme 2. Schematic reaction coordinate diagram for propene dimerization on Brønsted acid sites (H^+A^-) where the caps indicate the confining voids in zeolites. $\Delta G_{3,j}^\ddagger$ represents the measured free energy barriers for C-C bond formation from respective alkoxides $G_{3,j}^*$, where * and ‡ indicate bound or transition states, respectively and j indicates distinct attachment points.

The sole irreversible step in Scheme 1 forms a C-C bond via reactions between a reactant-derived bound alkoxide and a gas-phase alkene, in a step mediated by carbenium-ion transition states (Scheme 1, Step 2). The hexenes formed can isomerize (Scheme 1, Step 3) and then desorb (Scheme 1, Step 4) or desorb and then readsorb and isomerize; these two possibilities are indistinguishable because adsorption-desorption steps are fast, as shown by the thermodynamic equilibrium among all gaseous hexene isomers formed from propene reactants [49]. The equilibrated pool of hexoxide isomers, via quasi-equilibrated adsorption-desorption events, can also react with another alkene to form C_9 chains.

The rate of dimerization of alkene with i carbon atoms in accordance with Scheme 1 is given by:

$$r_i = \frac{\sum_j k_{ij} K_{ij} [C_i]^2}{1 + \sum_j K_{ij} [C_i] + \sum_n \langle K_n \rangle [C_n]} \quad (2)$$

where j denotes the distinct attachment points of the alkoxides derived from the reactant alkene. In Equation 2, n is the number of C-atoms, C_n is the molar concentration of the products formed,

and $\langle K_n \rangle$ is their equilibrium constant for alkoxide formation, ensemble-averaged over all alkoxide surface attachment points.

At conditions that lead to surfaces covered by bound alkoxides and to low conversions and high $[C_i]/\sum[C_n]$ ratios (<0.05 conversion and > 50 molar ratios at all conditions of this study), this equation becomes:

$$r_i = \frac{\sum_j k_{ij} K_{ij} [C_i]}{\sum_j K_{ij}} \quad (3)$$

The kinetic and equilibrium constants in this equation are functions of Gibbs free energies:

$$K_{ij} = e^{\left(\frac{-\Delta G_{ij}}{RT} \right)} \quad (4)$$

$$k_{ij} = e^{\left(\frac{-\Delta G_{ij}^\ddagger}{RT} \right)} \quad (5)$$

The terms $\Delta G_{ij}^\ddagger$ and ΔG_{ij} are given by:

$$\Delta G_{ij}^\ddagger = G_{ij}^\ddagger - G_{ij}^{(*)} - G_i^{(g)} \quad (6)$$

$$\Delta G_{ij} = G_{ij}^{(*)} - G_i^{(g)} \quad (7)$$

where the $\ddagger$, $*$, and g notation stand for the transition state, the bound alkoxides, and the gaseous alkenes, respectively. The equilibration among all bound alkoxides, a consequence of fast hydride shifts and of their equilibration with gaseous alkene reactants and the choice of the j th configuration as a reference leads to:

$$r_i = \frac{\sum_j k_{ij} \left(\frac{K_{ij}}{K_{i,ref}} \right) [C_i]}{\sum_j \left(\frac{K_{ij}}{K_{i,ref}} \right)} \quad (8)$$

Substitution of Equations 4-7 yields:

$$r_i = \frac{\sum_j e^{\frac{-(G_{ij}^\ddagger - G_{ij}^{(*)})}{RT}} [C_i]}{\sum_j e^{\frac{-G_{ij}^{(*)}}{RT}}} \quad (9)$$

The definition of $\langle G_i^\ddagger \rangle$ and $\langle G_i^{(*)} \rangle$ as the exponential averages of the TS and alkoxide free energies over all bound alkoxide configurations then gives:

$$e^{-\frac{\langle G_i^\ddagger \rangle}{RT}} = \sum_j e^{-\frac{G_{ij}^\ddagger}{RT}} \quad (10)$$

$$e^{-\frac{\langle G_i^{(*)} \rangle}{RT}} = \sum_j e^{-\frac{G_{ij}^{(*)}}{RT}} \quad (11)$$

These definitions then allow the dimerization rate of an alkene with i carbon atoms (Equation 9) proceeding through all configurations of bound alkoxides to be expressed as:

$$r_i = e^{-\frac{\langle G_i^\ddagger \rangle - \langle G_i^{(*)} \rangle - G_i^{(g)}}{RT}} [C_i] = k_i [C_i] \quad (12)$$

This rate equation accounts for all C-C bond formation TS structures, irrespective of the equilibrated alkoxide from which they formed, and for all bound alkoxides, irrespective of which TS they lead to in their conversion to products. This equation, however, does not account for the transition states that form all of the product isomers. Instead, we surmise, as is customary in transition state formalisms, that the exponential reactivity consequences of small differences in free energies among these TS structures (Eq. 5) will cause one dimer structure to form preferentially, while all others from via rapid hydride and methyl shifts upon readsorption. The resulting equation (Eq. 12) reflects a kinetic treatment that is general to all catalysts and alkenes with kinetically-relevant reactions involving bound species in quasi-equilibrium with their gaseous precursors and present at saturation coverages.

DFT-derived free energies of reactants, intermediates, transition states and products on TON (Fig. 6) are consistent with the assumptions required to obtain the functional form of the rate equation shown as Equation 12. The formation of C-C bonds via reactions of propene with secondary ($G_{3,2}^\ddagger$) and primary ($G_{3,1}^\ddagger$) propoxides to a product with the same skeletal backbone (2MP) were explored and the resulting TS structures are shown in Table 2. The TS free energies indicate that C-C bonds form predominantly from the secondary propoxide, which gives free energy values much smaller ($G_{3,2}^\ddagger = 103 \text{ kJ mol}^{-1}$) than its equilibrated primary analog ($G_{3,1}^\ddagger = 184 \text{ kJ mol}^{-1}$), in which case $\langle G_i^\ddagger \rangle$ (Eq. 12) merely reflects the value of $G_{3,2}^\ddagger$.

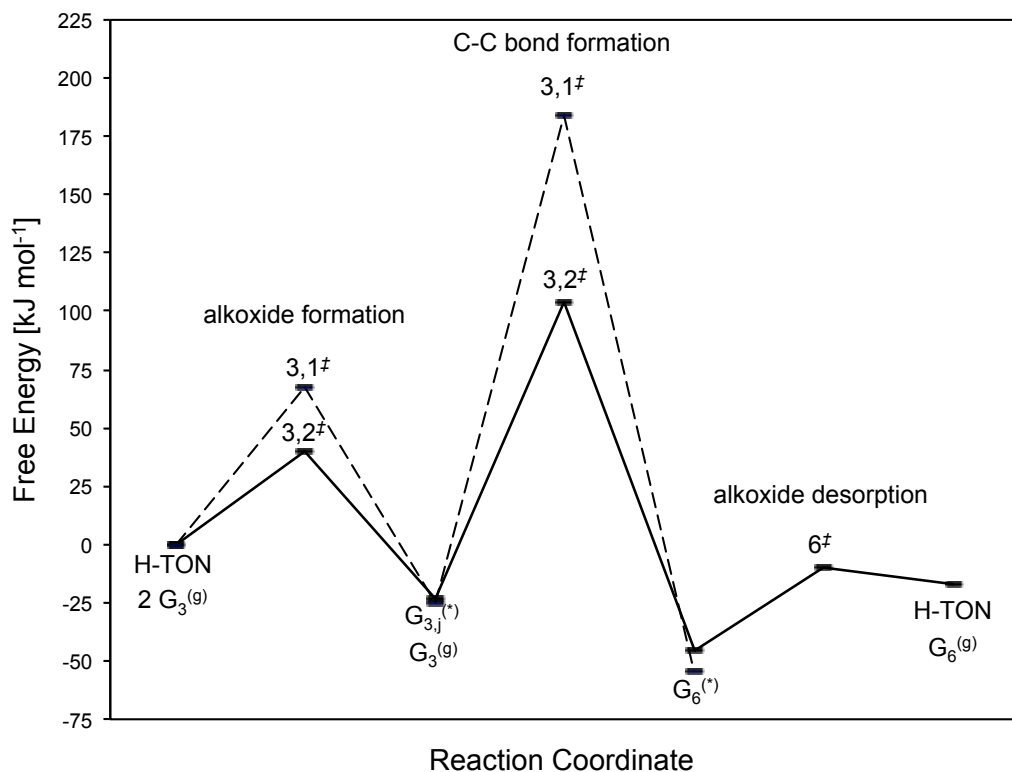
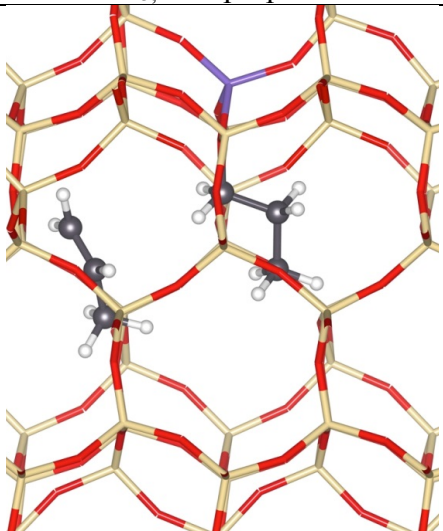
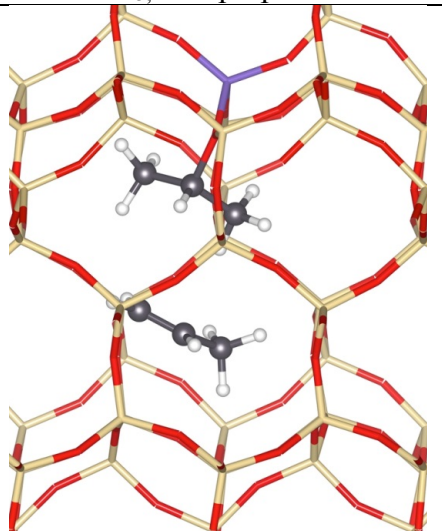
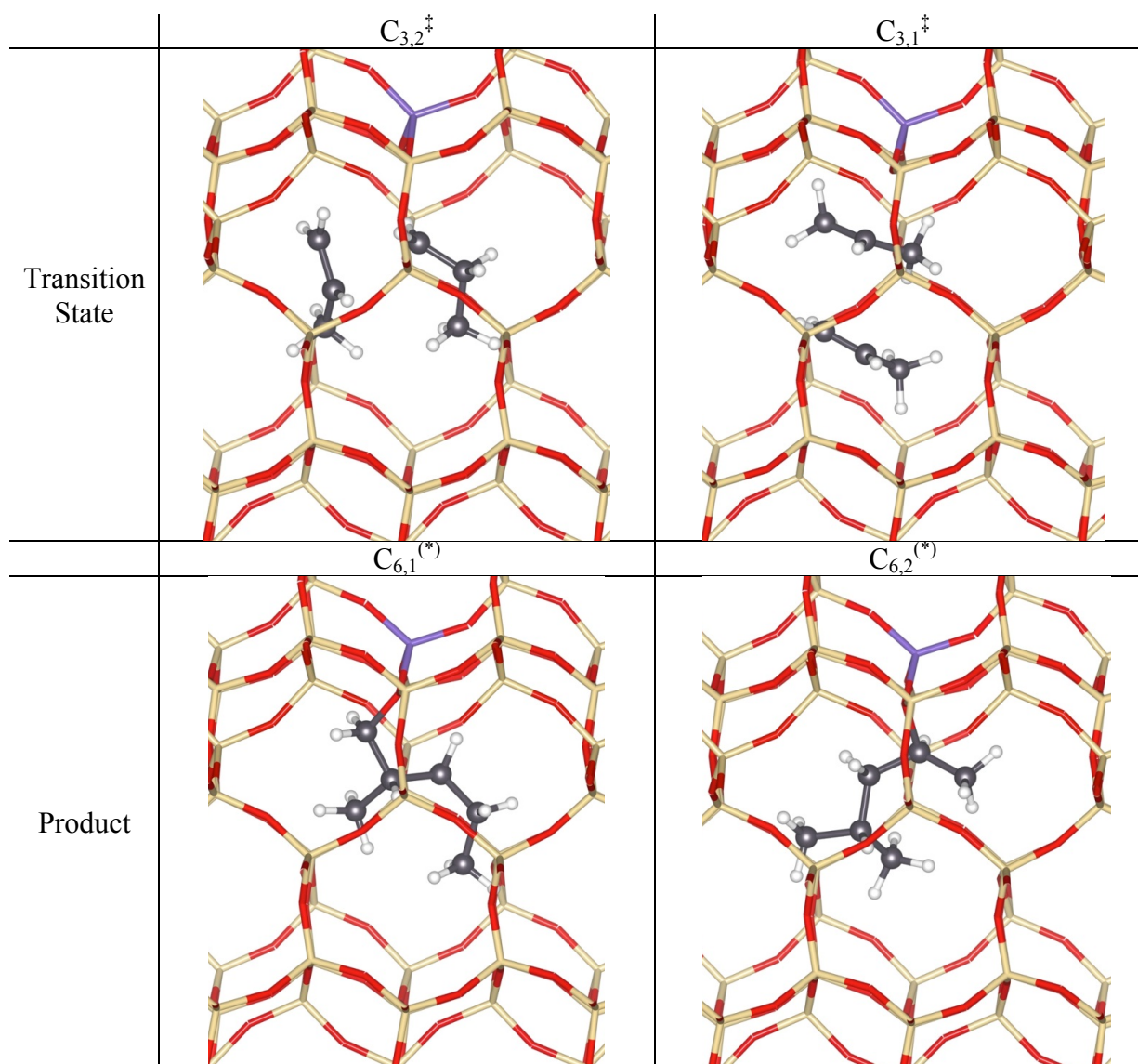


Figure 6. DFT-derived reaction free energy diagrams of propene dimerization on H-TON (RPBE+D3BJ; 503 K, 1 bar) where $i,j^\ddagger$ represent transition states for either alkoxide and C-C bond formation with i carbons and attachment j . $G_i^{(g)}$ and $G_{i,j}^{(*)}$ represent alkenes with i carbons in gaseous and alkoxide state, respectively. Energies are relative to a bare surface and gaseous reactants.

Table 2. DFT-derived structures of reactants, transition states and products involved in the C-C bond formation elementary steps from a primary propoxide and secondary propoxide on TON (RPBE+D3BJ).

	$C_{3,1}^{(*)} + \text{propene}$	$C_{3,2}^{(*)} + \text{propene}$
Reactant		



3.3.4. Consequences of confinement on alkene dimerization turnover rates

Propene dimerization turnover rates show a similar linear dependence on pressure for all solid acids, but the first-order rate constants vary significantly among the different framework structures, even for aluminosilicates that contain acid sites of similar strength (Fig. 1). These rate constants decreased monotonically as the size of the aluminosilicate voids increased (Fig. 8). Void sizes, in the context of Figure 7, are defined using strictly geometric features and more specifically by the characterization of size in terms of the largest sphere that can be fully inscribed within each framework [51]. The size of MFI voids is taken here as that of its channel intersections, because Al atom appear to reside predominantly at such locations at these Si/Al ratios [57,58]; moreover, turnover rates on MFI are similar to those for protons in BEA voids that resemble such intersections in size (Table 4). Measured dimerization rate constants (k_3 ; Eq. 12) reflect the energy of the ion-pair TS that mediates C-C bond formation relative to that of a smaller propoxide, present in an equilibrated mixture of binding configurations, and a gaseous propene.

These geometric descriptors and their consequences for reactivity reflect, in turn, the ability of the confining voids to stabilize the TS and the bound alkoxides to different extents. More complete and rigorous descriptions must replace such heuristic visualizations of pore space in terms of geometric constructs with van der Waals interaction energies derived from DFT functionals that properly describe them; such protocols would allow accurate assessment of “fit” for TS and alkoxide structures, diverse in size and shape among alkene reactants, within voids, also diverse in size and shape among microporous and mesoporous frameworks. In doing so, such void and molecular geometries are described in terms of the enthalpies and free energies of confinement, which rigorously determine reactivity (Eqs. 5 and 12).

The C-C bond formation TS on TON is significantly larger than for each of the two propoxide binding configurations, when such volumes are calculated using van der Waals radii for C and H (0.12 nm³ vs. 0.055 or 0.052 nm³). Their diameters, defined here as that of the sphere of equivalent volume $\langle d_{vdW} \rangle$, are 0.61 nm and 0.46-0.47 nm for the TS and propoxides, respectively. These size differences, and the accompanying changes in the external surface areas of these chemical species (Table 3), allow more effective van der Waals contacts with the framework for TS structures than bound propoxides. As a result, TS structures benefit from confinement more strongly than bound alkoxides, leading to reactivity enhancements as voids approach the size of the TS structures (Fig. 7). These TS and alkoxide dimensions, reported here from DFT-derived structures in TON vary only slightly among different frameworks, thus retaining its heuristic value as a geometric descriptor of size for the organic moieties in the diverse solid acids used in this study.

The calculated $\langle d_{vdW} \rangle$ of the transition state (0.61 nm) is larger than diameter of the pore in TON modeled by the largest inscribed sphere (0.57 nm), which indicates the inaccuracy of simplifying the pore network and transition states into a series of cylinders and spheres. The DFT-calculated dispersive energies are determined from methods that aim to capture long-range correlation interactions that regulate attractive van der Waals forces [22,23]. Here we use these dispersive energies from optimized structures as a more rigorous descriptor for confinement. Because these calculations include the interactions between all atoms, we subtract the contributions from the interactions between atoms of the catalyst and the interactions between the atoms within the hydrocarbon species. This results in the interaction between the entire organic moiety (either the alkoxide or the transition state) and the pore network (Eq. 13-14).

$$E_{vdW}^{(*)} = E_{ij}^{(*)} - E_{HZ} - E_i^{(g)} \quad (13)$$

$$E_{vdW}^{\ddagger} = E_{ij}^{\ddagger} - E_{HZ} - 2E_i^{(g)} \quad (14)$$

Here, all energies are the dispersive component of the electronic energies for the alkoxide ($E_{ij}^{(*)}$), the transition state ($E_{ij}^{\ddagger}$), the proton form of the catalyst (E_{HZ}) and the gas phase species ($E_i^{(g)}$). These dispersive interactions are about 100 kJ mol⁻¹ lower in energy for the propene dimerization transition state than either alkoxide precursor or their ensemble average (Eq. 11; Table 3), consistent with the preferential stabilization of the transition state, which leads to the observed effects of confinement (Fig. 7).

The dispersive interactions should also be dependent on the catalyst framework and void environment. Instead of optimizing full transition state structures in various zeolite frameworks, we approximate the dispersive interactions in other zeolites by transferring the structure of the transition state as optimized in TON into the MFI or FAU void at their T-12 and T-1 sites

(Section 2.4), respectively; this method lends itself as a probe for quickly screening zeolite frameworks, but is incomplete, as it does not ensemble average over all T-sites in the framework the way reactions average. The dispersive energy for the propene dimerization transition state ($E_{vdW}^\ddagger$) increases as the void becomes larger (TON<MFI<FAU; Fig. 8), indicating that fewer stabilizing dispersive interactions exist, which results in a lower first order rate constant. Good correlation between the experimentally measured rate constants and this descriptor for confinement (Eq. 14) is observed even without accounting for all of the T-sites and for flexibility of the zeolite framework and organic moiety that would appear in full DFT optimizations. It does, however, provide a descriptor of confinement, not in terms of geometry, yet instead in terms of energy, on which is what the rate constant depends. The concept of flexibility will be explored next by using reactants of different size (isobutene vs. propene) to understand how the framework responds to different moieties.

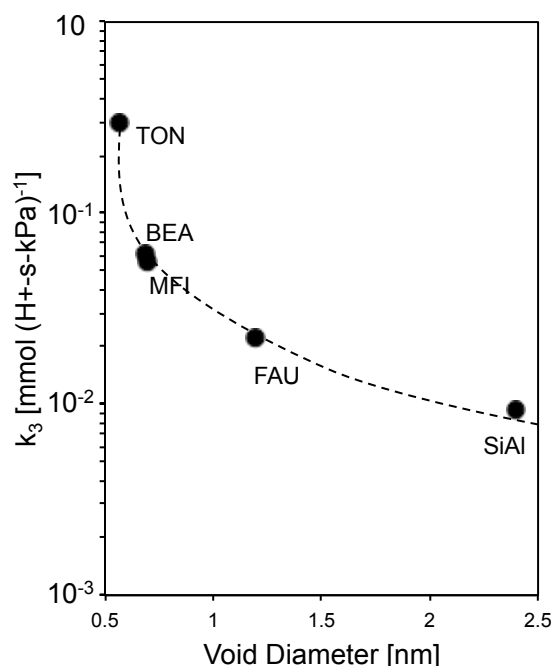


Figure 7. First-order rate constants (k_3 , per proton) for propene dimerization as a function of void diameter, defined as the largest sphere that can be inscribed within each framework type [503 K; <5 % propene conversion; dashed curve indicates a trend].

Table 3. DFT-derived van der Waals volumes, surface areas, diameters and dispersive energies of the two propoxide precursors and the C-C bond formation transition state structures from propene dimerization on H-TON. The diameters are calculated assuming a sphere of equivalent volume.

Structure in TON	V_{vdW} [nm ³]	SA_{vdW} [nm ²]	d_{vdW} [nm]	E_{vdW} [kJ mol ⁻¹]
p-propoxide (3,1*)	0.052	0.82	0.46	-117
s-propoxide (3,2*)	0.055	0.82	0.47	-120
C-C (3,2 [‡])	0.12	1.4	0.61	-215

Table 4. First-order rate constants for propene dimerization (k_{eff}) as a function of void diameter, as determined by modeling the void environment with cylinders and spheres of varying sizes for TON (Si/Al=40), MFI (Si/Al=40) and BEA (Si/Al=12.5) [503 K; <5 % propene conversion].

Zeolite	$k_{eff,3}$ [$\mu\text{mol (H}^+\text{-s-kPa)}^{-1}$]	Void Environment	Void Diameter [nm]
TON	300 $\pm$ 20	Channel	0.57
MFI	56 $\pm$ 4	Channel	0.57
		Intersection	0.70
BEA	61 $\pm$ 2	Channel	0.67

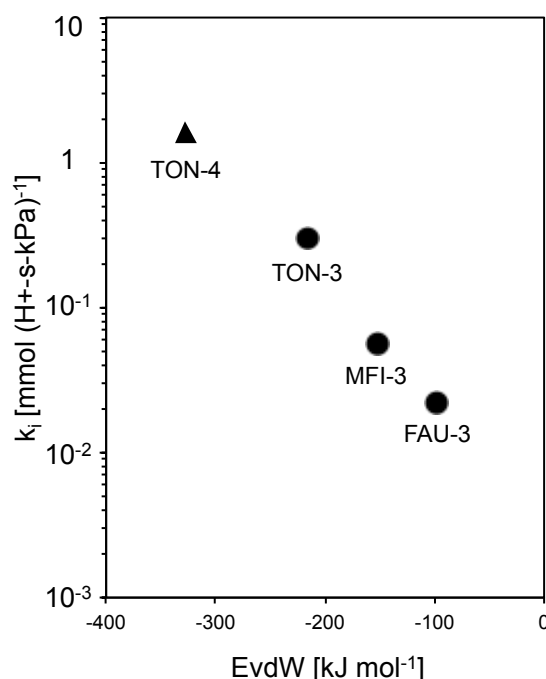


Figure 8. First-order rate constants (k_i , per proton; 503 K) for propene or isobutene dimerization as a function of E_{vdw} (D3BJ) defined in Equation 14.

Isobutene dimerization turnover rates are also proportional to reactant alkene pressure (Fig. 9) on TON. *In-situ* infrared spectra during isobutene dimerization are also consistent with this mechanism as they show the disappearance of O-H bands in TON, the emergence of butoxide-related bands and the absence of features associated with perturbed O-H stretches (8 kPa isobutene; Fig. 3 right, Spectra c; 503 K). DFT-derived Gibbs free energies on TON indicate that while isobutoxides attached at the primary ($C_{4,1}^{(*)}$) or tertiary ($C_{4,3}^{(*)}$) C-atom have similar free energies of formation ($\Delta G_{4j} = -19.9 \text{ kJ mol}^{-1}$ and $-12.0 \text{ kJ mol}^{-1}$ for primary and tertiary, respectively (503 K; 1 bar), C-C bond formation occurs only from the tertiary isobutoxide ($> 20 \text{ kJ mol}^{-1}$ lower in energy from the primary isobutoxide), which leads to a rate expression for consistent with Equation 13. Measured rate constants for isobutene dimerization on TON, however, are about five-fold larger than for propene (0.30 vs. 1.6 $\text{mmol (H}^+\text{-s-kPa)}^{-1}$). This difference in reactivity is due to a difference in proton affinity, where larger, more substituted transition states have greater proton affinities, and to a difference in van der Waals interactions. The transition state for isobutene is larger than that for propene (in terms of volume, surface area

and equivalent diameter; Tables 3 and 5) (structures for isobutene and propene compared in Fig. 11), resulting in additional stabilization, consistent with lower E_{vdw} by more than 100 kJ mol⁻¹ (Fig. 9).

The combination of various transition states and frameworks (propene and isobutene; TON, MFI, FAU) in one figure reflects the robustness of using this dispersive energy to describe confinement effects even with the approximations that were made. For example, this dispersive energy only accounts for the attractive interactions, but the organic moiety could be too close to the lattice oxygen and result in repulsion. The zeolite can partially mitigate these negative interactions by creating local distortions in the lattice. The extent of these distortions is quantified for the isobutene and propene transition states in TON because their structures were fully optimized using DFT treatments that account for van der Waals interaction (RPBE-D3BJ), while the structures for MFI and FAU used the organic component of transition state from TON and static crystals to obtain an approximation of E_{vdw} . Here, we quantify the distortions in terms of mean atom displacement between the transition state and the proton state. Due to the geometry of the TON pore network, we define a cylindrical coordinate system with the origin at the center of the 10-MR channel. Each lattice atom m has the coordinates of $(r_{\text{TS}}, \theta_{\text{TS}}, z_{\text{TS}})_m$ and $(r_{\text{H}}, \theta_{\text{H}}, z_{\text{H}})_m$. The change in average r for all oxygen atoms in the first shell of the cylinder is 0.34 pm for isobutene dimerization and 0.055 pm for propene dimerization, indicating TON deforms more while trying to accommodate the larger transition state. These distortions are small but energies of covalent bonds depend sensitively on bond length, suggesting an energy penalty that is factored into the overall optimization of the transition state.

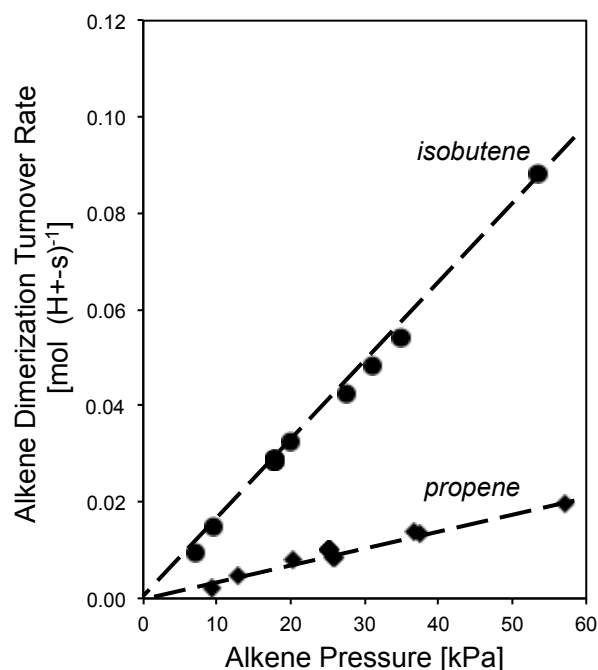


Figure 9. Alkene dimerization turnover rates as a function of propene (◆) and isobutene (●) pressure on TON [503 K; <5 % propene conversion; dashed lines represent linear regression fits]. The rate constant for isobutene dimerization is 5.3 times larger than that for propene, due to a larger, more stable transition state.

Table 5. DFT-derived van der Waals volumes, surface areas, diameters and dispersive energies of the two butoxide precursors and the C-C bond formation transition state structures from isobutene dimerization on H-TON. The diameters are calculated assuming a sphere of equivalent volume.

Structure in TON	V_{vdW} [nm^3]	SA_{vdW} [nm^2]	d_{vdW} [nm]	E_{vdW} [kJ mol^{-1}]
p-isobutoxide (4,1*)	0.074	1.00	0.51	-140
t-isobutoxide (4,3*)	0.071	0.99	0.52	-153
C-C (4,3 [‡])	0.15	1.7	0.66	-327

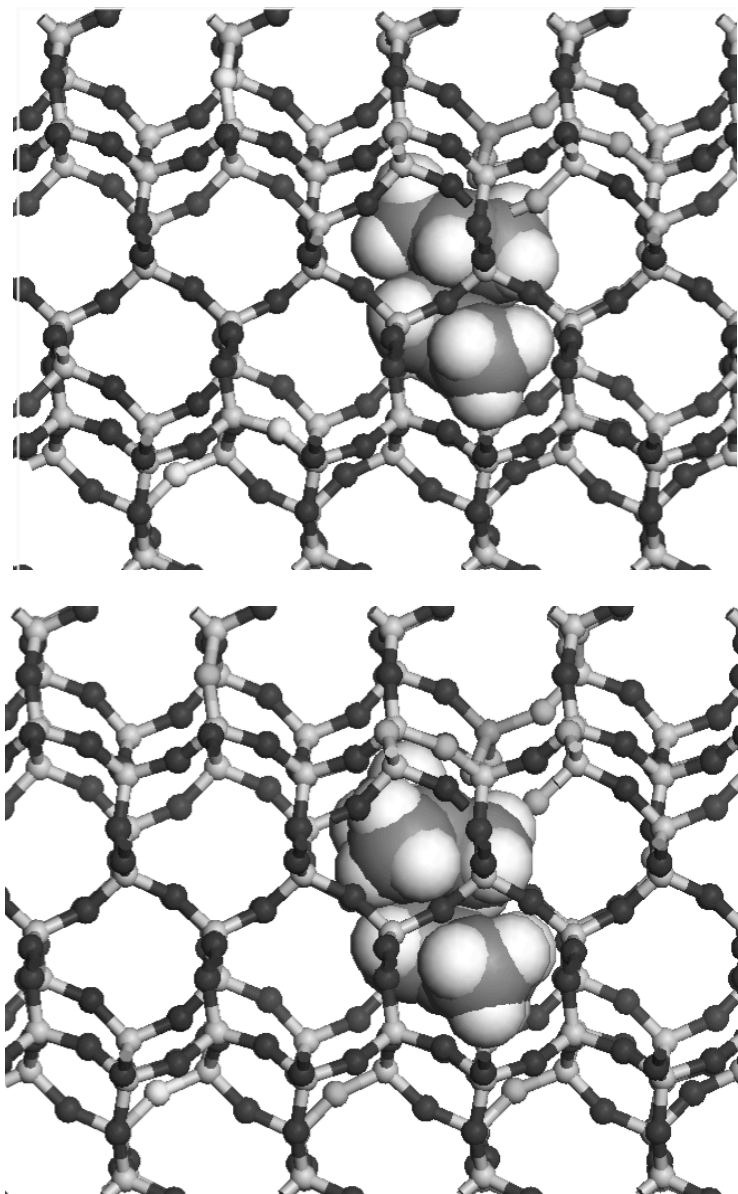
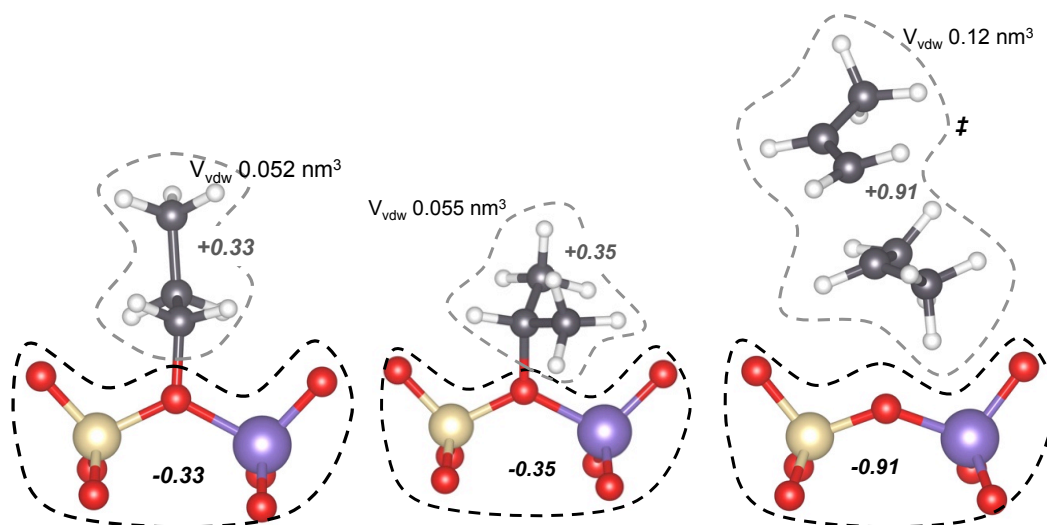


Figure 10. DFT-derived structures of transition states for C-C bond formation via secondary propoxide (top) and a tertiary butoxide (bottom) on TON (RPBE+D3BJ). The van der Waals radii for organic atoms is used to illustrate its occupied volume.

3.3.6. Consequences of acid strength on propene dimerization turnover rates

These effects of molecular size and of confinement on reactivity occur in parallel with the effects of the conjugate anion in the carbenium ion-pairs at the transition state. Deprotonation energy (DPE) is used as a surrogate for the acid strength of solid Brønsted acids. It represents the energy required to heterolytically cleave the O-H bond and move the proton to non-interacting distances, or how stable the anion is with the negative charge. C-C bond formation steps on solid acid catalysts involve fully protonated (ion-pair) transition states; the measured barrier reflects the energy difference between this charged transition state and the equilibrated alkoxide pool, which are covalently bound species. The nonzero values for calculated charge on the alkoxides (propoxides: +0.33-0.35; Scheme 3) is due to the inaccuracies of QUAMBO treating covalent bonds. Fully charged transition states ($\text{C-C}_{3,2}^\ddagger$: +0.91 (organic), -0.91 (anion)) benefit from stronger acids because stronger acids require less energy to separate charge and form ion-pair transition states than weaker acids.



Scheme 3. DFT-derived charge distributions and van der Waals volumes for the two propoxide precursors and the C-C bond formation transition state structures from propene oligomerization (H-TON, RPBE+D3BJ). The pore network was deleted after optimization for visual clarity.

Acid strength is varied in zeolites by changing the heteroatom (Al, Ga, Fe, B) and DPE values can be estimated from DFT using large cluster models [11]. Changing the heteroatom does not change the structure of the zeolite; thus the series of H-X-MFI samples probe the effects of acid strength on propene dimerization independently of confinement effects. Propene dimerization turnover rates were first order on all samples (Fig. S1; SI), but the effective first-order rate constants were influenced by the identity of the heteroatom. This is quantitatively consistent with their different DPE values (Fig. 11) and with the expectation that stronger acids would lead to lower activation energies for reactions with ion-pair transition states because stronger acids have a more stable conjugate anion.

Acid strength of unconfined protons was probed by using amorphous silica alumina (SiAl) as well as Keggin polyoxometalates with different central atoms that change both the number of charge balancing protons as well as the strength of each proton [9]. The effective first-order rate constants (normalized per proton) again decrease exponentially with increasing DPE (Fig. 11). Here, amorphous silica alumina is estimated to have the same DPE as H-Al-MFI. The DPE values for the POM clusters were calculated using surfaces covered propoxides, consistent

with the state of the catalyst during experimental conditions. This correction was not implemented for the zeolite DPE values, as each site is isolated and alkoxides at one site would not influence the acid strength at a different proton.

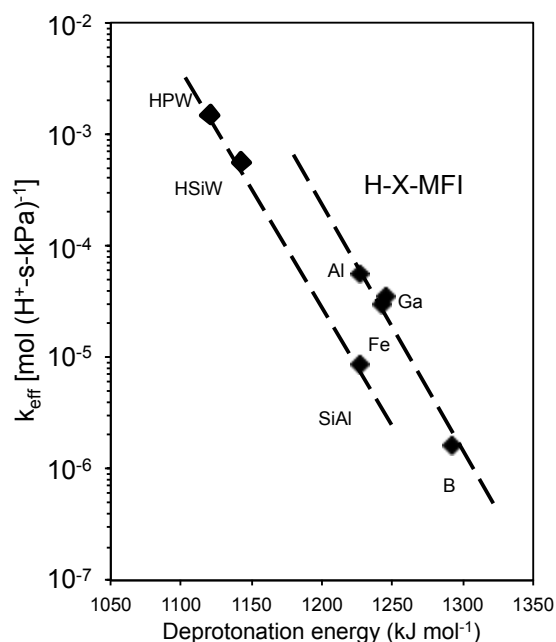


Figure 11. First-order rate constants for propene dimerization (k_{eff}) as a function of deprotonation energy for both unconfined and MFI-confined protons [503 K; <5 % propene conversion].

The trend lines in Figure 11 for unconfined and confined solid acids have similar slopes, indicating that, for a given solvating environment, stronger acids stabilize the charged transition states more than relevant neutral precursors, but a confined proton has a higher first-order rate constant than an unconfined one for a given acid strength. This decrease in activation energy is provided solely by solvation of the larger, ion-pair transition state relative to the smaller, covalently-bound precursors. The DFT-calculated formation energy of this precursor (relative to a bare proton and gas phase propene) is independent of DPE (Fig. 12), which is consistent with a fully formed alkoxide having significantly less charge than their transition state. The charge calculated using partial-charge decomposition also did not change with acid strength (Fig. 12), which is in good agreement with results reported for methoxide covered surfaces on Keggin POM clusters [9]. These energies were calculated using bare clusters and thus the DPE values used reflect this state. Alkoxide-covered clusters would have different energies, but the difference would be similar regardless of acid strength.

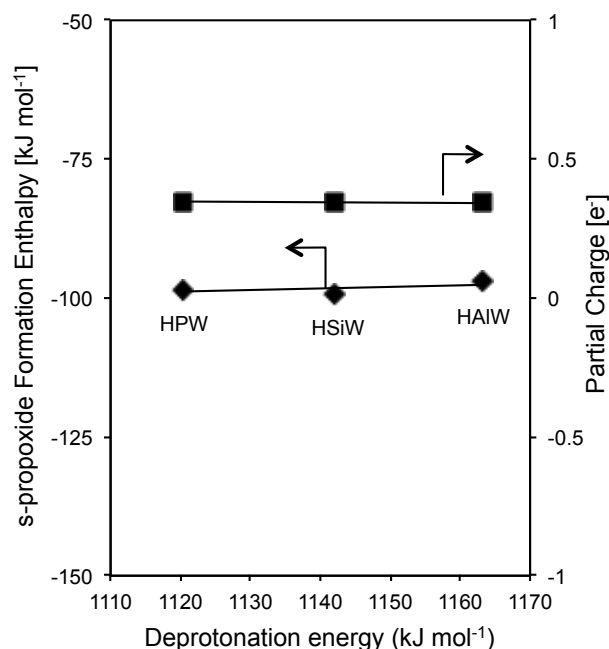


Figure 12. Calculated formation enthalpies (503 K) of secondary-propoxides on bare Keggin polyoxometalates as a function of deprotonation energy.

3.4. Conclusions

The effects of solvation and acid strength on the reactivity of Brønsted acids for propene and isobutene oligomerization were compared on microporous and mesoporous solid acids. Kinetic, spectroscopic and theoretical examination of the mechanism reveals C-C bond formation is kinetically limiting and occurs on surfaces covered with equilibrated pools of alkoxides attached to the lattice at different points resulting in different degrees of substitution (primary, secondary, tertiary). TON, a 10-MR zeolite, exhibited high reactivity due to increased solvation when compared to large pore zeolites and mesoporous samples of similar acid strengths because the transition state formed in the voids is larger than its alkoxide precursors. MFI (10-MR) showed reactivity more similar to 12-MR large pore zeolites (BEA) than to 10-MR TON, consistent with the acid sites being located in the large intersections of the sinusoidal and straight 10-MR channels. Isobutene coupling rate constants are higher than propene in TON, consistent with DFT-derived sizes and dispersive energies that are used as descriptors for the amount of van der Waals interactions between organic moieties and their inorganic hosts and their stabilizing effects. Stronger acids exhibited higher reactivity than weaker acids because their anionic conjugate bases better stabilize the positively charged carbenium ion transition state involved in C-C bond formation as compared to the covalently-bound alkoxide precursor. These results demonstrate mechanistic understanding of alkene oligomerization on solid acids and the effects of acid strength and confinement to increase reactivity of alkene chain growth pathways that extends to other light alkenes as well as plethora of zeolitic, mesoporous or supported polyoxometalate catalysts.

3.5. Supplemental Information

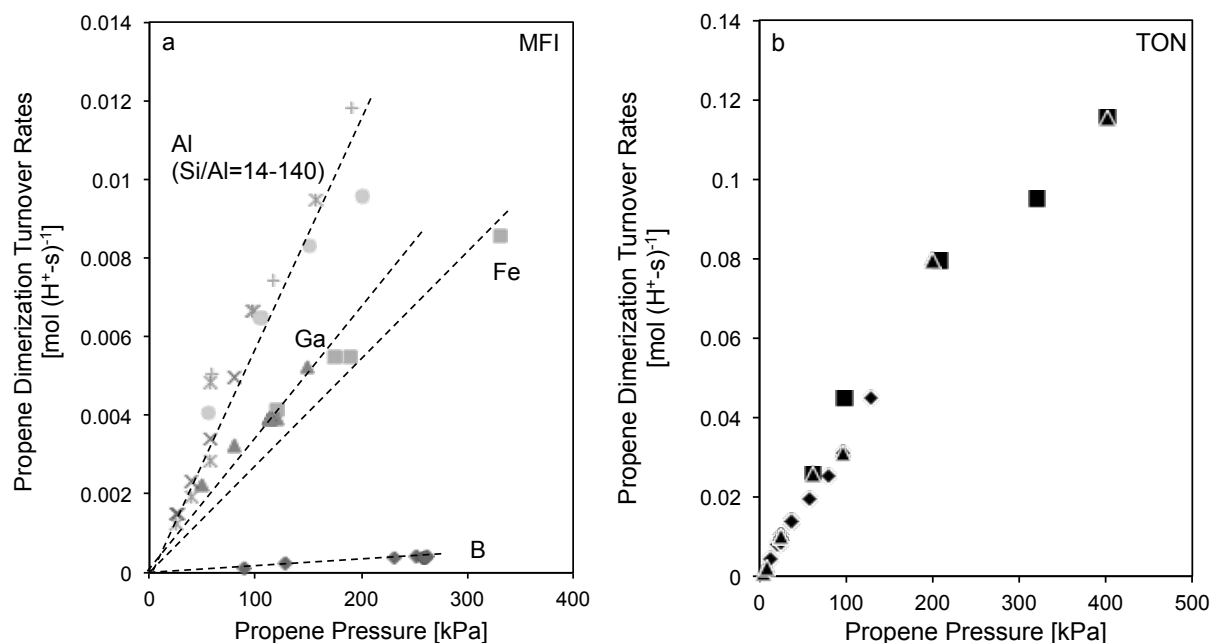


Figure S1. Propene dimerization turnover rates on (a) MFI (Al (Si/Al=14-140); Ga, Fe and B) and (b) TON (Si/Al=24-49) as a function of propene pressure [503 K; <5 % propene conversion; dashed lines represent linear regression fits].

Table S1. DFT-calculated vibrational frequencies in cm^{-1} for propene and isobutene derived alkoxides on TON (T-4) and MFI (T-12) [frequencies above 200 cm^{-1} are listed; RPBE-D3BJ].

TON				MFI
$C_{3,1}$	$C_{3,2}$	$C_{4,1}$	$C_{4,3}$	$C_{3,2}$
3106.4	3152.7	3102.2	3237.3	3148.7
3070.1	3105.2	3087.8	3222.1	3100.1
3060.8	3096.8	3075.1	3118.3	3078.6
3046.1	3071.2	3057.1	3103.7	3074.9
3041.1	3062.6	3053.2	3088.6	3045.3
3012.7	3010.6	3050.7	3069.9	3006.2
2985.8	3002.0	3029.7	3036.3	2999.5
1472.0	1473.1	2992.1	3027.3	1474.7
1461.0	1454.1	2983.7	2998.0	1453.5
1458.8	1448.8	1475.0	1487.5	1447.1
1452.6	1443.5	1468.2	1471.8	1440.5
1381.7	1386.7	1458.4	1459.2	1385.0
1366.6	1379.1	1451.7	1453.3	1375.8
1302.2	1367.3	1447.5	1448.0	1369.5
1295.5	1337.2	1396.2	1435.7	1326.8
1258.9	1181.3	1375.1	1393.3	1182.9
1156.3	1152.6	1362.1	1369.7	1155.2

1111.1	1083.2	1348.7	1368.3	1085.8
1024.9	924.2	1297.8	1262.2	923.1
909.5	921.5	1281.5	1250.2	920.2
876.1	887.4	1182.4	1127.1	887.9
864.4	746.6	1162.6	1028.9	766.7
740.2	699.6	1120.2	1024.7	708.4
660.4	453.2	956.2	956.6	441.2
522.7	418.3	940.8	924.7	428.0
314.6	377.9	919.1	909.0	398.2
286.5	233.2	903.1	799.5	229.1
229.3	219.8	880.9	715.8	224.7
216.1	208.6	812.6	608.0	215.5
		641.3	508.7	
		544.5	444.7	
		410.0	400.7	
		373.0	385.8	
		308.2	279.6	
		279.3	256.3	
		230.6	245.3	
		216.2	224.8	
		205.9		

Table S2. Weisz-Prater criterion calculated for TON and MFI at 503 K.

	MFI	TON
R_v [mol s ⁻¹ m ⁻³]	1.1	26
r_p [nm]	100	50
C_s [mol m ⁻³]	13	7.2
D_e [cm ² s ⁻¹]	4x10 ⁻¹¹	1x10 ⁻¹³
$\frac{R_v r_p^2}{C_s D_e}$	0.008	0.02

Table S3. Effectiveness factor calculated for TON and MFI at 503 K.

	MFI	TON
r_p [nm]	100	50
k [s ⁻¹]	0.09	3.6
D_e [cm ² s ⁻¹]	4x10 ⁻¹¹	1x10 ⁻¹³
$\eta = \frac{\tanh\left(r_p \left(\frac{k}{D_e}\right)^{1/2}\right)}{r_p \left(\frac{k}{D_e}\right)^{1/2}}$	1	1

3.6. References

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CHAPTER FOUR

Reactivity and Stability of Alkoxide Intermediates During Alkene Oligomerization

Abstract

Oligomerization reactions of alkenes on solid Brønsted acids are mediated by ion-pair transition states (TS) that can differ in both size and charge from their precursors, which for oligomerization are neutral alkoxides formed via quasi-equilibrated alkene protonation. We report kinetic and thermodynamic constants, extracted from turnover rates and *in-situ* FT-IR spectra, of these relevant TS and precursors in mixed alkene coupling reactions of ethene, propene, n-butene and isobutene over large pressure ranges (1-500 kPa) on microporous and mesoporous acids with different acid strength as well as void size and shape (H-TON (10-membered ring (MR)), H-MOR (12-MR), amorphous silica-alumina (SiAl) and Keggin polyoxometalate clusters supported on silica (HPW)). Measured equilibrium constants indicate bulkier alkoxides (e.g. tertiary-butoxides) are favored over less substituted ones in larger pore environments, but become sterically hindered within smaller, concave environments. Density functional theory (DFT) calculations that rigorously account for van der Waals interactions treatments accurately capture this trend of relative alkoxide stabilities as a function of carbon number as well as substitution (i.e. primary, secondary, tertiary), information that is experimentally inaccessible. These periodic calculations highlight the flexibility of the inorganic acid catalysts: the local environment distorts to maintain the covalent alkoxide bond while also increasing the van der Waals interactions with the alkoxide. These distortions (quantified in terms of O-atom displacement and bond angles for the alkoxide O-atom) increase with increasing chain length and substitution of the alkoxide but also cost energy, which factors into the overall optimization. Rate constants for alkene co-oligomerization increase with increasing TS size, because of the combined effects of more stable carbenium ions and more effective contact with the void walls. Local distortions are also present in the optimized structure of the TS and become too costly as the TS become larger than the size of the confining voids. This investigation into how the stabilities of bound species and TS involved in alkene co-oligomerization reactions are affected by proton environment and therefore affect turnover rates and selectivities allows for rigorous extrapolation to molecules of different size than those studied here.

4.1. Introduction

Solid Brønsted acids readily catalyze C-C bond formation in alkenes [1–3]; these reactions are mediated by ion-pair transition states of different size and charge than their precursors, leading to large effects of confinement and acid strength, respectively. Hydrocarbon reactions on solid acid catalysts involve adsorbed precursors whose stability often affect reactivity and selectivity. While alkane adsorption in zeolites has been well investigated [4–7], experimental insight into adsorption of alkenes remains difficult due to the rapid oligomerization [8]. Previous spectroscopic as well as theoretical studies indicate that protonation of adsorbed

alkenes (and alcohols) occurs readily to form covalent alkoxide species; carbenium ions exist only as transition states, not stable intermediates, within zeolite structures [9–12]. These studies also specify the general steps of alkoxide formation, but without accurate reliable experimental results, comparison to density functional theory (DFT) remains illusive.

The ion-pair transition states that mediate oligomerization reactions involve these alkoxides with another alkene. Key properties of these systems, and all acid-catalyzed reactions, include how the anion (formed after deprotonation of the inorganic catalyst) (i) accepts the negative charge (acid strength), which results in an electrostatic interaction with the organic cation (derived from reactants) [13,14], and (ii) provides van der Waals interactions, which are dependent on the size and shape of the organic component and the surrounding pore environment (confinement) [15–17]. Because confinement effects are extremely sensitive to size and shape, systematic control of either or both is needed to provide the detailed insights into reactivity to extrapolate to other reactions and catalysts.

This study reports stabilities of alkoxides and C-C bond formation transition states measured experimentally as equilibrium and kinetic constants, respectively, on microporous and mesoporous acids with different acid strength and void size and shape. Oligomerization reactions of ethene, propene, trans-2-butene and isobutene and co-oligomerization of mixtures (with propene) (1-500 kPa) on H-TON (10-membered ring (MR)), H-MOR (12-MR), amorphous silica-alumina (SiAl) and Keggin polyoxometalate clusters supported on silica ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$; HPW) indicate catalysis occurs on alkoxide covered surfaces with kinetically-relevant additions of an alkene to this intermediate, consistent with *in-situ* FT-IR spectra and density functional theory (DFT) calculations.

Mixed alkene oligomerization reactions give accurate values of relative alkoxide stabilities reflected in ratios of equilibrium constants; propoxide and ethoxide formation equilibrium constants can also be extracted from single feed experiments of propene at low pressures (< 4 kPa) and ethene. Measured equilibrium constants indicate alkoxide stability increases with chain length and substitution in larger pore environments (MOR, HPW), but bulkier alkoxides (e.g. tertiary-isobutoxide) become sterically hindered within smaller, concave environments (TON). DFT calculated Gibbs free energies of alkoxide formation, which are ensemble averaged for the multiple attachments points (primary, secondary and tertiary, when applicable), accurately capture trends measured on TON and HPW. These DFT treatments account for van der Waals interactions and reveal the flexibility of the inorganic acid catalysts. We show that the local environment distorts to increase van der Waals interactions between the organic alkoxide and the lattice oxygen and to maintain the covalent alkoxide bond. These distortions are quantified, relative to the native proton form, in terms of O-atom displacement, interaction energy between the inorganic atoms and angle of alkoxide attachment (Si-O-Al and O-W-O for TON and HPW, respectively). The values of all descriptors increase with increasing chain length and substitution of the alkoxide, which is consistent with less favorable formation of bulkier alkoxides on TON relative to HPW measured experimentally.

Rate constants for C-C bond formation extracted from alkene mixtures (C_2+C_2 , C_3+C_2 , C_3+C_3 , C_3+C_4 , C_4+C_4) provide an array of transition states that systematically vary in size as estimated from DFT-derived van der Waals volumes. Measured rate constants increase with increasing transition state size because of the combined effects of more stable carbenium ions and more effective contact with the void walls, which can become detrimental for transition states too large in size. The relative contribution of the two can be inferred from use of microporous (TON) and mesoporous catalysts (SiAl, HPW), the latter of which has negligible

van der Waals interactions between the inorganic and the organic. DFT calculations on TON indicate that the inorganic rearranges to increase van der Waals interactions with the cation, information that would be lost in treatments that neglect dispersive forces. Here, the pertinent descriptor is O-atom displacement because the moiety is no longer bound to the catalyst, rendering angle of the alkoxide bridge uninformative. These distortions involve either the lattice oxygen moving into the center of the 10-MR channel or away from it, depending on the transition state size, but again remain localized to near the organic moiety.

4.2. Experimental Methods

4.2.1. Alkene oligomerization turnover rates

TON (BP; Si/Al=39), MOR (Zeolyst; Si/Al=10), amorphous silica alumina (SiAl; Sigma-Aldrich) and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (synthesis described in [18]) were pelleted, crushed, and sieved to retain 180-250 μm aggregates. Alkene turnover rates were measured on samples (15-50 mg) placed within a tubular reactor with plug-flow hydrodynamics (316 stainless steel; 12 mm I.D.). The temperature was set using a three-zone resistively-heated furnace (Applied Test Systems Series 3210; Watlow controllers; 96 Series) and measured with a K-type thermocouple held within an internal concentric thermowell placed in the middle of the bed. NH_4 -TON, $\text{H}_{45}\text{Na}_{55}\text{MOR}$ [19] and SiAl were treated before catalytic rate measurements in a 5 % O_2 in He stream ($83.3 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, Praxair) by heating to 818 K (at 0.025 K s^{-1}) and holding for 3 h to convert the NH_4^+ to H^+ , and then cooled to 503 K. Keggin POM clusters (H-form) were treated in flowing He ($50 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$; 99.999 %, Praxair) by heating to 503 K (at 0.083 K s^{-1}) to remove adsorbed moisture. Mixtures of ethene (99.9 %, Praxair), propene (99.9 %, Praxair or 5% in He, Praxair), trans-2-butene (99.9 %, Praxair) and isobutene (99.9 %, Praxair) were sent to the reactor and the effluent was transferred through lines held above 373 K into a gas chromatograph (Agilent 6890). Reactant and product concentrations were measured using flame ionization detection after chromatographic separation with a methyl silicone capillary column (Agilent HP-1 column, 50 m x 0.32 mm x 1.05 μm film). Reactant pressures were changed by dilution into a He stream (99.999 %, Praxair) and the total system pressure was maintained using a dome-loaded regulator (Tempresco).

4.2.2. Infrared assessment of hydroxyl groups and adsorbed species during catalysis

Infrared spectra were collected using a Nicolet NEXUS 670 infrared spectrometer equipped with an Hg-Cd-Te (MCT) detector. Self-supported wafers (~20-40 mg) were sealed within a quartz vacuum infrared cell fitted with NaCl windows and treated in flowing dry air ($20.8 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, zero grade, Praxair) by heating to 818 K (at 0.033 K s^{-1}), holding for 3 h, and cooling to reaction temperature in flowing He. Ethene (99.9 %, Praxair), propene (99.9 %, Praxair) or isobutene (99.9 %, Praxair) were then introduced into the He flow (99.999 %, Praxair) at rates designed to give desired alkene pressures (3-70 kPa). Spectra were collected with 2 cm^{-1} resolution and $4000\text{-}400 \text{ cm}^{-1}$ by averaging 64 scans.

4.2.3. Density functional theory methods

Periodic density functional theory as implemented in the Vienna ab initio Simulation Package (VASP) [20–23], was used to determine optimized structures and energies for stable intermediate and transition states. Wavefunctions were represented by a periodic plane-wave basis set expansion (to a cut-off energy of 396 eV) and projector-augmented wave (PAW5)

pseudopotentials were used to describe electron-core interactions [24,25]. Exchange and correlation energies were calculated within the generalized gradient approximation using revised Perdew–Burke–Ernzerhof (RPBE) functionals [26–28] with dispersive energies and forces calculated by DFT-D3 during energy minimization [29,30]. A 1 x 1 x 1 Monkhorst–Pack k-point mesh was used to sample the first Brillouin zone [31].

TON was described using five unit cells (unit cells defined in [32]) in order to fully capture the details of the pore network, while also providing a vacuum region that prevents electronic interactions among periodic chemical species. The Al₂-O₃(H) (as numbered by [32]) was chosen as the location for alkene adsorption to form alkoxides. Keggin POM clusters were described by placing full clusters (~1 nm in diameter) at the center of 3 x 3 x 3 nm³ unit cells to prevent electronic interactions among neighboring cells.

Reaction paths of minimum energy were calculated using nudged elastic band (NEB) methods [33] with structures converged to energies within 1×10^{-4} eV and forces to within 0.3 eV Å⁻¹ to identify starting structures for TS structures, which were further refined using Dimer calculations [34]. Energies reported here include contributions from electronic energies (E_0), zero-point vibrational energies (ZPVEs), vibrational free energies (G_{vib}) and translational and rotational free energies (G_{trans} and G_{rot}) for gaseous molecules. ZPVE and G_{vib} values were determined from the frequencies in optimized structures. Low-frequency modes of weakly bound adsorbates give rise to significant inaccuracies in vibrational contributions to free energies; they were excluded from Gibbs free energy calculations. These modes were assumed instead to retain a fraction (0.7) of the translational and rotational entropies estimated by statistical mechanics for the gaseous alkene in question, which was shown to provide accurate estimates of adsorption entropies for adsorbed molecules on oxide surfaces [35]. All energies are referenced to the H-form of the catalyst and gas-phase alkenes.

4.3. Results and Discussion

4.3.1. Kinetic measurement of alkoxide stabilities

Propene and isobutene dimerization turnover rates, normalized per proton (Table 1), are proportional to alkene pressure on TON (10-500 kPa; 503 K) (Fig. 1a), which reflects a kinetically-relevant addition of a gas-phase alkene to a bound surface intermediate [1]. Turnover rates for propene dimerization deviate from first-order kinetics at low propene pressures (Fig. 1b), and ethene dimerization turnover rates are not proportional to ethene pressure even at much higher pressures. This change in kinetic behavior with increasing alkene pressure indicates that protons are not saturated with hydrocarbon species and thus turnover rates are described by:

$$r_{x+x} = \frac{\alpha[C_x]^2}{1+K_x[C_x]} \quad (1)$$

where α is a lumped rate constant that will be discussed in Section 4.3.3 and K_x is the equilibrium constant for the formation of an alkene derived surface species with x carbons. The presence of free protons during ethene dimerization is also evident from infrared spectra (Fig. 2; 503 K). The area under the 3600 cm⁻¹ band, which corresponds to the Brønsted O-H stretching frequency [36], decreases upon exposure to ethene and continues to decrease with increasing pressure; infrared bands characteristic of alkoxide species (–O–C_nH_{2n+1}) with saturated C-H bonds also appear at 1500-1450 cm⁻¹ [9,37,38], indicating that protons have reacted with alkenes to form alkoxides upon alkene adsorption. The formation of these alkoxides is consistent with

previous theoretical studies [11] and in Sections 3.3.1 and 4.3.2. The alkoxide fractional coverage (f ; Eq. 2) is calculated by:

$$f_p = \frac{Area\ OH_0 - Area\ OH_p}{Area\ OH_0} \quad (2)$$

where $Area\ OH_0$ is the area of the band near 3600 cm^{-1} for TON under an inert He environment and $Area\ OH_p$ is that band area under a given alkene pressure p . The fractional coverage of ethoxide increases to unity with increasing ethene pressure, becoming saturated near 50 kPa (Fig. 3). Propoxide and isobutoxide coverage, in contrast, reaches saturation more rapidly than ethoxide on TON (Fig. 3). The difference in alkene pressure needed to reach saturation indicates that the equilibrium constant for alkoxide formation is smaller for ethoxide than for propoxides or isobutoxides. Propene and isobutene do not saturate protons at low pressures (below 7 kPa; 503 K), consistent with the curvature in propene dimerization turnover data (Fig. 1b), but their relative abilities to protonate compared to ethene render it difficult to obtain enough reliable data at submonolayer coverages to regress equilibrium constants. The ethoxide coverage from FT-IR, however, was interpreted as a Langmuir isotherm, which is appropriate due to the isolated nature of acid sites in zeolites (Eq. 3):

$$f_{p,2} = \frac{K_2[C_2]}{1+K_2[C_2]} \quad (3)$$

where K_2 is the equilibrium constant for ethoxide formation. This equilibrium constant for both ethoxide and propoxide formation can also be measured by fitting the kinetic data in Figure 1 to Equation 1; the values from both ethoxide measurements are in agreement with each other (Fig. 4; C_2 and IR data points). Equilibrium constants for alkoxide formations (K_x), furthermore, can be obtained by measuring the formation rates of dimers and co-dimers from mixtures of alkenes, where propene is reacted with either ethene, trans-2-butene or isobutene. These experiments are completed at alkene pressures that lead to surfaces in which all Brønsted acids have reacted with alkenes to form a pool of alkoxides (Fig. 5), resulting in ratios of equilibrium constants (Eq. 3-5).

$$r_{3+3} = \frac{k_6[C_3]^2}{K_3[C_3] + K_x[C_x]} = \frac{k_{eff,6}[C_3]}{1 + \frac{K_x[C_x]}{K_3[C_3]}} \quad (4)$$

$$r_{3+x} = \frac{k_{3+x}[C_3][C_x]}{K_3[C_3] + K_x[C_x]} = \frac{k_{eff,3+x}[C_x]}{1 + \frac{K_x[C_x]}{K_3[C_3]}} \quad (5)$$

$$r_{x+x} = \frac{k_{x+x}[C_x]^2}{K_3[C_3] + K_x[C_x]} = \frac{k_{eff,x+x} \frac{[C_x]^2}{[C_3]}}{1 + \frac{K_x[C_x]}{K_3[C_3]}} \quad (6)$$

where k is the intrinsic rate constant for the dimerization of two alkenes with either 3 or with x carbons and concentration $[C_x]$ and k_{eff} is the rate constant extracted from kinetic analysis. These equilibrium constants depend on the Gibbs free energy of alkoxide formation ($\Delta G_{x,i}$), referenced to the H-form of the catalyst (G_H) and the gas-phase alkene with x carbons (G_x^g):

$$\Delta G_{x,i} = G_{x,i}^{alk} - G_x^g - G_H \quad (7)$$

These alkoxides, depending on their size and structure, can have different attachment points (primary ($i=1$), secondary ($i=2$) and tertiary ($i=3$); Scheme 1) and multiplicities for degenerate carbons (e.g. p-ethoxide has two identical C-atom attachment points). These alkoxide formation energies are inaccessible from experiments alone and will be calculated using density functional theory (Section 3.2), then ensemble averaged to include any accessible attachment points (i) and their multiplicity (j).

$$\overline{\Delta G_x} = -RT \ln \left(\frac{1}{\sum_j j} \sum_i j \exp \left(\frac{-\Delta G_{x,i}}{RT} \right) \right) \quad (8)$$

$$K_x = \exp \left(\frac{-\overline{\Delta G_x}}{RT} \right) \quad (9)$$

Here, $\overline{\Delta G_x}$ is the ensemble averaged Gibbs free energy of formation for alkoxide derived from alkene x .

Figure 4 shows the absolute values of the equilibrium constants on TON as calculated by multiplying the ratio of equilibrium constants (K_x/K_3) by that of propoxide formation fitted from low-pressure data. We note that (i) values of K_2 are similar despite different methods of measurement and (ii) all alkoxides are more stable than ethoxide. Further, n-butene-derived alkoxides has a slightly higher value than propoxides, indicating that increasing chain length aids in stabilizing the alkoxide. However, the isobutene-derived alkoxides are not more stable than those derived from n-butene, despite increased substitution, which may imply a steric effect with the small, concave environment of TON (10-MR; 0.46 nm x 0.57 nm [32]). This steric effect is investigated further through use of solid acids with confining voids of different size and shape (MOR and HPW).

MOR is a 12-MR zeolite with pores 0.7 nm x 0.65 nm in dimension [32]; it also has 8-MR side pockets, however, these protons are selectively titrated in this study with Na^+ (Table 1; [9]). Keggin HPW structures are 1.1 nm tungsten-oxide shells around a phosphate anion (PO_4^{3-}) supported on mesoporous silica (2.4 nm; Fig. 10). Figure 6a shows measured ratios of alkoxide equilibrium constants, renormalized to ethoxide, such that each alkoxide is compared to the smallest (and least stable) alkoxide studied for TON, MOR and HPW. All alkoxides are more stable than ethoxide ($K_x/K_2 > 1$) on both MOR and HPW, similar to TON. Unlike TON, however, isobutoxide is more stable than n-butoxide on both MOR and HPW. The interactions between the alkoxides and the surrounding atoms of the catalyst are much less on HPW than in TON because of the convex surface around the oxygen involved in the alkoxide. The convex nature of HPW and the larger pores of MOR alleviate any steric hindrance felt by isobutoxides adsorbed within TON, causing a large difference between the stabilities of isobutoxides on MOR or HPW compared with TON. Similar K_x/K_2 values for all alkoxides on MOR and HPW suggest the 12 MR channels of MOR are large enough not to impose steric hindrances in formation of bulkier alkoxides. This is also despite large differences in acid strength, here in terms of deprotonation energy (HPW: 1090 kJ/mol versus MOR (and all aluminosilicates): 1220 kJ/mol), indicating acid strength does not affect relative alkoxide stabilities. The absence of an acid strength effect is consistent with all measured equilibrium constants reflecting covalently-bound alkoxide species as opposed to charged carbenium ions. These combined results indicate that size and shape of the catalyst and the alkoxide affect relative thermodynamic stabilities, but the

details of how the alkoxides interact with the catalyst cannot be gleaned from experiments; we, thus, turn to density functional theory to obtain a better understanding of the chemical bonding between alkoxide structures and the catalyst.

4.3.2. Alkoxide stabilities from density functional theory

Density function theory (DFT) calculations are used to compare theory to the experimental results in Figure 6a; in order to do so, we must consider ZPVE and entropy to calculate free energies (Eq. 9) and the multiple attachments must be accounted for through ensemble averaging (Eq. 7-9). This rigorous accounting also provides the relative stability of alkoxides with different attachments but derived from the same alkene, information that cannot be measured from experiments alone. Figure 6b shows the calculated relative equilibrium constants for TON and HPW at 503 K, which is in good accordance with experimental trends (Fig. 6a). The optimized structures for TON are shown in Figure 7.

The total potential energies (E_{total}) of the alkoxides are broken down into a quantum mechanical (E_{QM}) and van der Waals (E_{vdW}) attractive component, the latter of which is calculated from the DFT-D3BJ method [29,30]:

$$E_{total} = E_{QM} + E_{vdW} \quad (10)$$

The total formation energies for each alkoxide backbone and attachment are referenced to its respective gas-phase alkene and the optimized H-form of TON. The relative formation energies with respect to ethoxide are all negative, i.e. more stable than ethoxide (Fig. 8), except t-isobutoxide, which is higher in electronic energy than either of the propoxides or n-butoxides. This higher energy is despite the van der Waals component continuing to decrease in energy as the alkoxide become longer and more substituted, congruous with increased interaction with the lattice oxygen. Compensation must occur, evident from higher QM values, otherwise the isobutoxide would have the lowest total energy. Whether the penalty is paid by the organic alkoxide or the inorganic catalyst is discussed next.

First, the alkoxide structure and properties are examined. The length of the C-O bond between the organic and the oxygen adjacent to the Al in TON (Figs. 7 and 10) or the terminal oxygen in HPW (Fig. 11) and the partial charge of the alkoxide are independent of chain length (Figs. 9a and 9b, respectively). The C-O bond length increases slightly with substitution for both catalysts (Fig. 9a), however, which is consistent with the partial charge of the alkoxide increasing commensurately (Fig. 9b). These slight trends (and absolute values) are similar on both TON and HPW (for both terminal and bridging oxygen, the latter is not shown here), indicating that any steric effects do not result in less covalent alkoxides. The similarity of charge is consistent with relative alkoxide stabilities that are independent of acid strength (Fig. 6a) because the similar bond length and charge on for all alkoxides (on HPW and TON) suggest the degree of covalency is equivalent for these neutral structures.

Similar alkoxide structures (in terms of bond length and partial charge) imply the catalyst itself must be contributing to the differences observed on different catalyst and the energetic penalty seen for isobutoxide. Comparing optimized structures of the H-form and alkoxide form, it is observed that the local environment responds to steric effects by distorting the inorganic structure apparently not to sacrifice the orbital overlap needed to form the covalent bond. The angle that involves the O-atom of the alkoxide, Si-O-Al bridge for TON and the O-W-O of the terminal oxygen for HPW (θ_z (Fig. 10) and θ_p (Fig. 11), respectively) is altered between the H-

form and alkoxide structure; Figure 9c shows the difference in these angles for TON and HPW. The distortion, in terms of this angle, on TON increases with increasing chain length or substitution of the alkoxide, with the t-isobutoxide disrupting the Si-O-Al bridge the most (optimized structure in Fig. 10; distortion highlighted by circle). The chain length of primary alkoxides derived from straight chain alkenes does not affect the host differently, but the p-isobutoxide is apparently bulky enough to change the θ_Z (an average of 9.5 for p-ethoxide, propoxide and n-butoxide vs. 11 for p-isobutoxide). The alkoxide chain length and substitution, however, alters the O-W-O angle in HPW much less than it alters the Si-O-Al angle in TON. The lack of strain in the terminal O-atom in HPW due to its convex nature facilitates formation of the bulky t-isobutoxide without disruption to the inorganic component. Thus, the extent of the distortion to accommodate the alkoxide is dependent on the catalyst and whether it is a concave or convex type surfaces (i.e. TON versus HPW).

These distortions were also quantified by comparing the interaction energy between the atoms of the inorganic catalyst (Si, Al and O) in the alkoxide form and the proton form (Scheme 2). The larger the deviation from the proton form, the more the inorganic host distorts upon alkoxide formation. The distortion energy is defined as:

$$\Delta E_{distortion} = |E_{Z*} - E_Z| = |(E_{Z*-alk} - E_{organic}) - (E_{Z-H} - E_H)| \quad (11)$$

where each term is the van der Waals component of the electronic energy calculated from D3BJ. Equation 10 is a function of the optimized inorganic component from the alkoxide (E_{Z*}) form and proton form (E_Z), which are defined as the difference in dispersive energy between the fully optimized structure (E_{alk-Z*} and E_{H-Z}) and the organic component ($E_{organic}$ and E_H , respectively). These energies are shown in Figure 12 and indicate the inorganic host adapts in the small, concave environment of TON to maintain the covalent bond of the alkoxide, especially for bulkier alkoxides. This increase in dispersive forces between atoms is consistent with movement of atoms in catalyst, which is quantified through the arithmetic mean of O-atom displacements from the proton to alkoxide forms of the inorganic component (Fig. 13). This displacement is described by:

$$d_O = \sqrt{(x_{alk} - x_H)^2 + (y_{alk} - y_H)^2 + (z_{alk} - z_H)^2} \quad (12)$$

where each O-atom n has the coordinates of $(x_{alk}, y_{alk}, z_{alk})_n$ and $(x_H, y_H, z_H)_n$ in the alkoxide and H-form, respectively. The trends for both interaction energy and O-atom displacement are similar for TON with increasing “bulkiness”, but change much less with “bulkiness” for HPW. The interaction energy and the O-atom displacement include the effects of movement to increase van der Waals interactions between the pore environment of TON and the organic alkoxide and not just the local distortion to maintain the orbital overlap for the C-O alkoxide bond, which is what the change in alkoxide attachment angle ($\Delta\theta$) describes. The combination of both effects leads to interaction energy and O-atom displacement values for p-isobutoxide in Figure 12 that are higher than either s-propoxide or s-n-butoxide, where $\Delta\theta_Z$ values for p-isobutoxide were lower than the normal s-alkoxides (Fig. 9c). The willingness to distort the local environment in order not to sacrifice the orbital overlap needed to form the covalent alkoxide bond, especially when bulky species are involved, is consistent with the sensitivity of potential energy to distances in these covalent bonds. The energetic penalty to deform the inorganic catalyst is in

part repaid through the electrostatic interactions between the organic alkoxide and the lattice oxygen, which are ubiquitous in microporous materials.

4.3.1. Reactivity of alkene coupling reactions and flexibility of zeolite frameworks

Chapter 3 discussed the effects of both confinement and acid strength on measured rate constants for propene dimerization using a diverse set of catalysts. It was found that the first-order rate constant, which reflects the addition of an alkene to a bound alkoxide, increases as the size of the pore approaches that of the organic component of transition state (TS) in question. This observance is due to the fact that the TS is larger and can create more van der Waals interactions with the lattice oxygen of the confining pore than its smaller precursors. Similarly, the rate constant increases with acid strength because the TS is charged while the alkoxide precursors are neutral. Conjugate anions of stronger acids can better stabilize the negative charge in the TS than those of weaker acids, which decrease the reaction energy barrier. These findings are extended, in this chapter, to a series of TS with varied sizes from the mixtures of ethene, propene and isobutene.

The regressed rate constants obtained from Equations 4-6 (data and fits in Fig. 5), where x is either 2 or 4 (ethene or isobutene co-fed with propene) are shown as a function of number of carbon atoms in the TS (Fig. 13a) on TON, SiAl and HPW. The increase in all rate constants on HPW compared to SiAl is due to their difference in acid strength (1090 kJ/mol [39] versus 1220 kJ/mol [14,40] for aluminosilicates, respectively), or the stability of the anion when it accepts the negative charge of the ion-pair TS. Comparison of these two samples removes effects of confinement because their mesoporous pores are not of molecular dimension (>2.4 nm) and therefore do not provide additional stabilization. The increase in the rate constant with carbon number, which is similar for both catalysts, reflects the stability of the organic moiety with the positive charge. The rate constants on TON (void diameter = 0.57 nm [32,41]) are higher than SiAl, again consistent with the effects of confinement for acids of similar strength [40], but varied pore size observed for bimolecular TS with respect to monomolecular precursors. The increase of rate constants with increasing number of carbon atoms in the TS on TON has the combined effect of stabilization of the cation due to confinement and the intrinsic property of the organic. The effects of confinement appear to diminish, however, as the TS continues to increase, possibly from repulsive interactions that occur when atoms in the organic moiety become too close to the lattice network of the pore. We will again turn to density function theory (DFT) to understand these effects on the molecular level.

Figure 14 shows the optimized TS for the 5 different coupling reactions (C_2+C_2 , C_3+C_2 , C_3+C_3 , C_3+C_4 , C_4+C_4) on TON. We utilized these structures in order to have a more quantitative descriptor of TS size than the number of C atoms. Figure 15a shows the C_3+C_3 removed from the pore and with the van der Waal radii of the C and H atoms. This moiety is enclosed in a surface (Fig. 15b) with a volume V_{vdW} ; the volumes of all TS optimized in TON are show in Figure 16a. We define the equivalent TS diameter (d_{x+x}) as the diameter of a sphere with the equivalent volume:

$$d_{x+x} = \left(\frac{3V_{vdW}}{4\pi} \right)^{1/3} \quad (13)$$

These diameters are given in Figure 16b; the measured rate constants are plotted against their values (Fig. 13b) they will be used as the descriptor TS size henceforth.

The optimized TS structures in Figure 14 indicate these are fully formed ion-pairs, as the covalent bond of the alkoxide has been completely broken. Moreover, the moiety moves toward

the center of the pore, apparently to gain as many stabilizing interactions with the lattice oxygen as possible, while at the same time, the inorganic host also moves. Because of the nature of the pore network in TON, we use a cylindrical coordinate system (with an origin in the center of the 10-MR channel; Fig. 17a) to quantify the distortions involved in the TS. Here, each lattice atom n has the coordinates of $(r_{TS}, \theta_{TS}, z_{TS})_n$ and $(r_H, \theta_H, z_H)_n$. The change in average r for all oxygen atoms in the first shell of the cylinder is shown in Figure 17b. The cylindrical coordinate system allow a directionality of the movement to interpreted and Figure 17b indicates the lattice oxygen move into the pore on average with smaller TS. This Δr becomes positive and continues to increase with increasing TS size, demonstrating the oxygen move into the second shell in order to accommodate the TS and increase van der Waals interactions. These distortions are fairly localized as evident from Figure 18 where the isobutene coupling TS is shown (two of the TS from the periodic system shown) from the top and the side. The oxygen atoms that have values of Δr greater than one standard deviation from the mean are highlighted in green. A distribution function that shows the distortion along the axis of the channel (z ; Fig. 19) indicates the distortions manly occur near the Al site (Z_{Al}) and the breadth of distribution is similar to that of the TS diameter, d_{x+x} .

These distortions, again, benefit the TS through additional van der Waals stabilizations, here quantified as a dispersive interaction energy:

$$\Delta E_{dispersion} = E_{TS} - E_Z - E_{HC} \quad (14)$$

where each term is the van der Waals component of the electronic energy calculated from D3BJ. E_{TS} is the total vdW energy for the TS, E_Z is that of the inorganic host and E_{HC} is that of the organic component (Scheme 3). These energy decreases with increasing TS size (Fig. 20a), even if normalized per C-number (Fig. 20b), indicating each carbon atom is obtaining more interactions with the lattice oxygen, which possibly arise from the increased distortions (Fig. 17b). These distortions cost energy and the penalty was quantified using the same equation developed for the alkoxides (Eq. 11; Fig. 21). It is again evident that the larger the organic moiety, the more energy is paid to locally distort the structure in order to obtain additional benefits of van der Waals interactions. This will continue until the amount of energy needed to distort the environment enough to “fit” a TS, will be too large and the combined ion-pair transition state (organic cation and inorganic anion) will be destabilized.

4.4. Conclusions

Relative alkoxide stabilities and reactivity for C-C bond formation were measured experimentally from co-oligomerization reactions of ethene, propene, n-butene and isobutene using microporous and mesoporous acids with different acid strength and void size and shape. The pertinent transition states (TS) and precursors were also investigated using density function theory (DFT) treatments that rigorously account for van der Waals interactions pertinent in microporous material. Bulkier alkoxides (derived from isobutene) are favored over less substituted ones in larger pore environments (MOR, HPW), but become sterically hindered within smaller, concave environments (TON). DFT treatments reveal stabilities of different alkoxide attachments (i.e. primary, secondary, tertiary) and the flexibility of the inorganic acid catalysts, information that is experimentally inaccessible. Measured rate constants of alkene coupling reactions increase with increasing TS size (due to larger and more substituted alkenes) irrespective of acid strength or confinement, however selectivity to TS that are near the size of

the pores in which they are formed is decreased relative to mesoporous acids without pores of molecular dimension. The local environment around the organic moieties (either alkoxide or TS) distorts to increase the van der Waals interactions with the lattice oxygen and the organic atoms and also, in the case of the alkoxide, to maintain the covalent C-O alkoxide bond. These distortions are quantified in terms of O-atom displacement, bond angles and dispersive interaction energy of inorganic atoms; all metrics indicate that distortions increase with increasing chain length and substitution of the alkoxide and TS, but also cost energy, which factors into the overall optimization.

4.5. Figures, Tables and Schemes

Table 1. Proton density for HPW, TON and MOR samples used in this study.

Catalyst	H ⁺ density (mmol g ⁻¹)
H-TON	0.22 ¹
H ₄₅ Na ₅₅ MOR	0.53 (0.44 12-MR) ²
SiAl	0.014 ³
H ₃ PW ₁₂ O ₄₀ /SiO ₂	0.043 ³

¹from decomposition of NH₄⁺ exchanged sample [1].

²from [19].

³from 2,6-di-tert-butylpyridine titration [1].

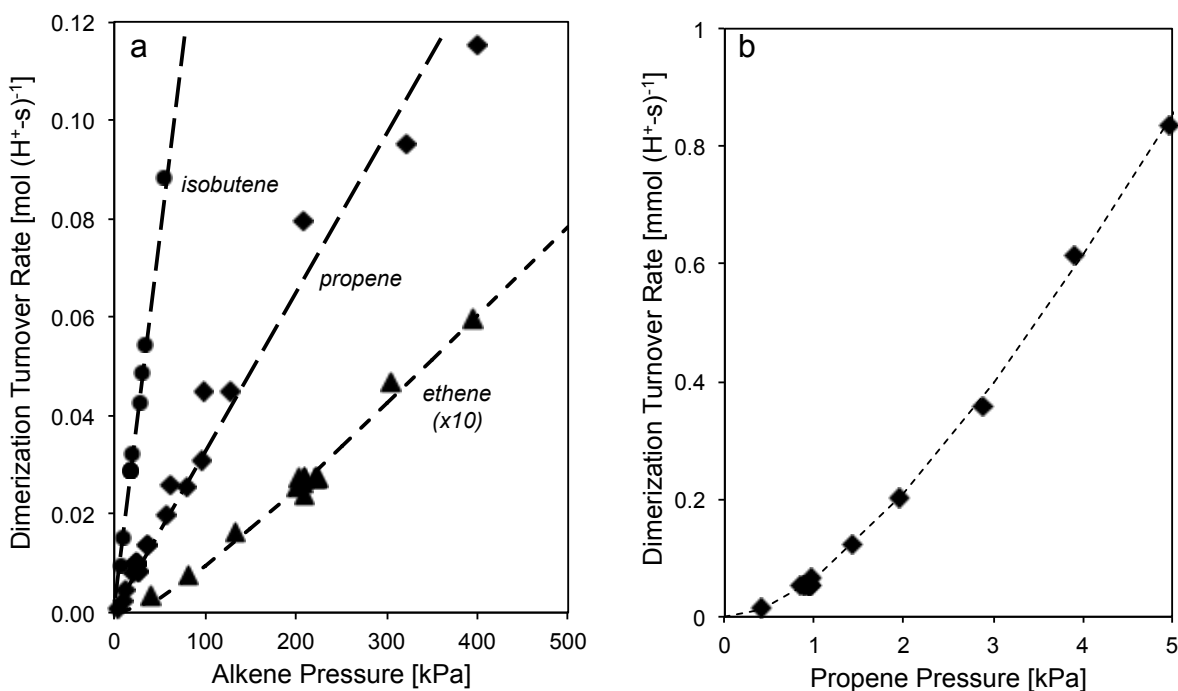


Figure 1. A: Alkene dimerization turnover rates on TON for (C₂H₄ (▲; multiplied by 10 to be visible on the same axis), C₃H₆ (◆) and i-C₄H₈ (●) as a function of alkene pressure. B: Propene oligomerization turnover rates on TON at low pressures. [503 K; <5 % alkene conversion; dashed lines represent linear regression fits].

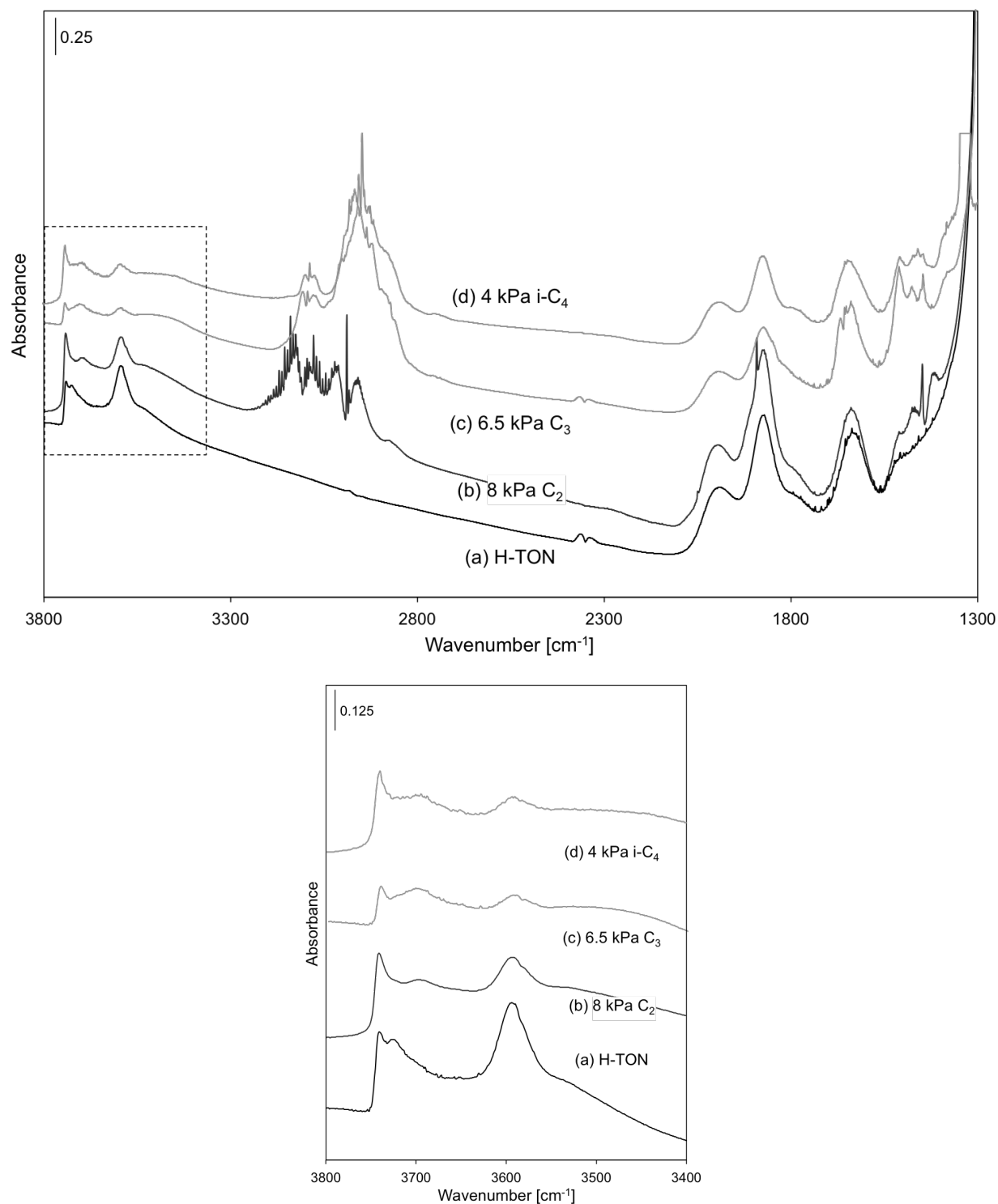


Figure 2. Full infrared spectra of TON (top) and zoomed in portion from dashed box (bottom) at 503 K in H-form (a), 8 kPa C_2H_4 (after 0.18 ks; b), 6.5 kPa C_3H_6 (after 0.18 ks; c) and 4 kPa i- C_4H_8 (after 0.18 ks, d).

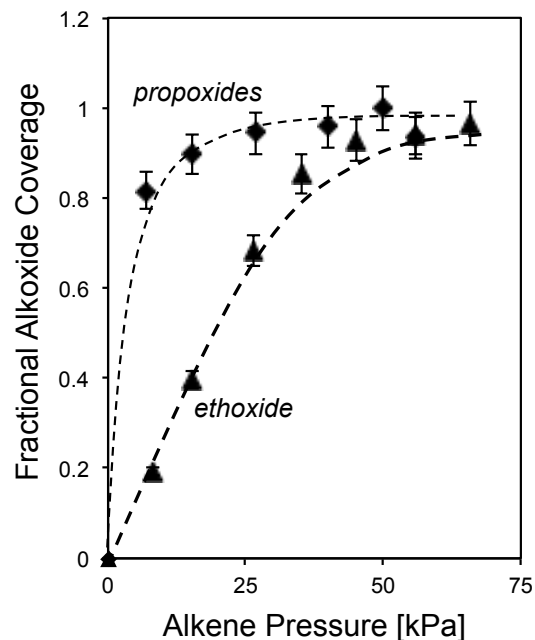
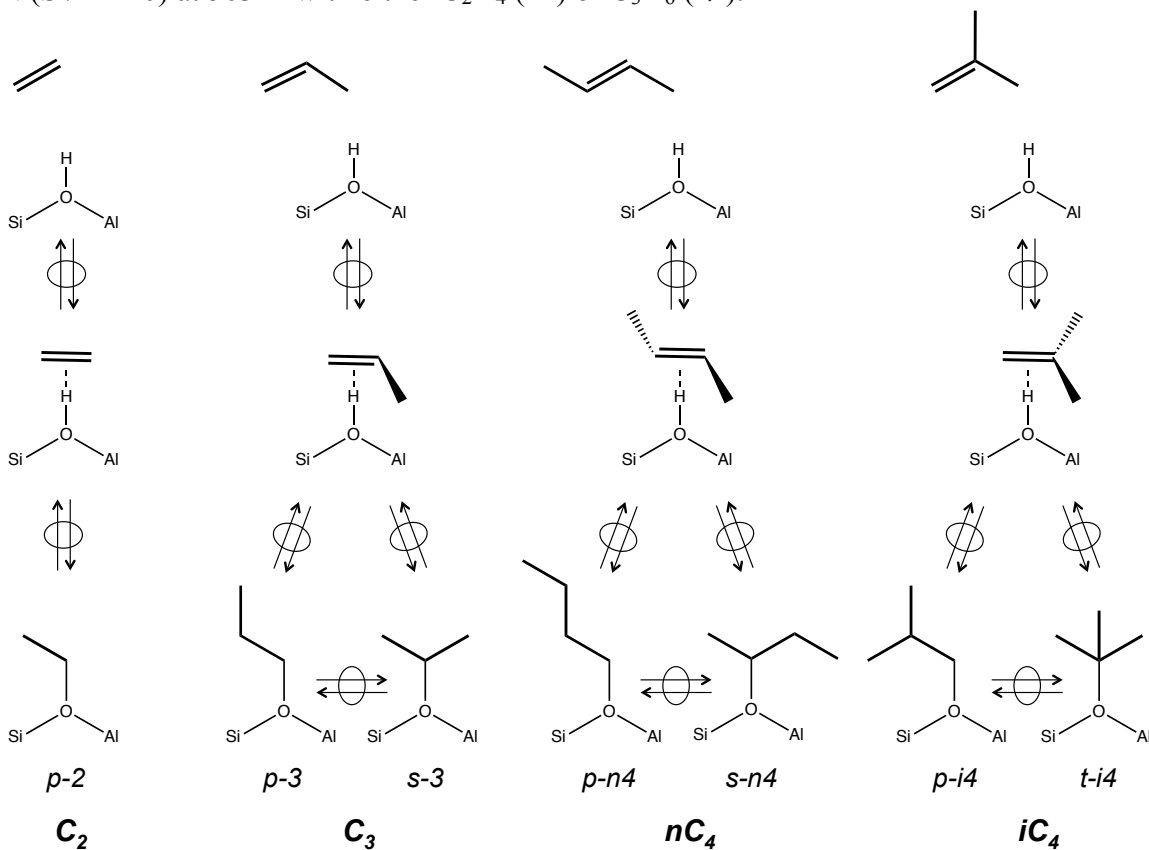


Figure 3. Fractional alkoxide coverage measured from 3600 cm^{-1} band in infrared spectra of TON (Si/Al=40) at 503 K with either C_2H_4 (▲) or C_3H_6 (◆).



Scheme 1. Alkoxide formation with available attachments from ethene, propene, trans-2-butene and isobutene via hydrogen-bonded intermediate on an aluminosilicate.

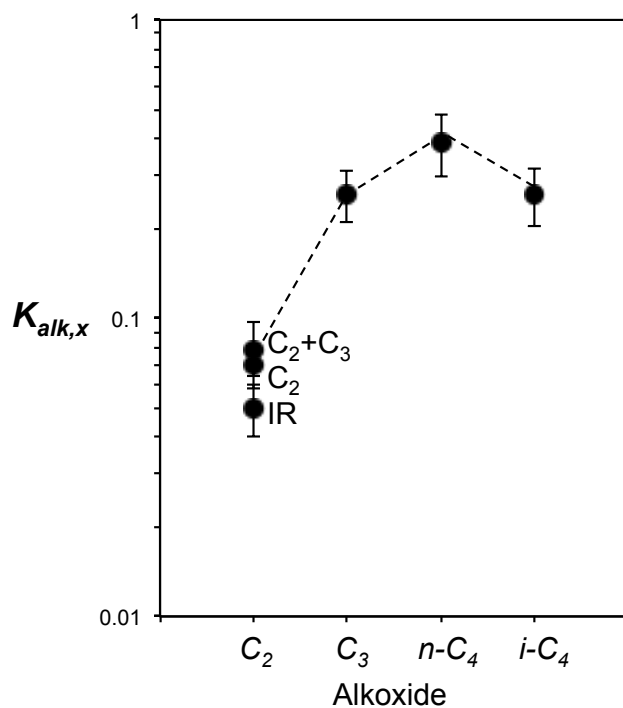


Figure 4. Measured equilibrium constants for alkoxide formation on TON [503 K; <5 % alkene conversion; dashed lines connect data points to guide the eye]. Parameters from least squares fit of co-oligomerization rate equations with respect to propoxide and multiplied by propoxide formation measured from low-pressure kinetic data. Ethoxide formation also measured from IR and fitting single feed oligomerization kinetic data.

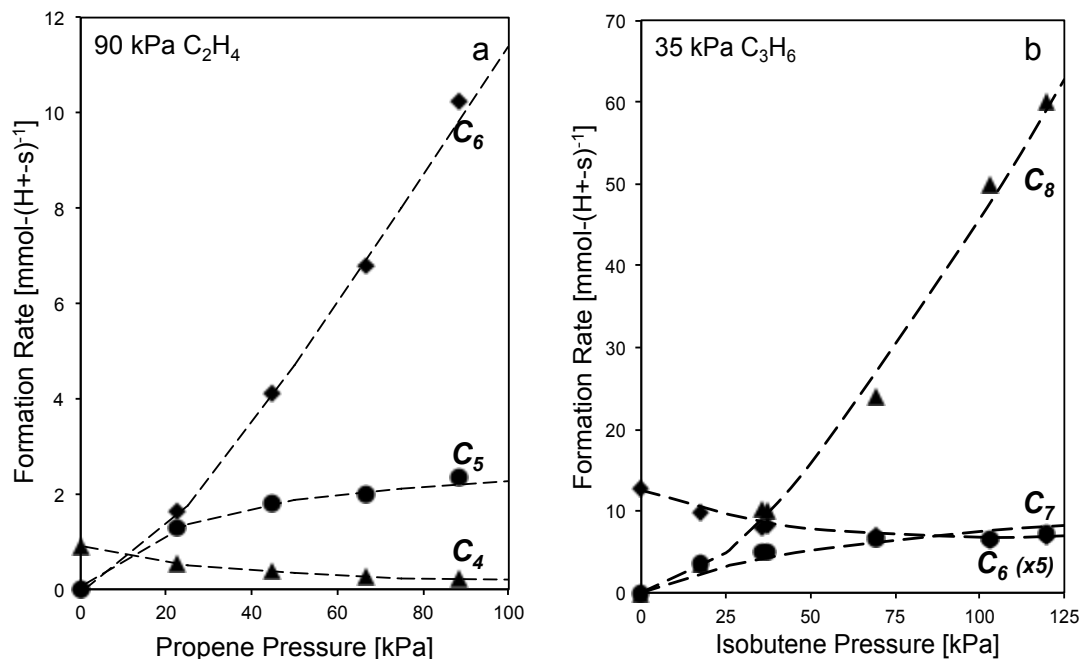


Figure 5. Formation rates of dimers and co-dimers from ethene and propene (a) and isobutene and propene (b) mixtures [503 K; <5 % alkene conversion]. Dashed lines indicate regression fit from Equations 6-8.

Table 2. DFT calculated thermodynamic values for alkoxides on TON and HPW.

Alkoxide	TON		HPW	
	ΔH_{alk} [kJ mol ⁻¹]	ΔG_{alk} [kJ mol ⁻¹]	ΔH_{alk} [kJ mol ⁻¹]	ΔG_{alk} [kJ mol ⁻¹]
ethoxide	-93.8	-17.7	-98.1	-22.5
p-propoxide	-99.1	-21.8	-81.5	-9.50
s-propoxide	-105	-23.2	-100	-31.0
p-n-butoxide	-119	-18.5	-82.9	-5.10
s-n-butoxide	-119	-28.4	-93.1	-31.1
p-isobutoxide	-91.5	-23.7	-76.9	13.1
t-isobutoxide	-58.3	3.88	-116	-38.1

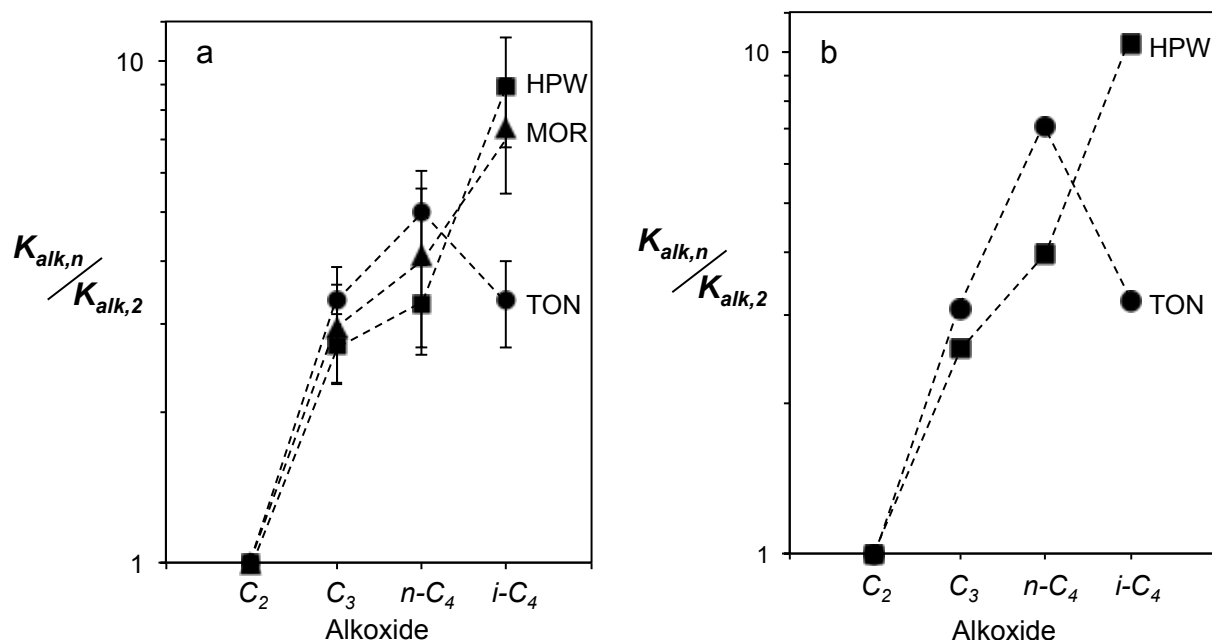


Figure 6. A: Measured relative equilibrium constants with respect to ethoxide on TON (●), MOR (▲) and HPW (■) [503 K; <5 % alkene conversion; dashed lines connect data points to guide the eye]. Parameters from least squares fit of rate equations with respect to propoxide were re-normalized to ethoxide. B: Calculated relative alkoxide stability with respect to ethoxide on TON (●) and HPW (■) [dashed lines connect data points to guide the eye]. Multiple attachment points were ensemble averaged according to the alkoxide ΔG at 503 K. All energies are referenced to H-TON and respective gas-phase alkene analog.

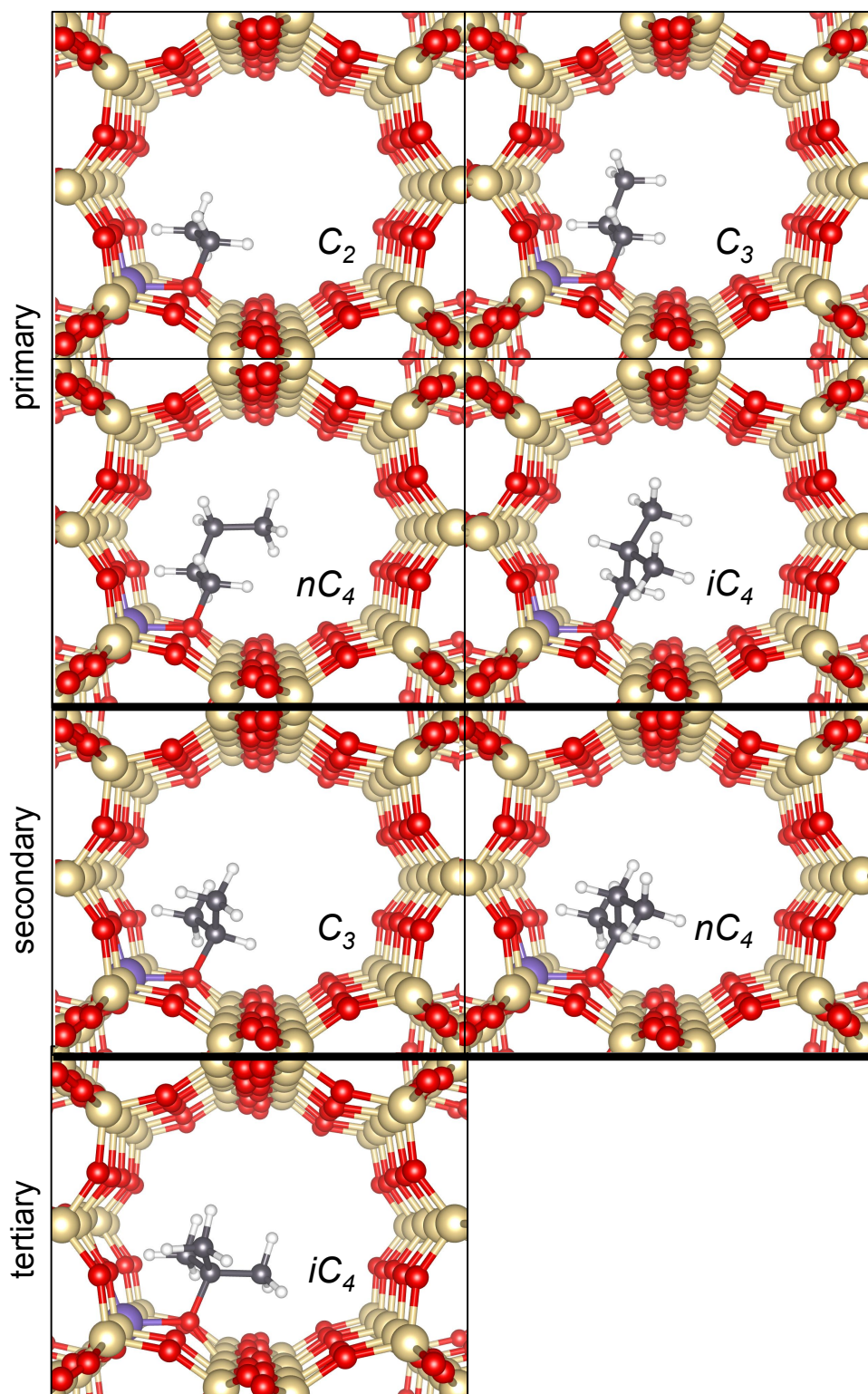


Figure 7. DFT-derived alkoxide structures in TON [Al₂ site] with increasing chain length and substitution of alkene precursor from left to right (C₂H₄, C₃H₆, n-C₄H₈ and i-C₄H₈). Primary alkoxides are shown in the top 2 rows, secondary in the 3rd row and tertiary in the bottom row.

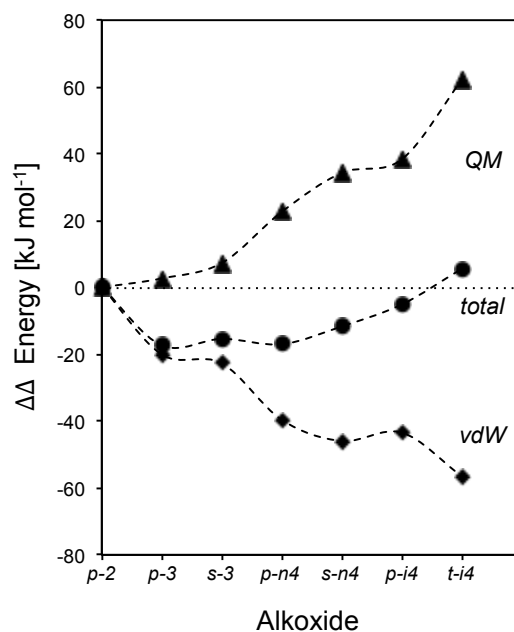


Figure 8. Calculated alkoxide total electronic energies (●) and its two components (van der Waals (vdW; ◆) and quantum mechanical (QM; ▲)) for p-propoxide, s-propoxide, p-n-butoxide s-nbutoxide, p-isobutoxide and t-isobutoxide relative to ethoxide on TON. Energies are referenced to H-TON and the gas-phase alkene analog [dashed lines connect data points to guide the eye].

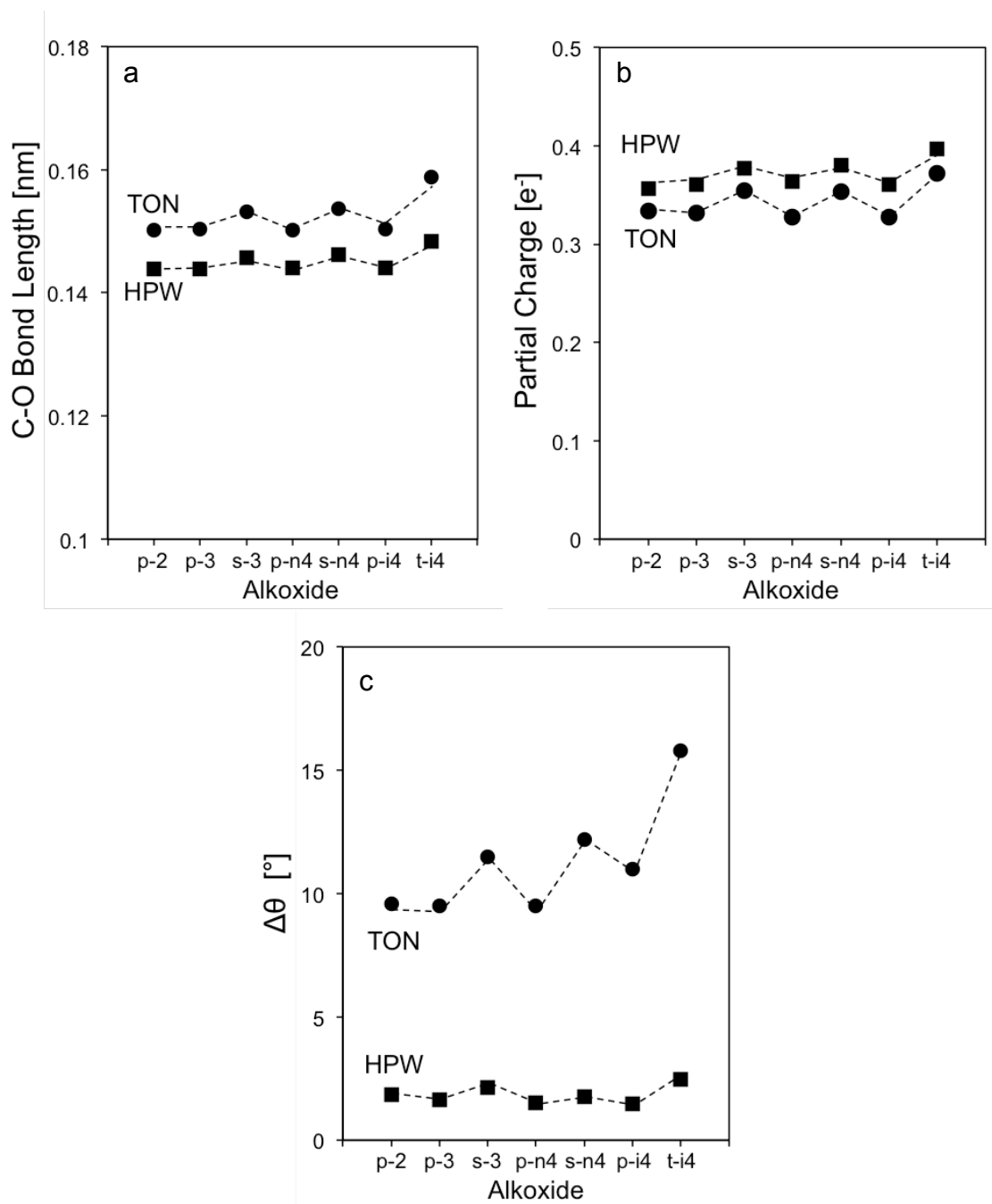


Figure 9. Properties of optimized alkoxide structures on TON (Al₂; ●) and HPW (terminal; ■): C-O bond length (a), partial charge of organic atoms (b) and Δθ between H-form and alkoxide form of Si-O-Al bridge in TON and O-W-O in HPW (c) [dashed lines connect data points to guide the eye].

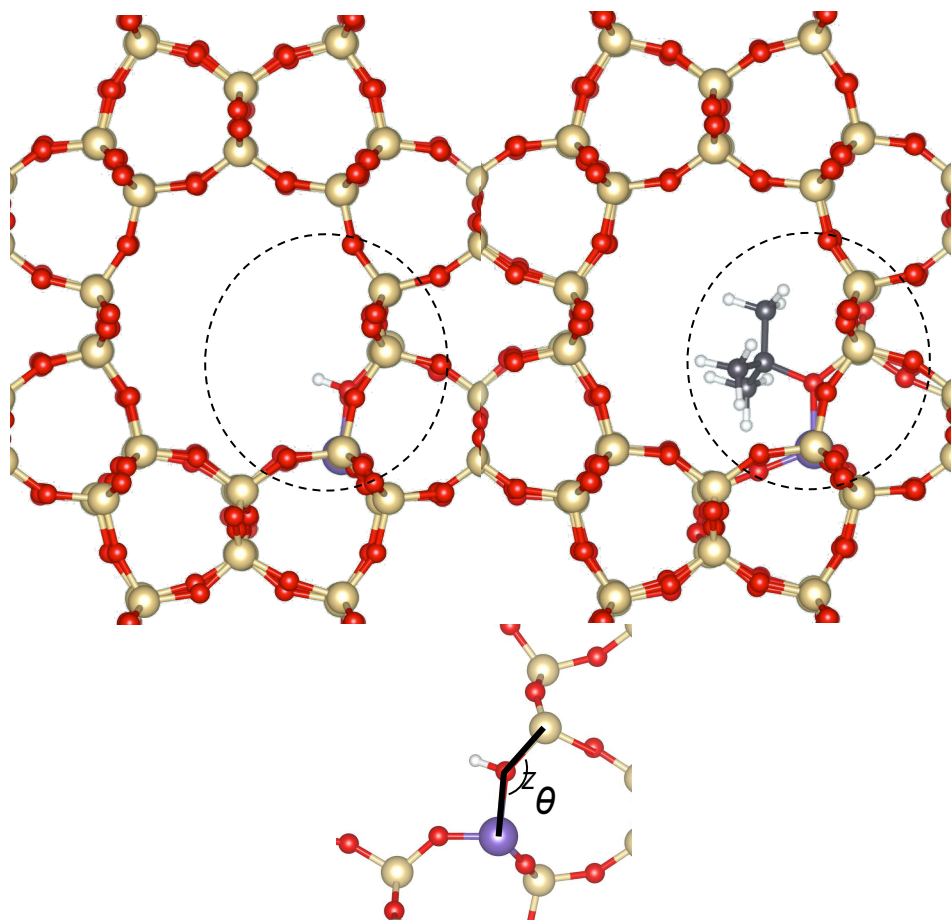


Figure 10. Structures of TON [Al₂ site] in H-form (top left) and t-isobutoxide (top right) with portion of most displacements highlighted in the dashed circle. The Si-O-Al bridge (bottom) shows the angle used for characterization in Figure 9.

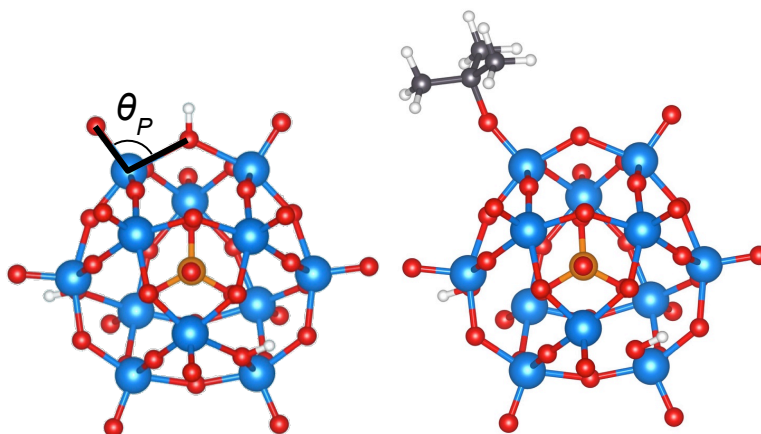
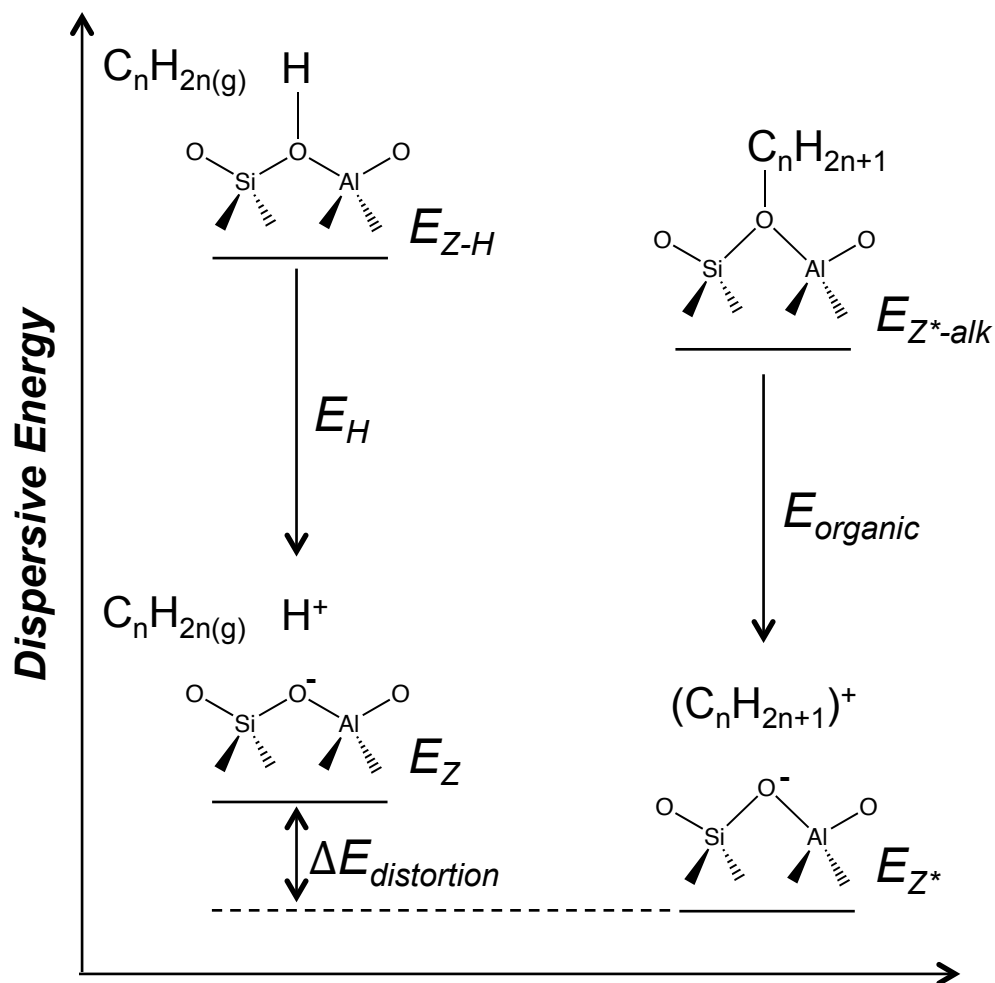


Figure 11. Structures of HPW in H-form (left) and t-isobutoxide (right) with O-W-O angle (left) shows the angle (θ_P) used for characterization in Figure 9.



Scheme 2. Thermochemical cycle description of distortion energy (Eq. 11) in terms of dispersive energies. The distortion energy ($E_{\text{distortion}}$) depends on the difference in dispersive energy between optimized inorganic component from the alkoxide (E_{Z^*}) and proton (E_Z) form, which are defined as the difference in dispersive energy between the full optimized structure ($E_{\text{alk-Z}^*}$ and $E_{\text{H-Z}}$) and the organic component (E_{organic} and E_H , respectively).

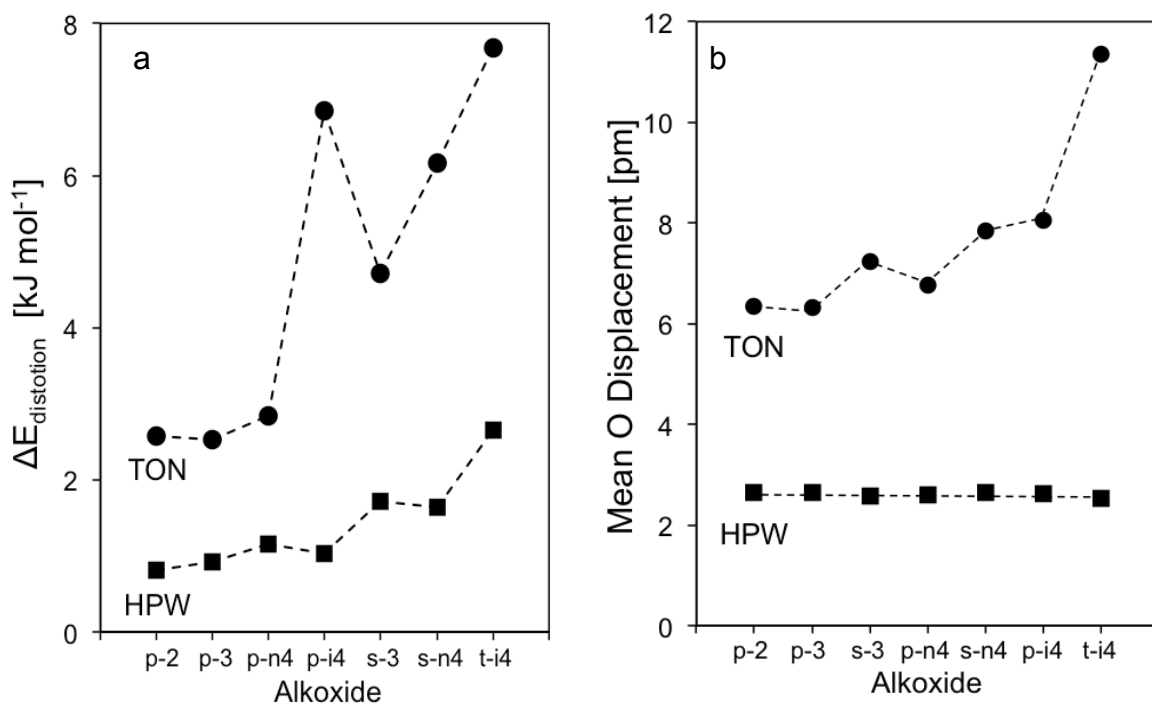


Figure 12. Distortion energies (Eq. 11; a) and mean displacements of oxygen atoms (Eq. 11; b) of alkoxide formation on TON [Al2; ●] and HPW [terminal; ■] relative to the H-form of each catalyst [dashed lines connect data points to guide the eye].

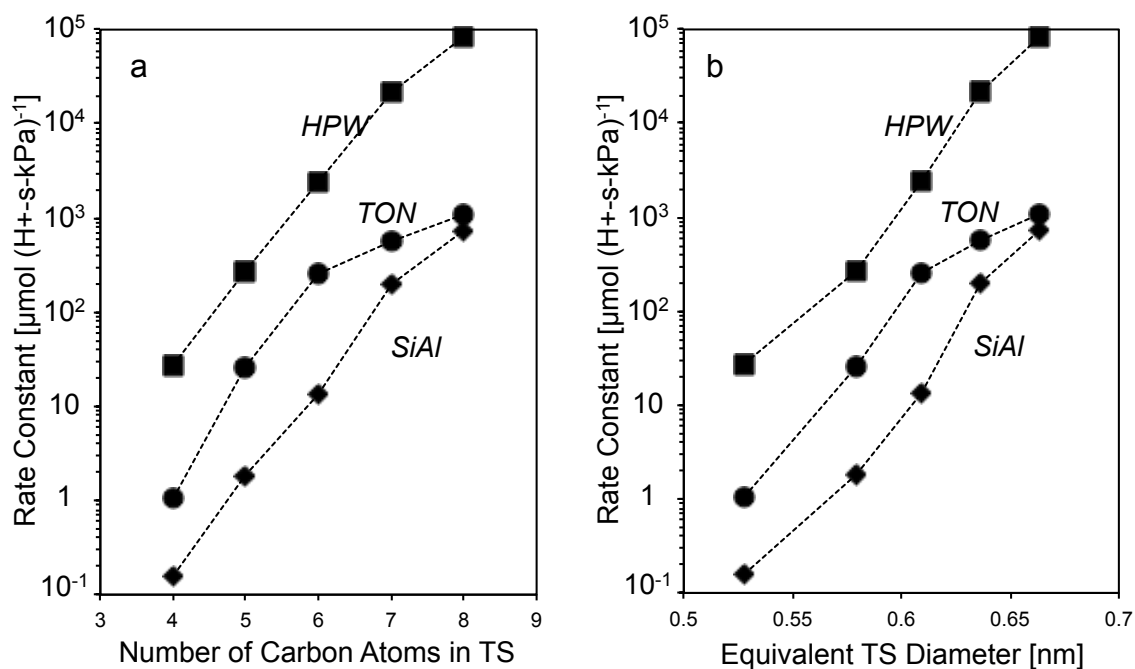


Figure 13. Measured rate constants from alkene coupling reactions of (ethene + propene) and (propene + isobutene) on TON (●), SiAl (◆) and HPW (■) as a function of (a) number of carbon atoms in the transition state (TS) and (b) diameter of a sphere with equivalent DFT-derived volume on TON [503 K; <5 % alkene conversion; dashed lines connect data points to guide the eye].

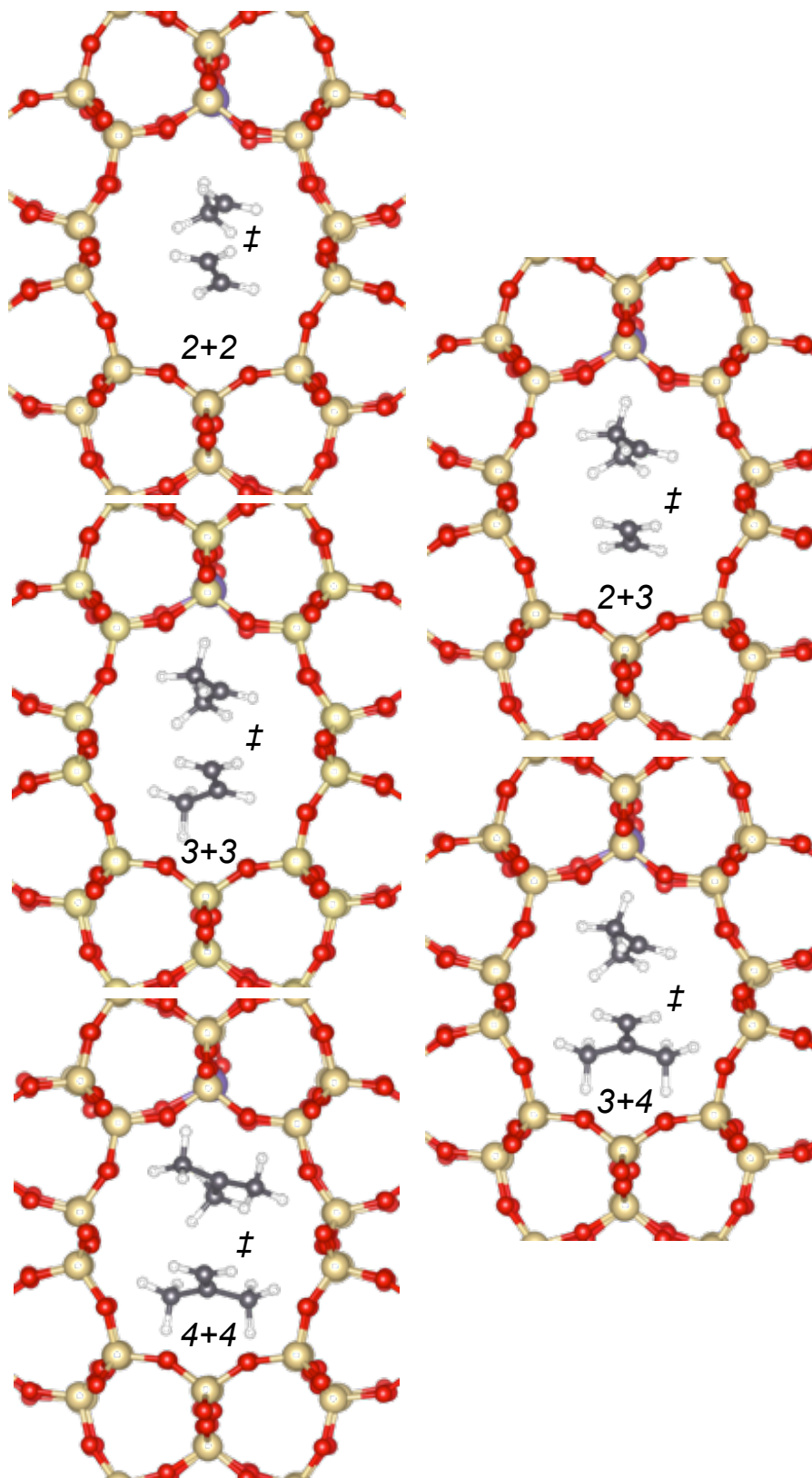


Figure 14. DFT-derived TS structures of alkene coupling reactions in TON [Al₃ site] with increasing chain length and substitution of alkene precursors [RPBE-D3BJ].

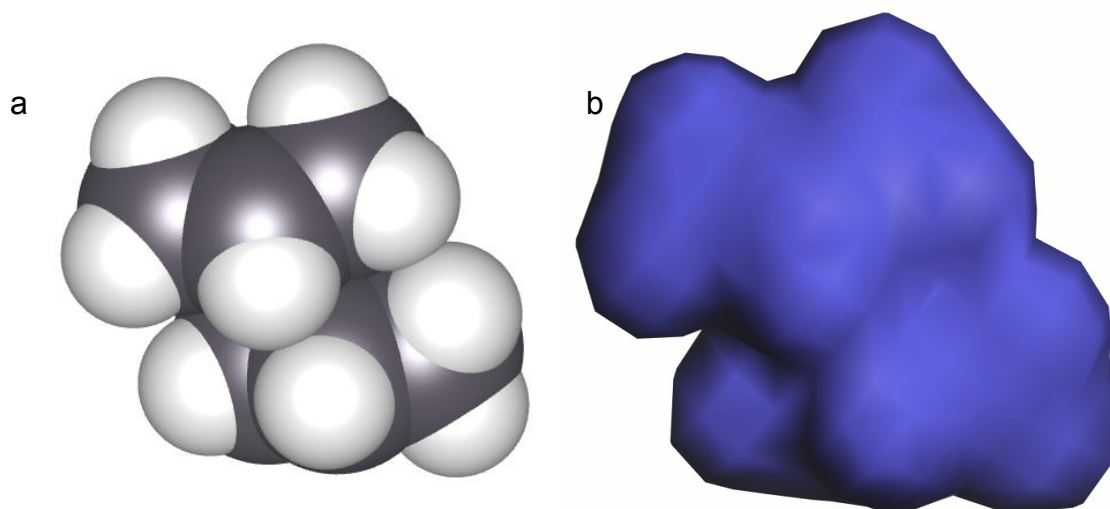


Figure 15. DFT-derived TS structure of propene addition to secondary propoxide in TON [Al₃ site] with van der Waals radii (a) and equivalent V_{vdW} (b) calculated from enclosed volume of a Connolly surface.

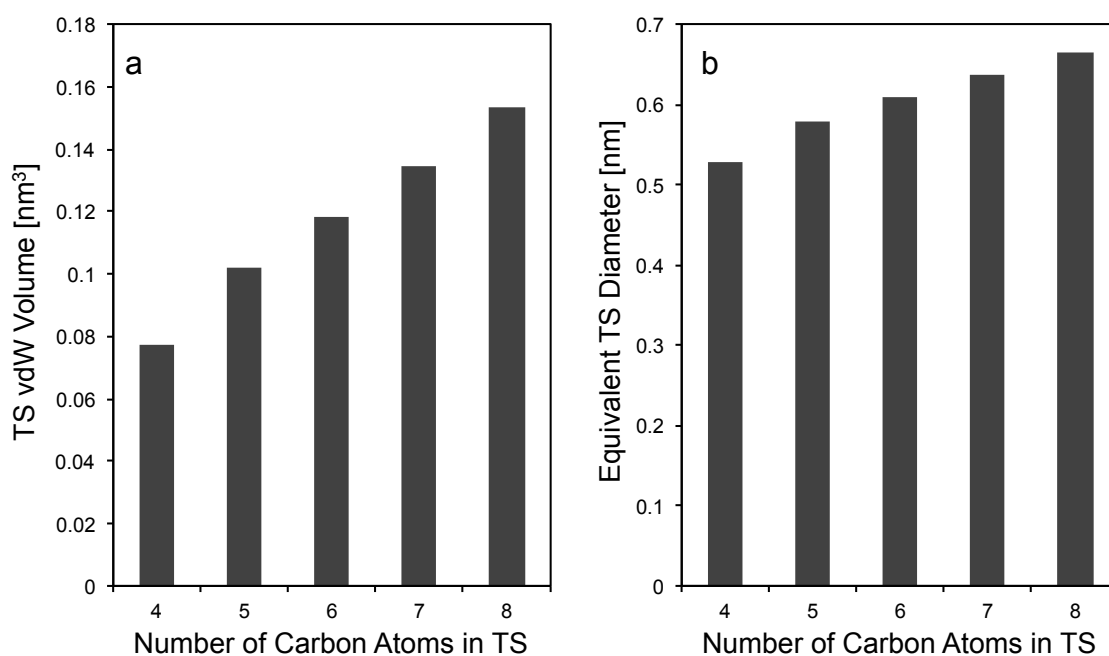


Figure 16. DFT-derived V_{vdW} of TS in Figure 13 (a) and calculated diameter of a sphere with equivalent diameter (Eq. b).

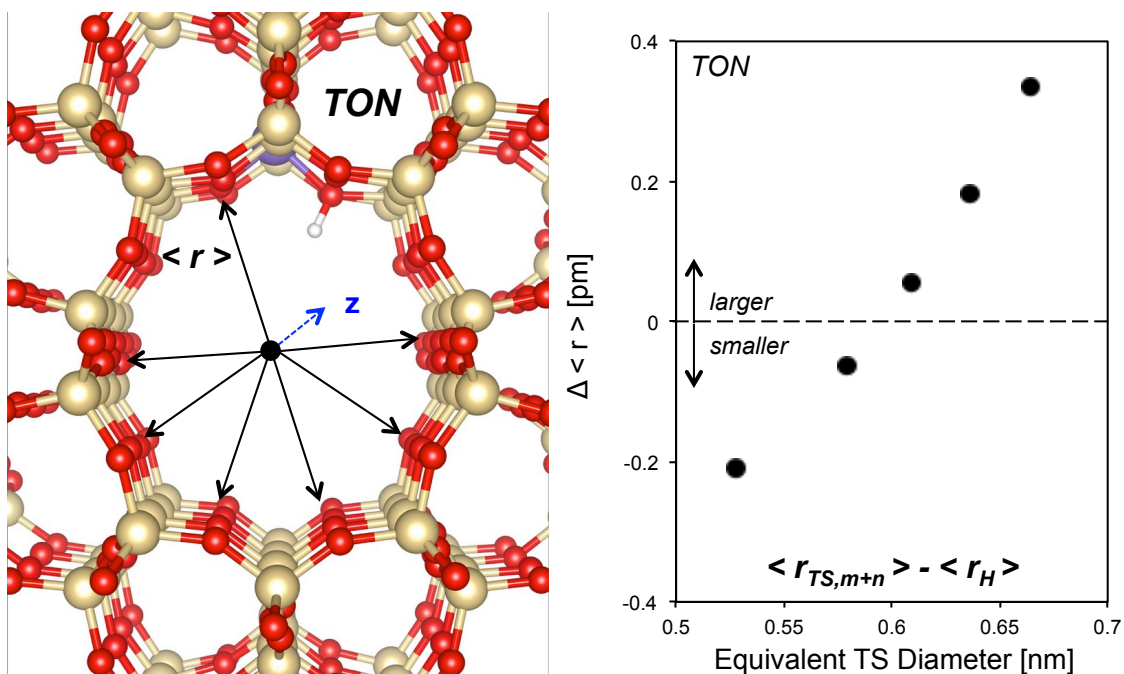


Figure 17. Cylindrical coordinates for TON zeolite (left) and Δr [pm] between H-form and TS of lattice oxygen in the first shell of the pore network.

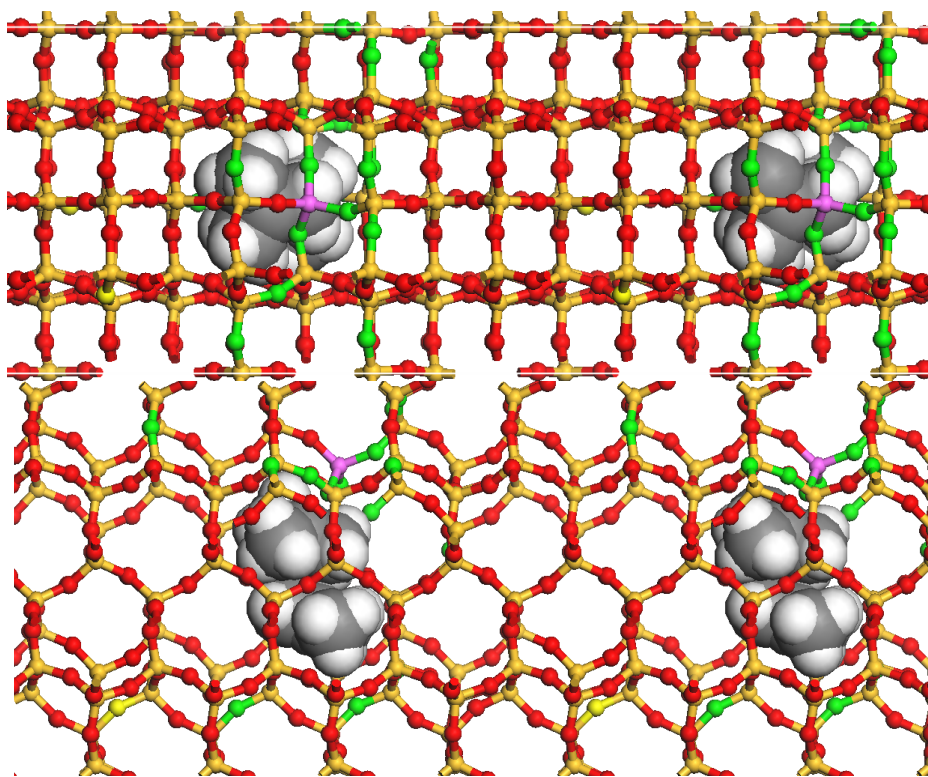


Figure 18. Locality of distortion from C_8 TS on TON as viewed from the top and the side. O-atoms highlighted in green have Δr values more than one standard deviation from mean.

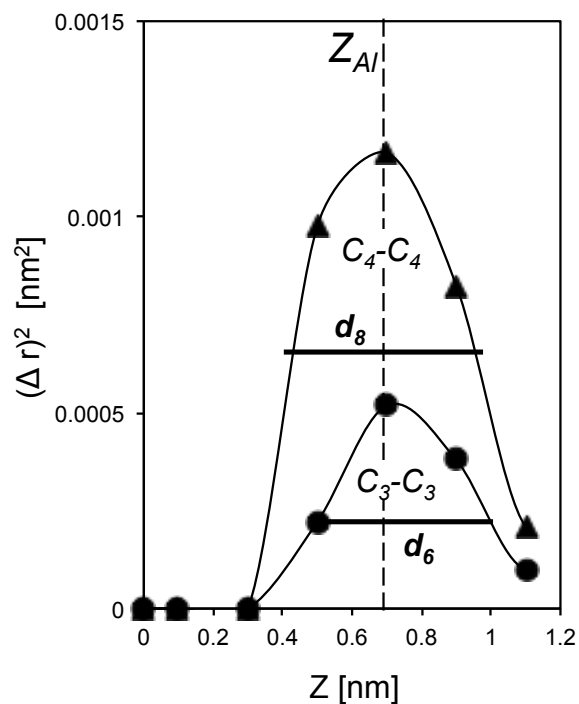
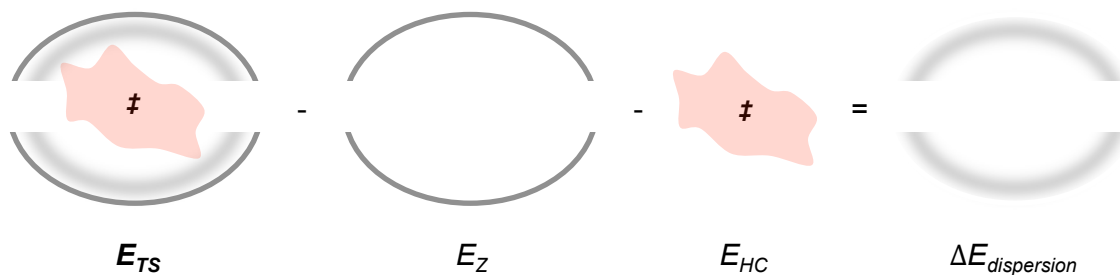


Figure 19. Deviation in lattice oxygen r between TS and H-form $(\Delta r)^2$ for C_8 and C_6 formation on TON as a function of Z (down the channel). Z_{Al} is the location of the Al and d_8 and d_6 are the respective TS diameters, which are similar to the breadth of the distortions.



Scheme 3. Schematic showing the chemical meaning of $\Delta E_{dispersion}$, where all terms are the D3BJ component of the optimized energy, E_{TS} is the total vdW energy for the TS, E_Z is that of the inorganic host and E_{HC} is that of the organic component.

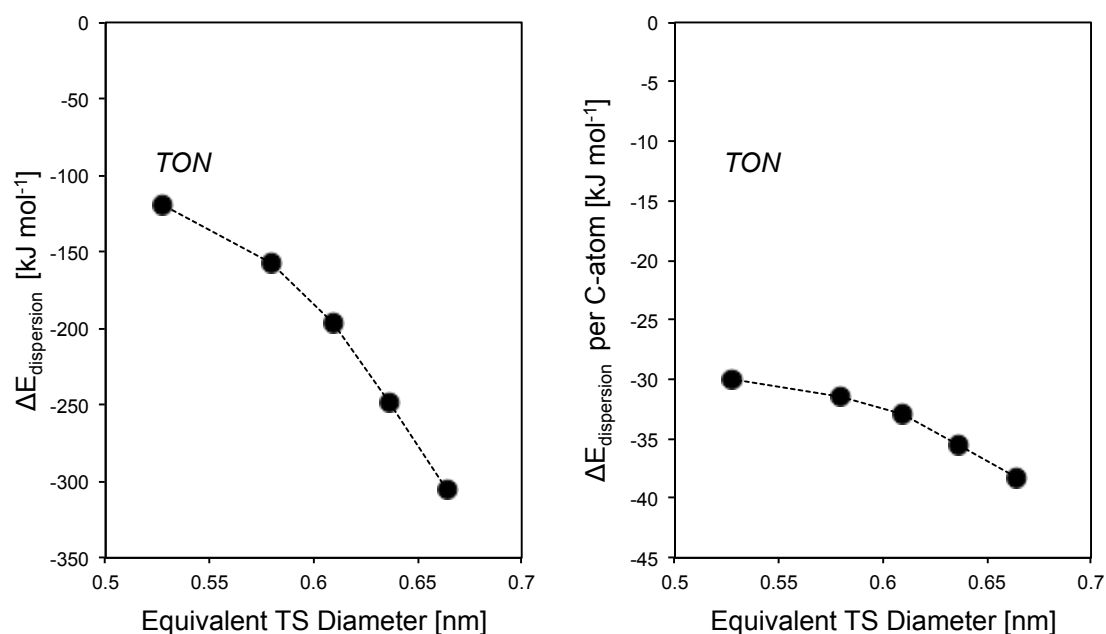


Figure 20. DFT-derived dispersive interaction energy of the TS (Eq. 14; a) and this value normalized by number of carbon atoms in the TS (b).

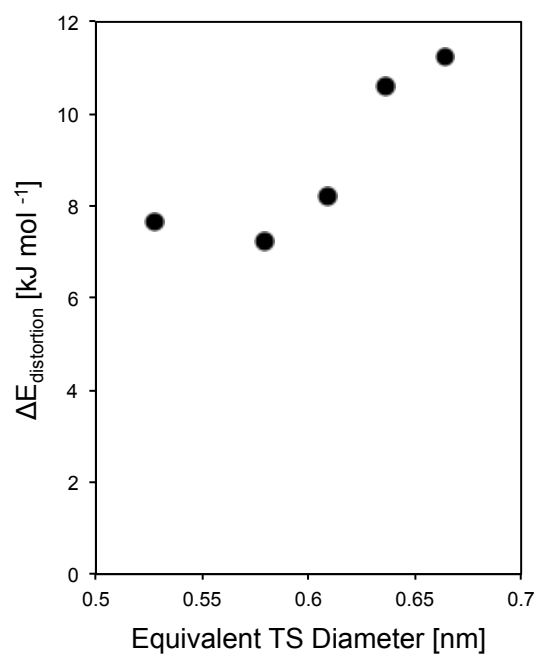


Figure 21. Distortion energies (Eq. 11) for TS in Figure 13 on TON relative to the H-form.

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CHAPTER FIVE

Incorporation of Light Alkanes into Alkene Oligomerization Cycles on Solid Brønsted Acid Catalysts

Abstract

We report light alkane (2-methylbutane, isobutane and n-butane) incorporation into alkene oligomerization pathways (alkylation), the rate of which is limited by the acid-catalyzed hydride transfer (HT) reactions between the alkane and growing chains, providing a route of termination from the cycle. Turnover rates for alkane formation increase linearly with reactant alkane pressure (10-250 kPa) on all zeolitic and mesoporous acids when measured during propene oligomerization (10 kPa alkene). Individual HT rates for the formation of hexane isomers (2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, n-hexane) are obtained because rapid hydride and methyl shifts result in an equilibrated isomer pool of the propene dimers both in the gas-phase as well as on the surface as alkoxides. The resulting first-order rate constants depend on zeolite void diameter; they increase with void size, reaching a maximum on BEA and then decrease as van der Waals contacts become less effective with further increases in void size (e.g. FAU, SiAl). The transition states that mediate HT, however, are significantly larger than those involved in dimer formation via oligomerization reactions as determined from density functional theory (DFT); as a result, HT steps become nearly undetectable for medium pore zeolite structures. These transition states are ion-pair in nature and are measured with respect to neutral precursors (alkoxides), leading to higher rates on stronger acids (here, Keggin polyoxometalate clusters on silica) because the anion of stronger acids better stabilizes the negative charge in the transition state compared to weaker acids. HT also occurs with propene-derived alkoxides, which dominate the surface under these conditions, and with alkoxides derived from secondary β -scission reactions (C_4 and C_5 molecules). This pool of hydride acceptors, combined with use of different hydride donors, yields a large array of transition states, which are assessed with DFT to benchmark what dictates intrinsic reactivities.

5.1. Introduction

Upgrading undervalued, light alkanes through reactions with low molecular weight alkenes (alkylation) is an industrial process that typically uses liquid Brønsted acids, either sulfuric acid or hydrofluoric acid [1,2]. The use of solid acids provides an environmentally friendly and non-corrosive alternative, but their deactivation and lower reactivity, however, have limited their application. Upgrading light alkenes on solid Brønsted acids to larger, fuel-like hydrocarbons involves concurrent oligomerization, isomerization, β -scission, hydride transfer and cyclization reactions [3–5]. Integration of light alkanes into these pathways is mediated by hydride transfer reactions that provide a route of termination from the cycle and increase the paraffinic content of the reactor effluent [6–8]. These reactions, as well as the other aforementioned acid catalyzed hydrocarbon reactions, are mediated by ion-pair transition states of various sizes, which lead to effects of confinement on turnover rates (per accessible proton) over a wide range of solid acid catalysts, including zeolites and mesoporous aluminosilicates.

Propene oligomerization turnover rates are proportional to propene pressure (5-450 kPa), which reflect kinetically-relevant additions of a propene molecule to a propoxide bound at each proton [9]. Incorporation of co-fed isobutane into this oligomerization pathway is limited by a hydride transfer step between isobutane and a bound alkoxide resulting in turnover rates that are proportional to isobutane pressure on all zeolitic and mesoporous acids. The first-order rate constants for C₆ alkane formation via hydride transfer to bound propene dimers, are dependent on void diameter, however, density function theory (DFT) estimates indicate these transition state sizes are significantly larger than those for dimer formation via oligomerization reactions; as a result, the ratio of the first-order rate constant for C₆ alkane formation to that for propene dimer formation increases with void size and only becomes larger than one for large pore (12-MR) zeolites and mesoporous aluminosilicates.

The likelihood of a given hydride transfer step is dependent on the stability of both the acceptor (a bound alkoxide) and the hydride donor in the transition state. Thus, measured kinetic rates decrease as the alkoxide becomes smaller, e.g. propane formation from propoxide proceeds more slowly than C₆ alkane formation from propene dimers, because fewer stabilizing van der Waals contacts can be made with the pore walls. Further, alkoxides of intermediate chain length are available for hydride transfer on samples where β -scission reactions occur readily, leading to broadening of the carbon number distribution [3]; again, smaller alkoxides (e.g. C₅) lead to lower formation rates of the corresponding alkane. Substitution of the alkoxide also affects its reactivity for a hydride transfer step; first-order rate constants for the structural isomers of C₆ alkanes (2-methyl pentane, 3-methyl pentane, 2,3-dimethyl-butane and n-hexane) differ and can only be measured because isomerization reactions between alkoxides of different backbones are in equilibrium with their corresponding gas phase alkenes [3]. Moreover, the substitution of the hydride donor affects the rate of the hydride transfer step, where 2-methylbutane and isobutane incorporate more easily than n-butane due to their ability to stabilize charge at a tertiary carbon (instead of secondary). Applications of the results and conceptual understandings gleaned here indicate promising routes for the production of higher molecular weight hydrocarbons for fuels by utilizing undervalued, light alkenes and alkanes.

5.2. Experimental Methods

5.2.1 Catalytic rate measurements

BEA, MFI, MOR TON, FAU, mesoporous silica-alumina and Keggin POM clusters dispersed on mesoporous colloidal silica with material properties tabulated in previous studies [3,9] (Table 1) were pelleted, crushed, and sieved to retain 180-250 μm aggregates. Alkene turnover and alkane formation rates were measured on samples (15-50 mg) placed within a tubular reactor with plug-flow hydrodynamics (316 stainless steel; 12 mm I.D.) in a three-zone resistively-heated furnace (Applied Test Systems Series 3210; Watlow controllers; 96 Series). The temperature measured with a K-type thermocouple held within an internal concentric thermowell placed in the middle of the bed. Keggin POM clusters (H-form) were treated in flowing He (50 cm³ g⁻¹ s⁻¹; 99.999 %, Praxair) by heating to 503 K (at 0.083 K s⁻¹) to remove adsorbed moisture. Aluminosilicates were treated before catalytic rate measurements in a 5 % O₂ in He stream (83.3 cm³ g⁻¹ s⁻¹, Praxair) by heating to 818 K (at 0.025 K s⁻¹) and holding for 3 h to convert the NH₄⁺ to H⁺, and then cooled to 503 K. n-Butane (99.9 %, Praxair), isobutane (99.9 %, Praxair) or 2-methyl-butane (99.5 % HPLC grade, Sigma-Aldrich) were fed into a stream of propene (99.9 %, Praxair, Praxair) and He. Liquid 2-methyl-butane was evaporated into a

flowing He stream (UHP Praxair) using a high-pressure syringe pump (Teledyne Isco Series D). Reactants were sent to the reactor and the effluent was transferred through lines held above 373 K into a gas chromatograph (Agilent 6890), where concentrations were measured using flame ionization detection after chromatographic separation with a methyl silicone capillary column (Agilent HP-1 column, 50 m x 0.32 mm x 1.05 μ m film). Reactant pressures were changed by dilution into a He stream (99.999 %, Praxair) and the total system pressure was maintained using a dome-loaded regulator (Tempresco).

5.2.2. Density functional theory methods

Periodic density functional theory as implemented in the Vienna ab initio Simulation Package (VASP) [10–13], was used to determine optimized structures and energies for stable intermediate and transition states. A periodic plane-wave basis-set expansion to a cutoff energy of 396 eV was used to represent the wave functions for valence electrons and projector-augmented wave (PAW) pseudopotentials were used to describe electron-core interactions [14,15]. Exchange and correlation energies were calculated within the generalized gradient approximation using revised Perdew–Wang (PW91) functional [16]. A 1 x 1 x 1 Monkhorst–Pack k-point mesh was used to sample the first Brillouin zone [17].

Keggin POM clusters were described by placing full clusters (~1 nm in diameter) at the center of cubic unit cells (3 nm in edge length) to prevent electronic interactions among neighboring cells [18,19]. Reaction paths of minimum energy were calculated using nudged elastic band (NEB) methods [20] with structures converged to energies within 1×10^{-4} eV and forces to within 0.3 eV $\text{\AA}^{-1}$. NEB TS structures were further refined using Dimer calculations [21] with convergence criteria of within 1×10^{-6} eV for energies and 0.05 eV $\text{\AA}^{-1}$ for forces on each atom. The structures of bound intermediate and TS were determined at the proton location of the bridging oxygen.

5.3. Results and Discussion

5.3.1. Effects of confinement on hydride transfer rates during oligomerization catalysis

Oligomerization on Brønsted acid catalysts proceeds via a kinetically relevant addition of a gas-phase alkene to a bound alkoxide (Scheme 1) on alkoxide covered surfaces as indicated from kinetic, spectroscopic and theoretical studies (Eq. 1) [9].

$$r_{oligo_i} = \frac{k_{oligo,i}[C_i][C_i^{alk}]}{\langle K_i \rangle [C_i]} = \frac{k_{oligo,i}K_i[C_i]^2}{\langle K_i \rangle [C_i]} = \frac{k_{oligo,i}K_i}{\langle K_i \rangle} [C_i] \quad (1)$$

Here, $k_{oligo,i}$ is the rate constant for oligomerization between an alkene (C_i) and an alkoxide (C_i^{alk}) with i carbons. The alkoxide is equilibrated with the gas-phase via an adsorption constant, K_i , while the surface is covered in a mixture of equilibrated alkoxides with different attachment points $\langle K_i \rangle$ (discussed in detail in Chapters 3 and 4). Evidence for the equilibrations of both the reactant-derived and product alkoxides with their alkene analogs will be discussed in Section 5.3.2.

During oligomerization, the only way a given alkoxide can leave the surface is through desorption. Co-fed light alkanes, however, can remove alkoxides via hydride transfer (HT) (isobutane and propene mixtures: Scheme 1). This provides a way to not only control chain length by removing chains before they can continue to grow, but also a way to incorporate

relatively unreactive alkanes at modest temperatures (503 K). The C₄ species can either desorb to form the alkene, react with propene to form C₇ alkenes or, with subsequent HT reactions, form alkylate, which is a high octane number blending species.

Formation rates of C₆ alkanes (normalized by the number of protons) are proportional to isobutane pressure (Fig. 1; 9 kPa propene; 503 K) on a diverse set of microporous and mesoporous catalysts, consistent with a kinetically relevant HT between hydride donor (here, isobutane) and its acceptor (an alkoxide). This is described by Equation 2:

$$r_{HT_{ni}} = \frac{k_{HT,ni}[C_n^o][C_i^{alk}]}{\langle K_3 \rangle [C_3]} = \frac{k_{HT,ni}K_i[C_n^o][C_{ij}]}{\langle K_3 \rangle [C_3]} = \frac{k_{HT,ni}K_i}{\langle K_3 \rangle} \frac{[C_i]}{[C_3]} [C_n^o] \quad (2)$$

where $k_{HT,ni}$ is the rate constant for HT from an alkane (C_n^o) with n carbons and an alkoxide (C_i^{alk}) with i carbons, which occurs on the same propoxide covered surface as oligomerization. The isobutane is also involved in other reactions, as indicated by selectivity to C₇ alkenes and alkanes over C₆ species increasing with increasing isobutane pressure (Fig. 2) and the formation of propane from the surface propoxides (Fig. 4; BEA). C-C bond cleavage β -scission that occur concurrently with C-C bond formation and HT yield a distribution of products with intermediate carbon number (Fig. 3; BEA), the extent of said events varies on the catalyst framework (Chapter 2). The alkoxides derived from these products are also available for HT and follow a similar mechanism to that of propene dimers as indicated by formation rates proportional to isobutane pressure (Fig. 4; BEA); their relative rates will be discussed in Section 5.3.2. Isobutane can also be incorporated into alkene conversion pathways with physical mixtures of Pt/SiO₂ and zeolites to form locally isobutene, which can dimerize or couple with reactant propene. This increases the total rate of isobutane consumption (Fig. S1; SI), but does not increase the hydride transfer indicated by similar hexane formation rates.

Figure 1 shows that while similar pressure dependences are observed on all catalysts, their relative rates vary. The particular catalysts are all aluminosilicates, meaning they have similar acid strength [22], but the size of their confining voids varies significantly. The linearity of these rates indicate the hexene concentrations are linear because oligomerization conversion is unaffected by isobutane and that the rate of hexoxide depletion is much less than the rate of their formation. We must, therefore account for the amount of hexenes and propene in order to obtain true rate constants that only consist of kinetic and thermodynamic constants (Eq. 2).

The true first order rate constants for HT between isobutane and hexoxides or propoxides are plotted in Figure 5 (a: $k_{HT,4,6}$; b: $k_{HT,4,3}$) as a function of void diameter, where the void diameter is that obtained for modeling the pore network as a series of spheres and cylinders [23,24]. The rate constants increase for both alkoxide acceptors as the void size decreases until it reaches a maximum (BEA for hexoxide and MOR for propoxide). This is because the bimolecular transition state is larger than its monomolecular precursor and thus can have more stabilizing van der Waals interactions with the lattice oxygen. The change in the maximum in Figure 5 is also a size effect, where transition state sizes can be approximated from density functional theory (DFT). The transition state for hexoxide HT involves 10 carbon atoms with an average diameter of 0.8 nm, while that for propoxide HT has only 7 carbon atoms with an average diameter of 0.7 nm (Fig. 6). As void size continues to decrease, the measured rate constant also decreases, indicating the transition state is destabilized in these voids due to its size. The maximum value of the rate constant with respect to void size should appear when the void size is similar to the transition state size. The discrepancy between these sizes is because the

transition state and the container have both size and shape, which is not captured in a one-dimensional length. For example, alkoxides of longer chain lengths have long tails that need to fit within the pore even if they do not directly interact with the hydride (Fig. 7). While better descriptors are needed to understand the molecular recognition of these environments, average diameters suffice for initial approximations.

Rate constants on acids with greater acid strength in terms of deprotonation energies (DPE; [18,22]) are two orders of magnitude higher than weaker acids when the protons on both materials experience similar confinement (HPW on mesoporous silica and mesoporous SiAl; 1085 versus 1220 kJ mol⁻¹ DPE, respectively). The difference in charge between the fully formed ion-pair transition state (DFT-derived charge in organic=+0.96; Fig. 6) and that of the alkoxide (DFT-derived charge in organic=+0.3) leads to the preferential stabilization of the transition state by the anion of a stronger acid, which better accepts the negative charge.

This HT transition state is much larger in size than the transition state for oligomerization (0.8 nm versus 0.6 nm; Fig. 6). The ratio of the HT to hexoxides rate constants to those measured on the same samples during oligomerization (Eq. 3) (0 kPa isobutane; Chapter 2; [9]) are unaffected by void diameter for larger pore acids, but decrease rapidly as the pore size gets smaller (Fig. 7). The larger transition state for HT no longer fits adequately in the smaller voids, destabilizing its energy relative to the oligomerization transition state (Eq. 4).

$$\gamma_i = \frac{k_{HT,ni}K_i}{k_{oligo,3}K_3} = \exp \left(-\Delta G_{\gamma_i}/RT \right) \quad (3)$$

$$\Delta G_{\gamma_i} = G_{HT,ni}^{\ddagger} - G_{oligo,3}^{\ddagger} - G_n^{(g)} - G_i^{(g)} - 2G_3^{(g)} \quad (4)$$

The size may be different between these two transition states, but they are both ion pairs with similar charge (Fig. 6). This results in similar γ values on HPW and SiAl. Therefore, they are similarly affected by acid strength because a given conjugate anion cannot selectively stabilize one ion-pair transition state over another when they are in the same sized void (here, a mesoporous void).

5.3.2. Effects of chain length and substitution of the acceptor and the donor during hydride transfer

Rapid methyl and hydride shifts among alkoxide intermediates results in equilibrated mixtures of all skeletal, regio and stereoisomers within a given carbon number. Approach to equilibrium parameters are given by:

$$\eta_{ij} = \frac{\left(\frac{C_{ij}}{C_{i,ref}} \right)}{K_{i,ref \leftrightarrow j}} \quad (5)$$

where $K_{i,ref \leftrightarrow j}$ is the equilibrium constant for conversion of the reference isomer of choice with i carbons to the j isomer, present at a concentration C_{ij} . The values of the equilibrium constants for hexene were calculated from ratios of isomer concentrations at high conversion because these ratios were mostly independent of conversion (range: 0.001-0.5), pressure or catalyst choice, yet did not have approach to equilibrium values of either 0 or 1 when using tabulated sources

[25,26]. Further, the tabulated Gibbs free energies for isomer formation varied among these literature sources, by as much as 15 kJ/mol (at 503 K) in some cases, leading to widely different η values depending on the source used.

Approach to equilibrium values for the hexene isomers formed from propene oligomerization on TON, MFI, BEA, SiAl and HSiW using the calculated equilibrium constants are near unity, even at very low conversions (less than 0.01 fractional propene conversion; Fig. 9; approach to equilibrium for C5s in Fig. S2). These isomers are grouped according to their skeletal backbones: 2-methylpentenes (2-MP), 3-methylpentenes (3-MP), linear hexenes (n-H) and 2,3-dimethylbutenes (23-DMB). The only isomers that do not have η values of unity are the 23DMB isomers, the bulkiest skeleton, in TON, which has the smallest channels; this is an artifact of transport limitations and not kinetic in origin as evident from increasing values with increasing conversion or acid site density as well as isotopic scrambling experiments described elsewhere [3]. The fact that these isomers reach equilibrium with gas-phase thermodynamics is also consistent with equilibrated adsorption and desorption events to communicate between the alkoxides and their alkene analogs.

The alkoxides with the different backbones are all available to undergo hydride transfer with isobutane (Scheme 2). The rates of formation of 2-methylpentane (2MP), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB) and n-hexane (nH) are all proportional to isobutane (Fig. 10; BEA), as well as for pentane isomer formation (2-methylbutane (2MB) and n-pentane (nP)). A rate expression, similar to Equation 2 is written for each isomer:

$$r_{HTn,ij} = \frac{k_{ij}[C_n^o][C_{ij}^{alk}]}{K_3[C_3]} = \frac{k_{ij}K_{ij}[C_n^o][C_{ij}]}{K_3[C_3]} = \frac{k_{ij}K_{ij}}{K_3} \frac{[C_{ij}]}{[C_3]} [C_n^o] \quad (5)$$

$$\sum_j r_{HTn,ij} = r_{HTn,i} \quad (6)$$

where $k_{HTn,ij}$ is the rate constant for HT from an alkane (C_n^o) with n carbons and an alkoxide isomer j (C_{ij}^{alk}) with i carbons that is equilibrated with the gas-phase via K_{ij} . It is the equilibrium among the isomers that allows the individual rates of formation to be measured. The first order rate constants, after incorporating the propene and isomer (C_{ij}) pressures (Fig. 11), do not indicate how many alkoxides are there, or how reactive they are. It instead reports what matters for reactivity, which is the product of the two and the difference in energy reflected in their combined rate constant (Eq. 7-8).

$$\gamma_{ij} = \frac{k_{HTn,ij}K_{ij}}{k_{oligo,3}K_3} = \exp \left(-\Delta G_{\gamma_{ij}} / RT \right) \quad (7)$$

$$\Delta G_{\gamma_{ij}} = G_{HTn,ij}^\ddagger - G_{oligo,3}^\ddagger - G_n^{(g)} - G_{ij}^{(g)} - 2G_3^{(g)} \quad (8)$$

The rate constants in Figure 11 are grouped according to the number of carbon atoms and generally increase with increasing chain length on BEA, HPW and SiAl. The increased values for HPW compared to SiAl for all alkoxide acceptors are consistent with their HT transition states benefiting from the more stable conjugate anion of the stronger acid, while the increased

values for BEA compared to SiAl reflect the effects of confining the large transition states in the microporous pores of BEA. Different backbones have different first order rate constants, indicating an effect of substitution on the measured energy. The selectivity among formation of these alkane isomers, however, is not dependent on acid strength or confinement (Fig. 12), which suggests the transition states to form each of the alkanes benefits similarly.

We again turn to DFT to try to understand these reactivity differences. The optimized structures of the transition states for hydride transfer between isobutane and either secondary n-hexoxide or tertiary 2-methylpentoxide on HPW indicate the highest energy point occurs at different times along the reaction coordinate (Fig. 13); the hydride has already passed in the case of 2-MP formation, but has not yet passed for nH formation. The energy ΔG_{vij} can be dissected into components via a thermochemical cycle (Scheme 3). First, the alkoxide must dealkylate from the surface, producing a protonated gas phase analog (dealkylation energy; DAE). The hydride is then transferred from the isobutane to the protonated species (hydride transfer energy; HTE). Now, the alkane has been formed and the positive charge resides on the isobutyl moiety. This cation is brought closer to the conjugate anion to help stabilize the charge (interaction energy; IE). The transition state structures in Figure 13 suggest that the bulk of the energy for nH formation is due to the dealkylation of the sec-hexoxide, while 2MP is actually limited by the hydride transfer. These results indicate that the chain length and substitution of the hydride acceptor affects both the overall energy of the transition state, as reflected by different measured first order rates constants (Fig. 11), but also which part of the hydride transfer is the most energy intensive.

The rate of hydride transfer is also affected by the chain length and substitution of the hydride donor. Total C₆ alkane formation rates on BEA are all proportional to reactant alkane pressure for 2-methylbutane, isobutane and n-butane (Fig. 14) when co-fed with 9 kPa propene, however the magnitude of the rates decreases with decreasing chain length and substitution. The resulting first order rate constants for the individual C₃, C₄, C₅ and C₆ alkane isomers are in Figure 15. The trend in rate constants with hydride donor is consistent with differences in dehydridation energies (Fig. 16), which is the energy required to remove the hydride. This measure of the stability of the moiety as a cation is directly related to the hydride transfer energy (HTE) in Scheme 3. Optimized transition state structures for the hydride transfer between n-butane or isobutane and tertiary 2-methylpentoxide on HPW (Fig. 17) indicate the point of highest energy along the reaction coordinate, which tracks the path of the hydride passing, is the same, only the energies differ. The step in the thermochemical cycle (Scheme 3) that is limiting for both transition states is that of the hydride transfer, because the alkoxide is the same. Therefore, these trend with the dehydridation energy.

5.4. Conclusions

Alkane incorporation via hydride transfer and alkylation into alkene chain growth pathways represents an attractive route to produce transportation fuels from undervalued feedstocks. Both oligomerization and hydride transfer are mediated by ion-pair transition states of similar charge but differing size and shape, and serve as probes to understand effects of catalyst properties on reactivity and selectivity. Turnover rates of alkane formation are proportional to reactant alkane pressure (isobutane, n-butane, 2-methylbutane) when co-fed with propene, indicating that hydride transfer between the hydride donor and surface bound alkoxides mediates incorporation. The resulting first order rate constants depend sensitively on confinement provided by voids of molecular size in zeolitic acids and on acid strength, because the ion-pair transition states are of

different size and charge, respectively, than their neutral alkoxide precursors. We probe here through rigorous kinetic analyses and relevant theoretical treatments how the strength and confinement of Brønsted acid sites (within microporous and mesoporous acids with different void size and shape) influence the relative stability of precursors and transition states involved in C-C bond formation (oligomerization) and hydride transfer (alkylation) reactions of alkene-alkane mixtures. In doing so, our work has provided previously absent assistance for designing acids with the most effective strength and location of protons in a way that allows systematic extrapolations to molecules of size and structure different from those examined here.

5.5. Figures, Tables and Schemes

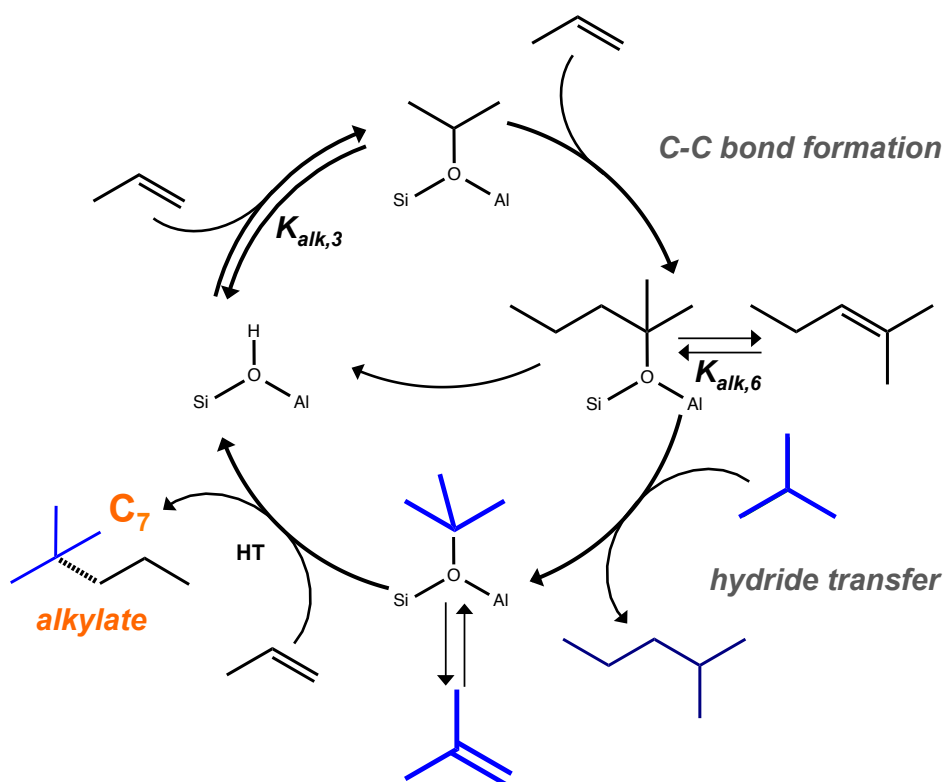
Table 1. Source, Si/Al ratio and proton counts for solid acids used in this study

	Sample	Source	Si/T* Ratio ¹	H ⁺ /T* Ratio
	(*T=Al unless otherwise noted)			
a	BEA	Zeolyst	11.8	0.39 ²
	BEA	Zeolyst	43	1.0 ²
	MOR	Zeolyst	10	0.86 ²
	MFI	Zeolyst	43.8	1.0 ²
	TON	BP	24	0.40 ²
	LZ-210	Engelhard	7.5	0.37 ²
	Silica-Alumina	Sigma-Aldrich	5.5	0.25 ³
b	Sample	POM content on Silica (wt %)	POM surface density (POM nm ⁻²)	Protons (H ⁺ /POM) ³
	H ₃ PW ₁₂ O ₄₀	5	0.04	0.72

¹from elemental analysis (ICP-OES).

²from decomposition of NH₄⁺ exchanged sample.

³from 2,6-di-tert-butylpyridine titration.



Scheme 1. Alkane incorporation into propene oligomerization pathway on solid Brønsted acids.

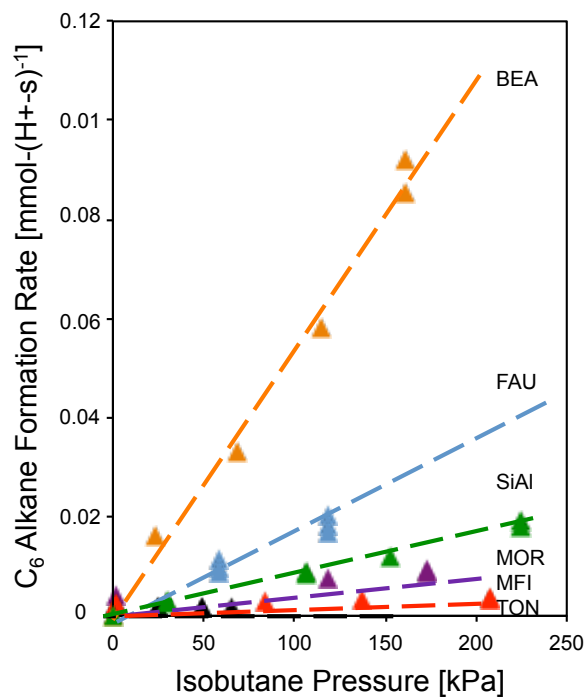


Figure 1. C₆ alkane formation rates as a function of isobutane pressure on aluminosilicates of various channel dimensions (BEA, FAU, SiAl, MOR, MFI, TON) [9 kPa propene, 503 K <5 % alkene and alkane conversion].

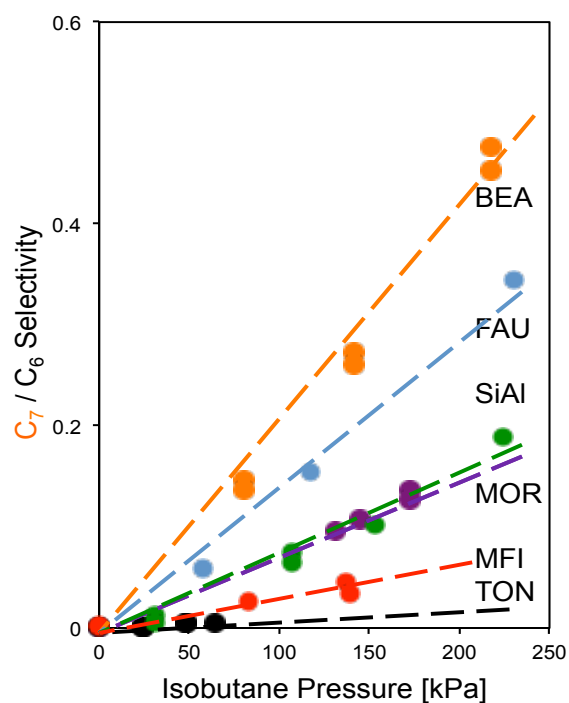


Figure 2. C7 to C6 selectivity as a function of isobutane pressure on aluminosilicates of various channel dimensions (BEA, FAU, SiAl, MOR, MFI, TON) [9 kPa propene, 503 K <5 % alkene and alkane conversion].

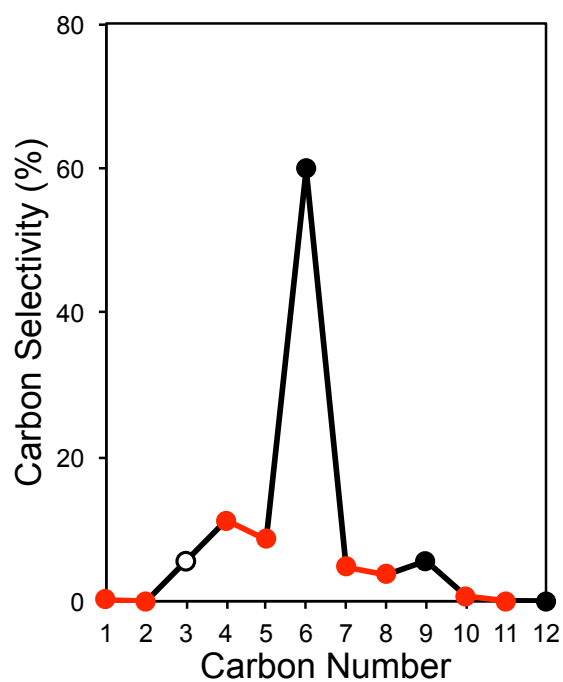


Figure 3. Carbon number selectivities of chains formed in C₃H₆ oligomerization reactions on BEA [503 K, 60 kPa, 0.4 % conversion].

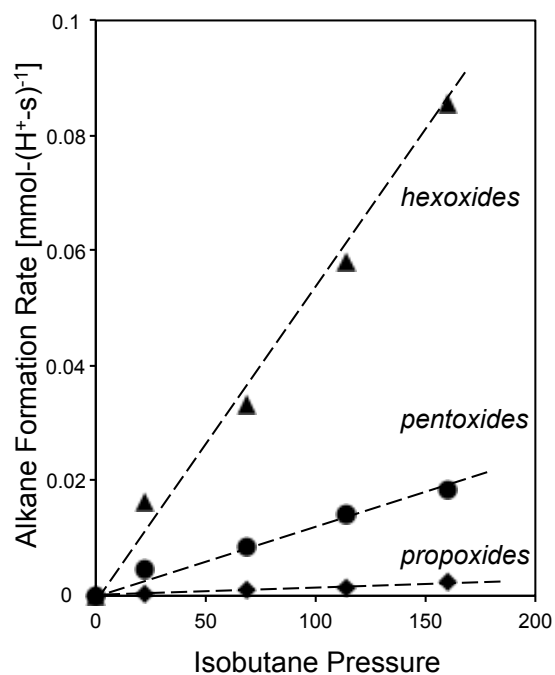


Figure 4. C6, C5 and C3 alkane formation rates from hexoxides, pentoxide and propoxides, respectively, as a function of isobutane pressure on BEA [9 kPa propene, 503 K <5 % alkene and alkane conversion].

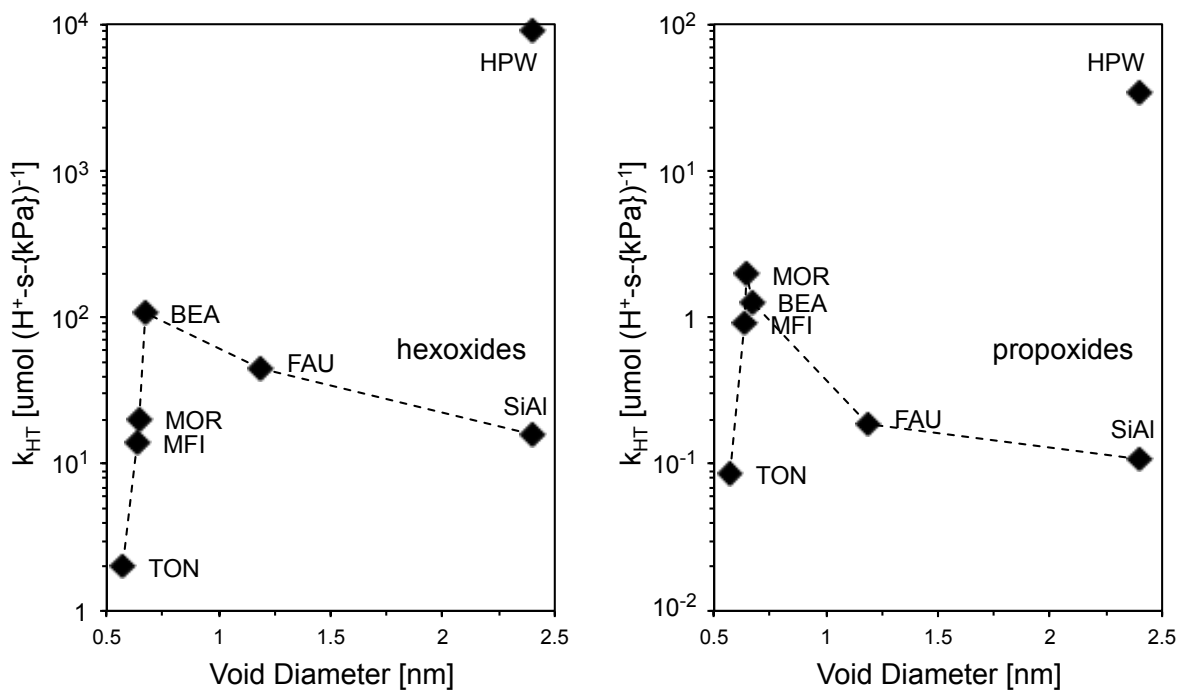


Figure 5. First-order rate constant for hexoxides (a) and propoxides (b) formation as a function of void diameter [9 kPa propene, 503 K <5 % alkene and alkane conversion].

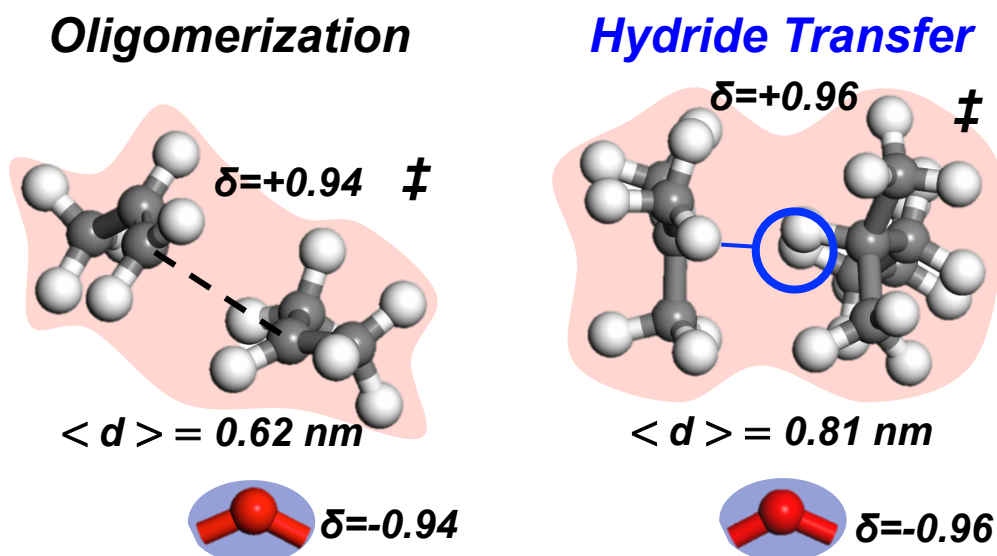


Figure 6. DFT-derived transition state structures for oligomerization (C-C bond formation between secondary propoxide and propene) and hydride transfer (isobutane and tertiary 2-methylpentoxide). Charges from QUAMBO and estimated sizes are included [HPW; PW-91].

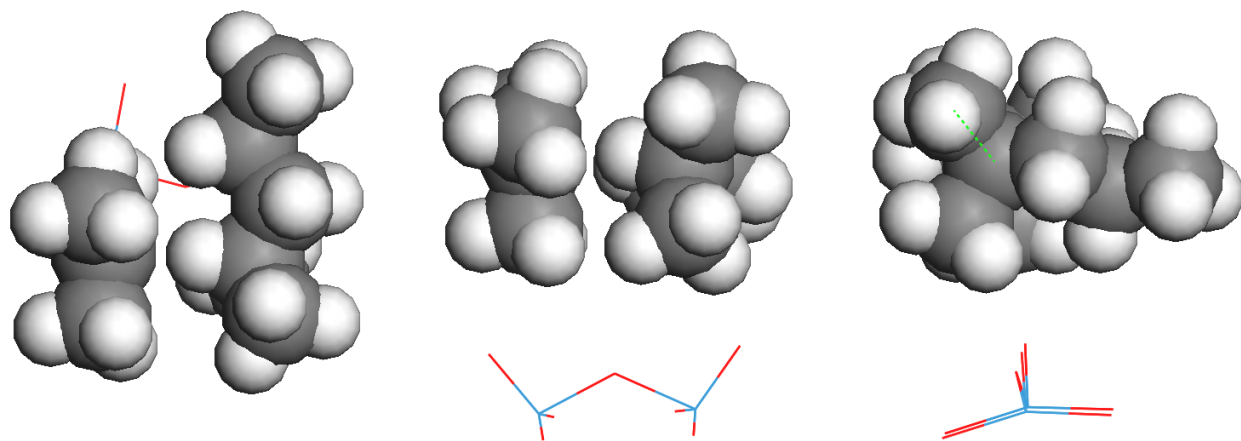


Figure 7. DFT-derived transition state structure for hydride transfer between isobutane and tertiary 2-methylpentoxide [HPW; PW-91].

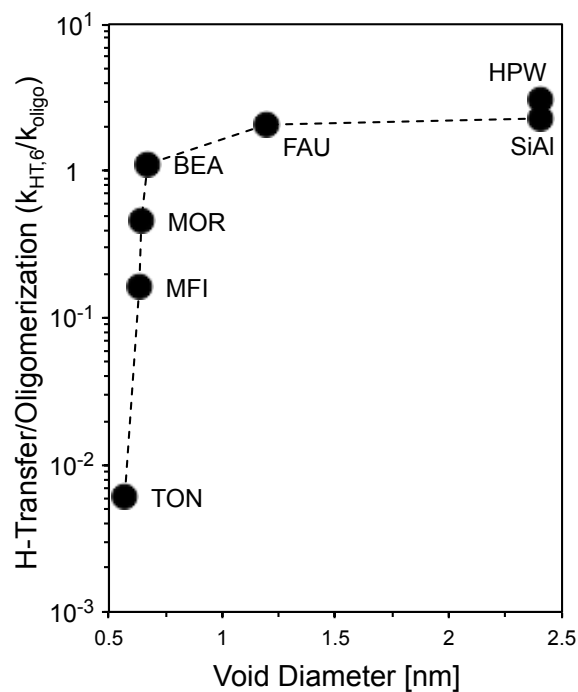
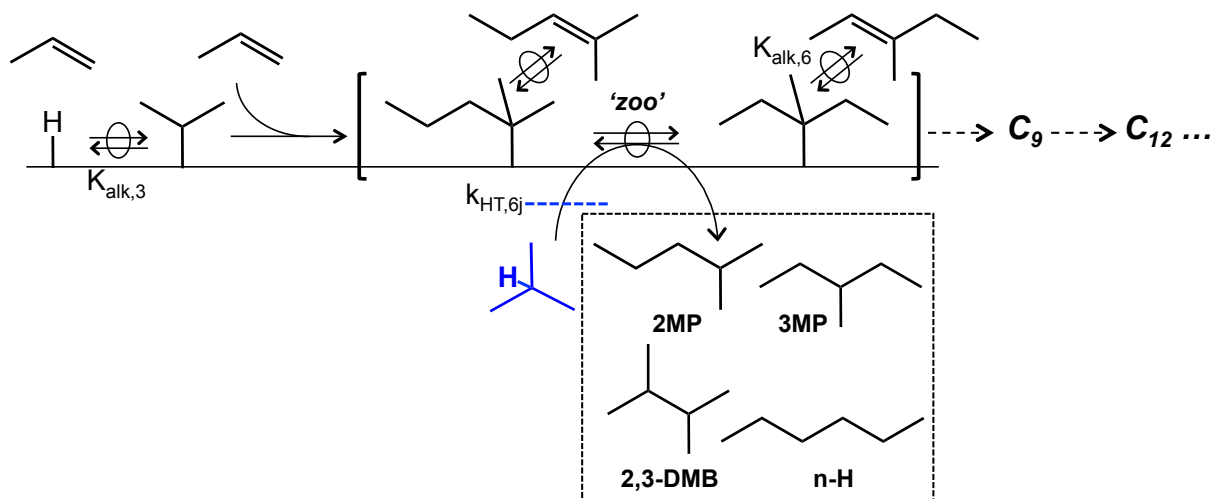


Figure 8. Hydride transfer to oligomerization selectivity (ratios of rate constants) as a function of void diameter [9 kPa propene, 503 K <5 % alkene and alkane conversion].



Scheme 2. Alkane incorporation into equilibrated isomer pools.

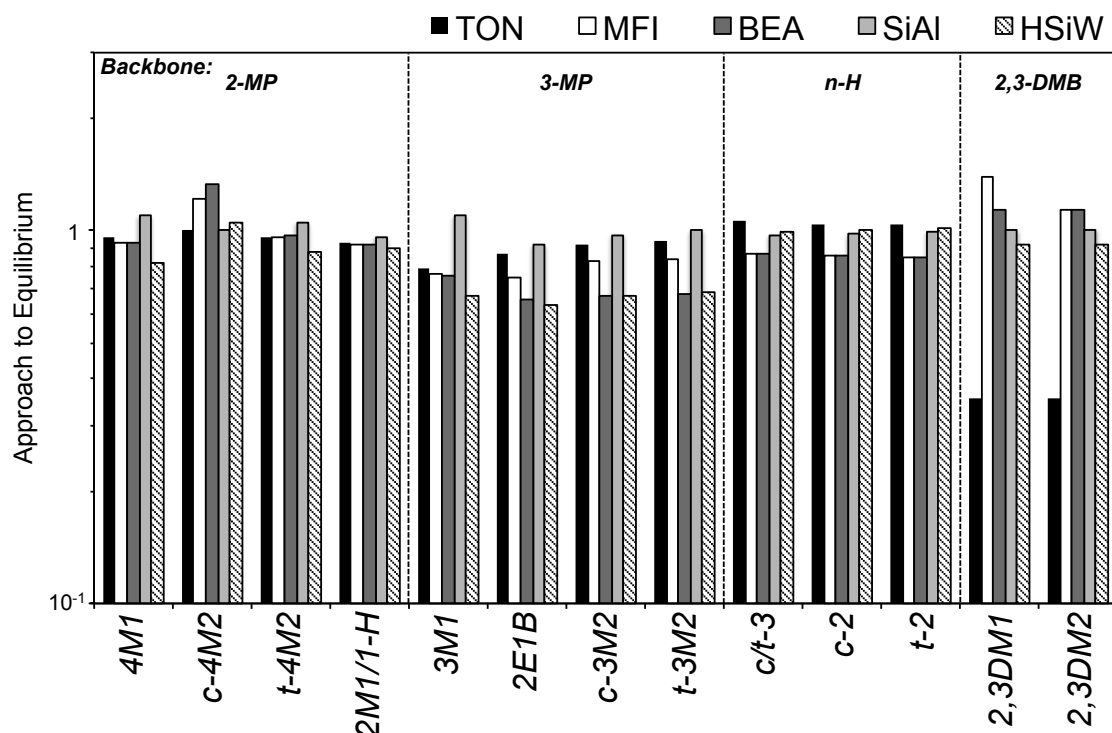


Figure 9. Approach to equilibrium for the formation of hexene isomers with respect to 2-methyl-2-pentene on the samples tested with their fractional conversions given: TON (0.005), MFI (0.009), BEA (0.004), SiAl (0.005) and HSiW (0.003) using calculated equilibrium constants for SiAl at a fractional conversion of 0.14. [503 K, 60 kPa]. Isomers are separated according to their backbone structures 2-methylpentene (2-MP), 3-methylpentene (3-MP), linear (n-H) and 2,3-dimethylbutene (2,3-DMB).

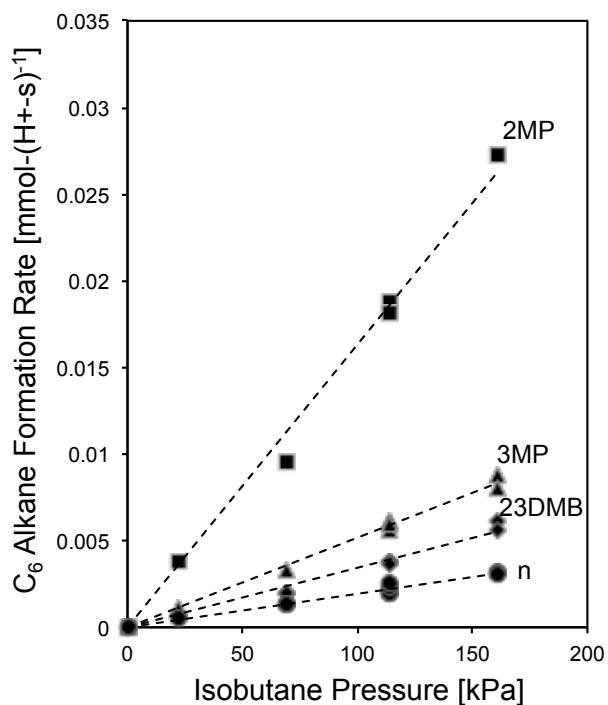


Figure 10. Formation rates of 2MP (squares), 3MP (triangles), 23DMB (diamonds) and n-hexane (circles) as a function of isobutane pressure on BEA [9 kPa propene, 503 K <5 % alkene and alkane conversion].

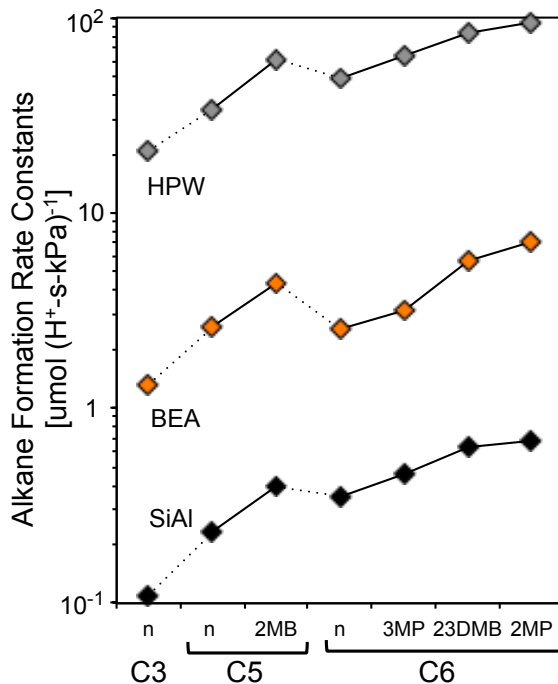


Figure 11. First-order rate constant for alkane formation from hydride transfer between isobutane and propoxide or all skeletal isomers of pentoxides and hexoxides on BEA, HPW and SiAl [9 kPa propene, 503 K <5 % alkene and alkane conversion].

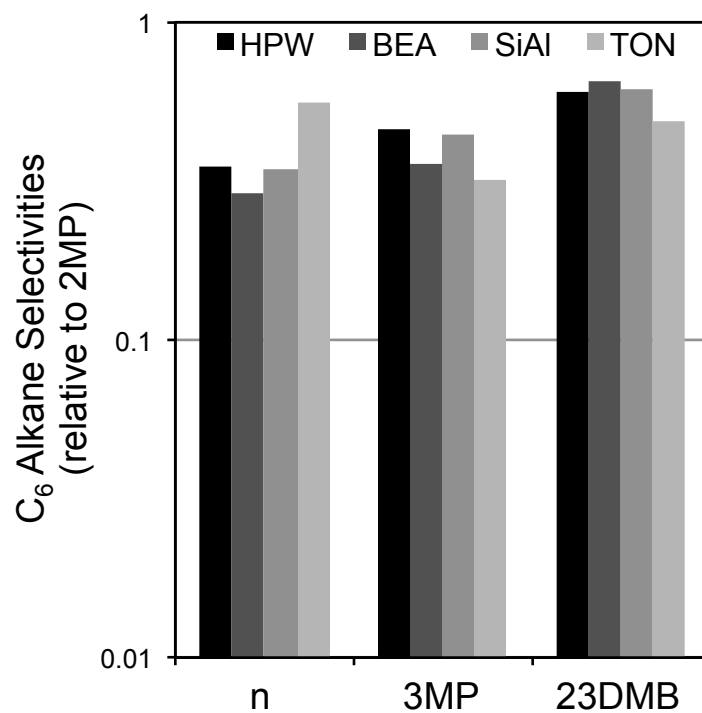


Figure 12. C₆ isomer alkane formation selectivities (rate constant ratios relative to 2MP) on HPW, BEA SiAl and TON [9 kPa propene, 503 K <5 % alkene and alkane conversion].

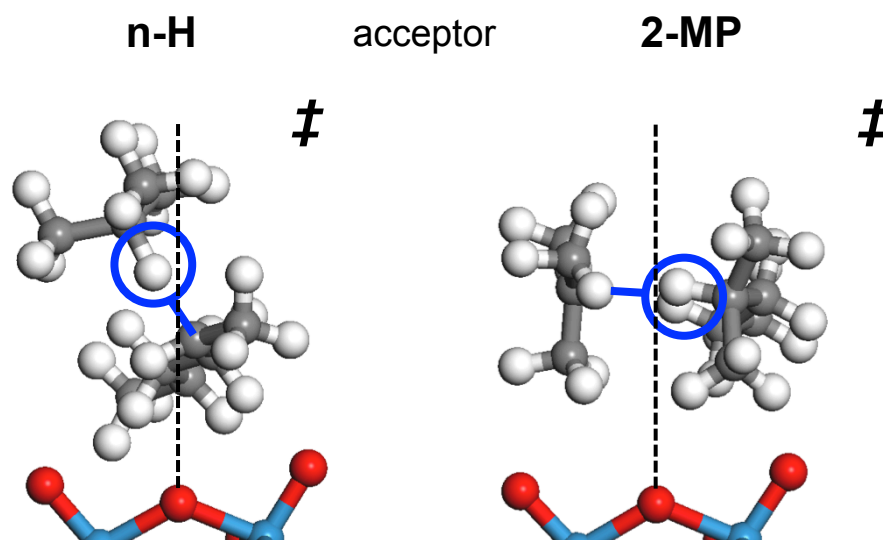
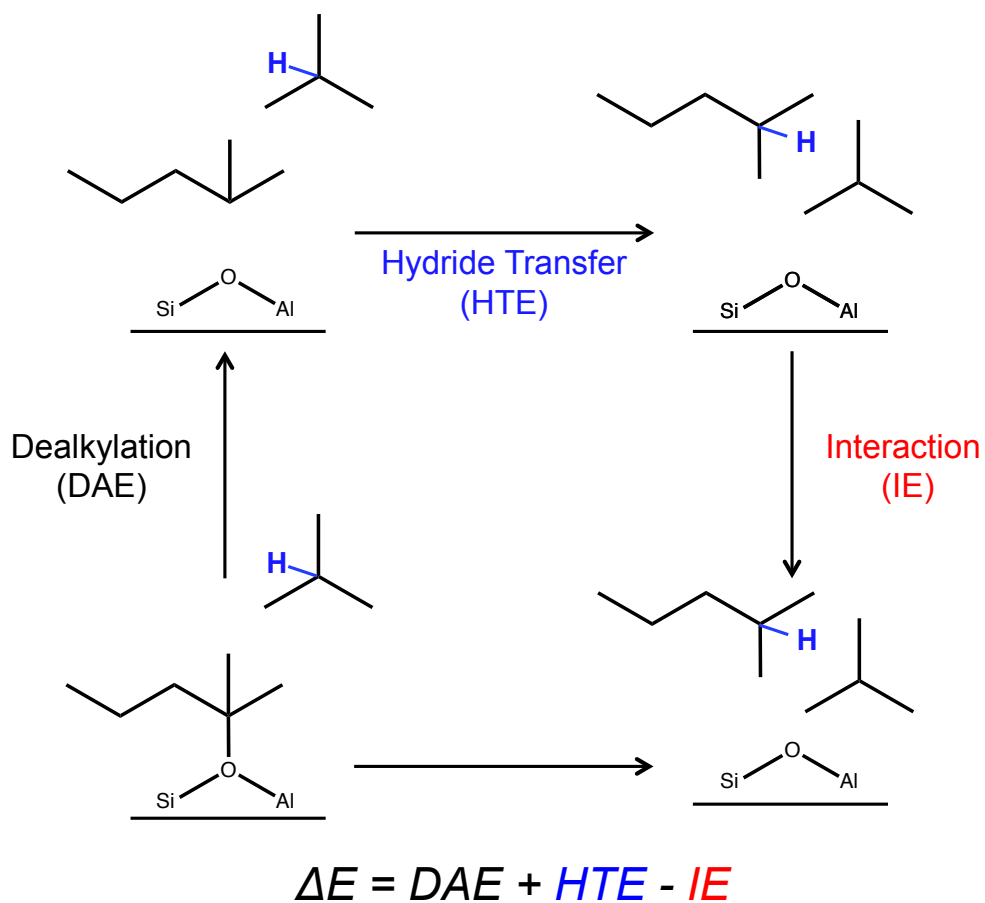


Figure 13. DFT-derived transition state structures for hydride transfer between isobutane and secondary hexoxide (left) or tertiary 2-methylpentoxide (right).



Scheme 3. Thermochemical cycle for hydride transfer between isobutane and tertiary 2-methylpentoxide in terms of dealkylation energy (DAE), hydride transfer energy (HTE) and interaction energy (IE).

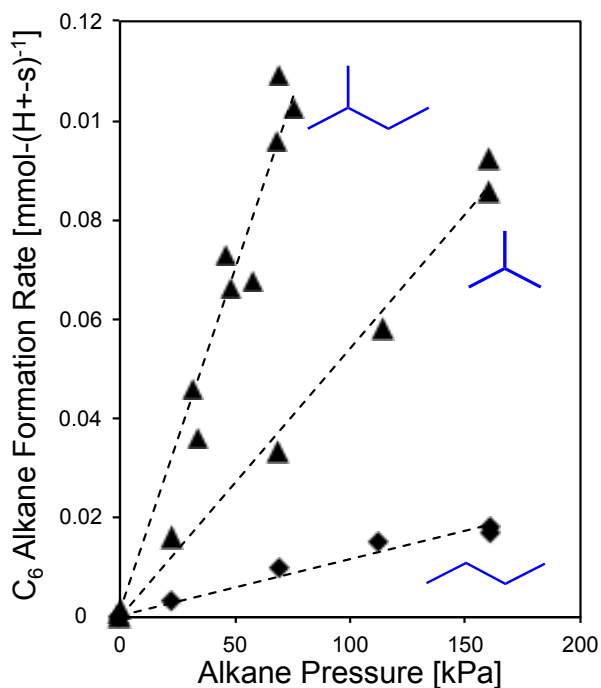


Figure 14. C6 alkane formation rates from hydride transfer between hexoxides and 2-methylbutane, isobutane or n-butane as a function of alkane pressure on BEA [9 kPa propene, 503 K <5 % alkene and alkane conversion].

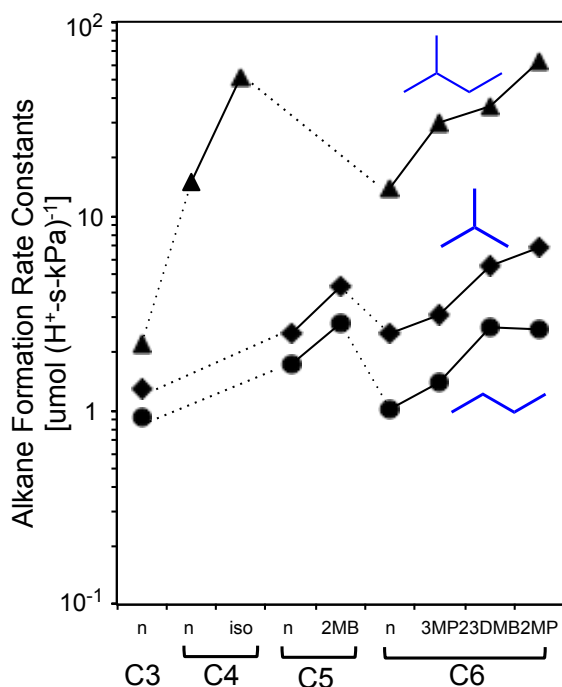


Figure 15. First-order rate constant for alkane formation from hydride transfer between 2-methylbutane, isobutane or n-butane and propoxide or all skeletal isomers of pentoxides and hexoxides on BEA [9 kPa propene, 503 K <5 % alkene and alkane conversion].

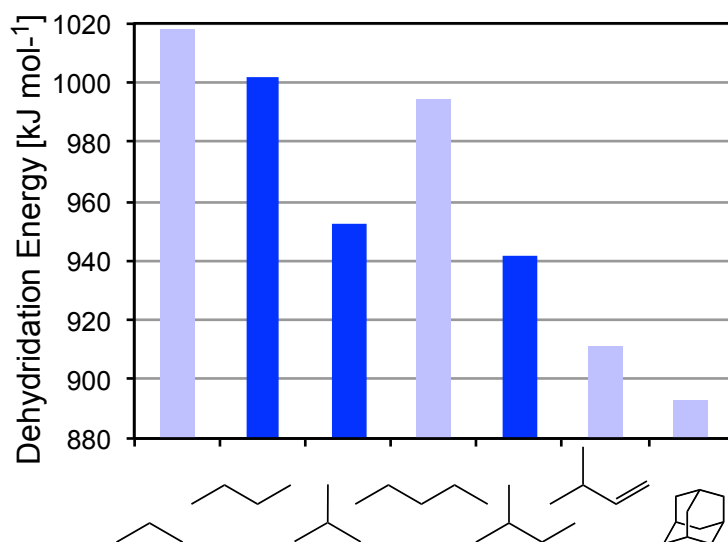


Figure 16. DFT-derived dehydrodation energies (Eq. x) for various hydrocarbons.

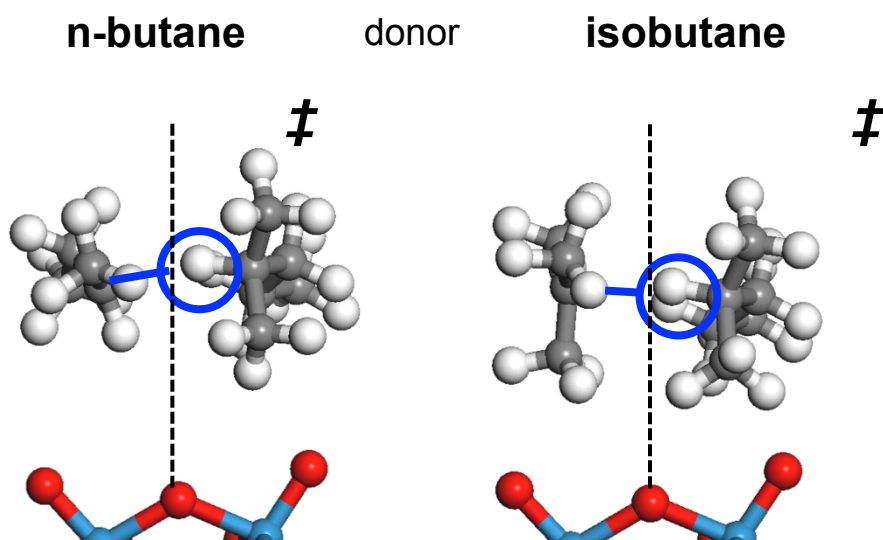


Figure 17. DFT-derived transition state structures for hydride transfer between n-butane (left) or isobutane (right) and tertiary 2-methylpentoxide.

5.6. Supplemental Information

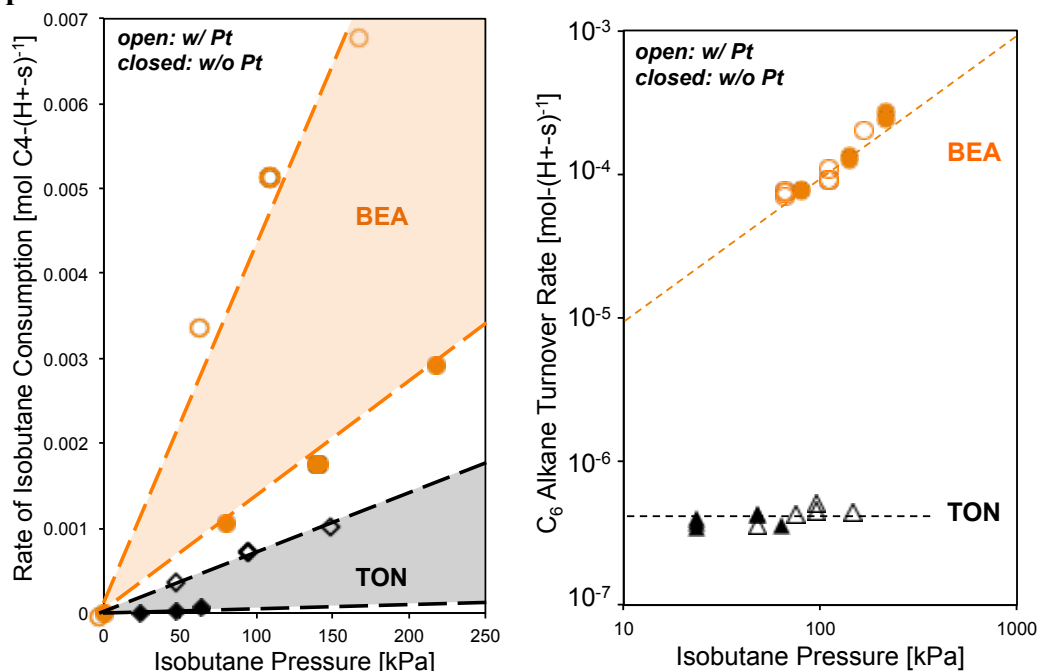


Figure S1. Isobutane consumption (a) and C_6 alkane formation (b) rates as a function of isobutane pressure with (open data points) and without (closed data points) Pt/SiO_2 physically mixed with BEA (circles) and TON (diamonds) [503 K, 60 kPa].

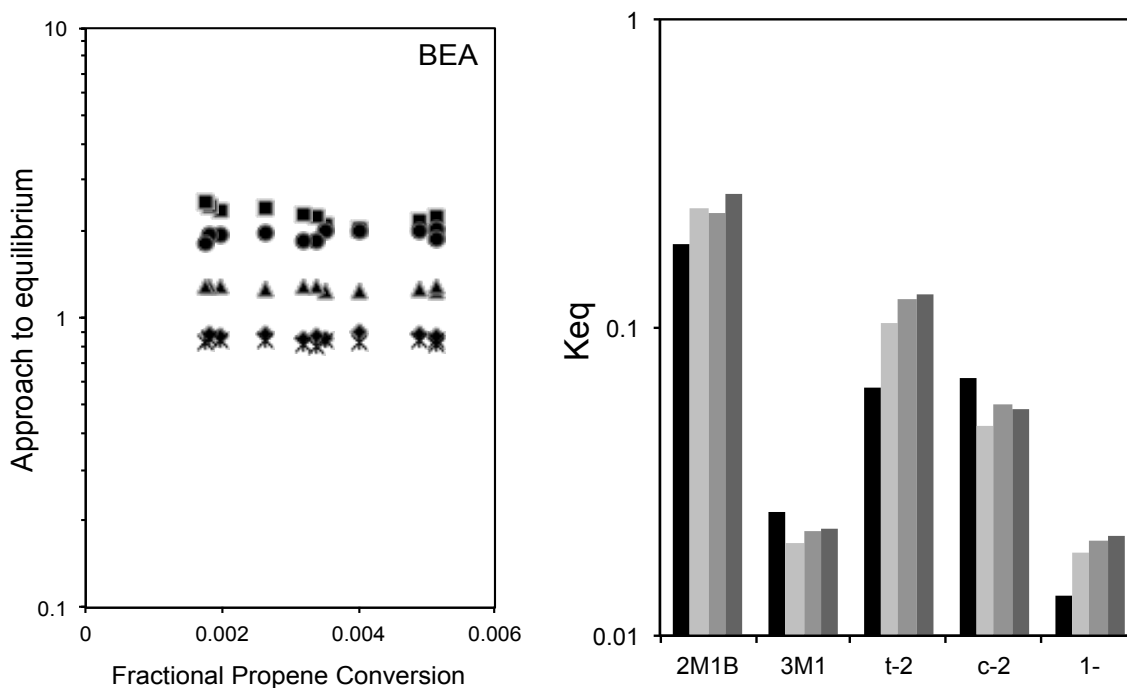


Figure S2. A: Approach to equilibrium for the formation of pentene isomers with respect to 2-methyl-2-butene on BEA using tabulated data from [25] [503 K, 60 kPa]. Values are not unity but are independent of conversion. **B:** Calculated equilibrium constants for the isomerization of 2-methyl-2-butene to other pentene isomers (2-methyl-1-butene, 3-methyl-1-butene, t-2-pentene, c-2-pentene, and 1-pentene).

c-2-pentene, 1-pentene) at 503 K, 60 kPa C₃H₆ on SiAl, BEA and TON (with increasing gray darkness, respectively). Tabulated values from [20] are shown in black.

5.7. References

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