

Effects of Void Environment and Acid Strength on Alkene Oligomerization Selectivity

Michele L. Sarazen,[†] Eric Doskocil,[‡] and Enrique Iglesia^{*,†}

[†]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, United States [‡]BP Products North America Inc., 150 West Warrenville Rd., Naperville, Illinois 60563, United States

Supporting Information

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 conversion (ethene, propene, isobutene; 2–400 kPa alkene; 473–533 K) were examined on microporous (TON, MFI, MOR, BEA, FAU) and mesoporous (amorphous silica–alumina (SiAl), MCM-41, Keggin POM) Brønsted acids with a broad range of confining voids and acid strength. Skeletal and regioisomers equilibrate under all conditions of pressure and conversion and on all catalysts, irrespective of their acid strength, void size, or framework connectivity, consistent with rapid



hydride and methyl shifts of alkoxides intermediates and with their fast adsorption-desorption steps. Such equilibration is evident from detailed chemical speciation of the products and also from intramolecular isotopic scrambling in all oligomers formed from 2-13C-propene on TON, MFI, SiAl, and POM clusters. Previous claims of kinetic control of skeletal isomers in oligomerization catalysis through shape-selective effects conferred by void environments may have used inaccurate tabulated thermodynamics, as we show in this study. The void environment, however, influences the size distribution of the chains formed in these acid-catalyzed alkene reactions. One-dimensional microporous aluminosilicates predominantly form true oligomers, those expected from dimerization and subsequent oligomerization events for a given reactant alkene; such chains are preserved because they cannot grow to sizes that would inhibit their diffusion through essentially cylindrical channels in these frameworks. Amorphous SiAl and colloidal silica-supported POM clusters contain acid sites of very different strength; both exhibit size variations across the void space, but at length scales much larger than molecular diameters, thus preserving true oligomers by allowing them to egress the void before β -scission events. Mesoporous acids of very different strength (POM, SiAl) give similar true isomer selectivities, as also observed on MFI structures with different heteroatoms (X-MFI, where X = AI, Ga, Fe, B), which also differ in acid strength; this insensitivity reflects oligomerization and β -scission reactions that involve similar ion-pair transition states and therefore depend similarly on the stability of the conjugate anion. Three-dimensional microporous frameworks contain voids larger than their interconnecting paths, an inherent consequence of intersecting channels and cagewindow structures. As a result, oligomers can reach sizes that restrict their diffusion through the interconnections, until β -scission events form smaller and faster diffusing chains. These undulations are of molecular dimensions and their magnitude, which is defined here as the ratio of the largest scale to the smallest scale along intracrystal diffusion paths, determines the extent to which oligomerization-scission cycles contribute to the size distribution of products. These contributions are evident in the extent to which chain size and the number of ¹³C atoms in each molecule formed from 2-¹³C-propene approach their binomial distributions, as they do on microporous acids with significant undulations. The general nature of these conclusions is evident from the similar effects of void shape and connectivity and of acid strength on selectivity for ethene, propene, and isobutene reactants

KEYWORDS: oligomerization, β -scission, skeletal isomerization, zeolites, Brønsted acid catalysis

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

Received: July 27, 2016 Revised: September 2, 2016 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 have a tendency 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 , where n = 2, 3, 4; pressure (P), 2-400 kPa; temperature (T), 473-533 K) 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 data reported here, taken at very low conversions, preclude the effects of deactivation, which occurs predominantly through the binding of larger oligomers, formed via subsequent alkene addition steps to growing chains. The detailed chemical speciation of the isomers formed and the rate of intramolecular scrambling of ¹³C atoms within the oligomers derived from 2-13C-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, despite their large differences in reactivity, void structure, proton density, and acid strength. Such distributions are not dependent on conversion, residence time, or 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 (1D) 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, threedimensional (3D) 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 was not dependent on acid strength, irrespective of whether active protons reside within mesoporous voids (POM, MCM-41/SiAl) or in MFI microporous channels (X-MFI, where X = AI, Ga, Fe, B). The acid strength of 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 the acid's 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 are dependent 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 products, 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, which is a conclusion that required the systematic reconsideration of previously reported formation Gibbs free energies for hexene isomers.

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

Table 1. Framework Structure, Source, Si/Al Ratio, and
Proton Counts for the Solid Acids Used in This Study

acid	source	Si/Al ratio ^a H	$^{+}/Al$ (H $^{+}/u.c.$) ratio
BEA	Zeolyst	11.8	$0.40 (2.0)^{b}$
MFI	Zeolyst	16.6	$0.65 (3.6)^{b}$
MFI	Zeolyst	29.2	$0.78(2.5)^{b}$
MFI	Zeolyst	43.8	$1.0(2.1)^{b}$
MFI	Zeolyst	173	$0.64 (0.36)^{b}$
MFI	Sud-Chemie	14	$0.71 (4.3)^{b}$
MFI	Tri-Cat	25	$0.35 (1.3)^{b}$
MOR	Zeolyst	10	$0.86 (2.9)^{b}$
TON	BP	39	$0.55 (0.36)^{b}$
TON	BP	49	$0.50 (0.26)^{b}$
TON	BP	24	$0.38 (0.40)^{b}$
FAU	Engelhard	7.5	$0.37 (8.5)^{b}$
silica—alumina	Sigma—Aldrich	5.5	0.25 ^c
Al-MCM-41	Sigma—Aldrich	39	0.3 ^c
acid	source	Si/T ratio ^a	H ⁺ /T ratio ^b
Ga-MFI	BP	45	0.86 (1.8)
B-MFI	BP	43	0.77 (1.7)
Fe-MFI	ref 14	61	0.85 (1.3)
	POM content on silica (wt %)	POM surface dens (POM nm ⁻²)	ity protons (H ⁺ /POM) ^c
$H_{3}PW_{12}O_{40}$	5	0.03	2.5
$H_4SiW_{12}O_{40}$	5	0.03	1.9
^a From elemental analysis (ICP-OES; Galbraith Laboratories). ^b From decomposition of NH_4^+ exchanged sample. ^c From 2.6-di- <i>tert</i> -			

butylpyridine titration.

with NH_4 cations, using procedures described elsewhere. 12 The number of protons in each sample was measured from the amount of NH₃ evolved upon heating NH₄⁺-exchanged samples. Transmission electron microscopy (TEM) images were taken on a Philips/FEI Tecnai 12 microscope operated at 120 kV for crystal size estimates by suspending the samples 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 m² g⁻¹; pore volume, 1.5 cm³ g⁻¹). The number of protons in Keggin POM clusters and mesoporous aluminosilicates (MCM-41, SiAl) was determined from the amount of a noncoordinating titrant (2,6-di-tert-butylpyridine) required to fully suppress rates during 2-methylpentane isomerization¹³ 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 μ m aggregates before use in catalytic experiments.

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 was set by a backpressure regulator (Tempresco). NH_4^+ -zeolites and mesoporous aluminosilicates were treated in 5% O₂ in helium (83.3 cm³ g⁻¹ s⁻¹, Praxair) by heating to 818 K (at a rate of 0.025 K s⁻¹) and holding for 3 h to convert NH_4^+ cations to H⁺ and then cooled to reaction temperature. Supported Keggin POM clusters in their H-form were treated in flowing helium (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 helium 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, Model 6890). Reactant and product concentrations were measured by flame ionization detection after chromatographic separation (methyl silicone Agilent HP-1 column, 50 m \times 0.32 mm \times 1.05 μ m); 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, Models 7890 A and 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. 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 the 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 that were the same as true oligomers (see eq 1):

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

where $[C_{m:n,t}]$ is the total molar concentration of product with m·n carbons formed from a reactant with n carbons and $[C_{m:n,b}]$ is the molar concentration of species with m·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·n carbons that have not undergone β -scission ($[C_{m:n}]$) were used to calculate a true oligomer selectivity parameter that is defined by the following expression:

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

2.3. Mechanistic Provenance of Oligomerization Products and Their Intramolecular ¹³-C Scrambling in Oligomerization Products of 2-¹³C-Propene. Kinetic and isotopic tracer experiments were carried out in a glass batch reactor,¹⁷ the contents of which were recirculated using an oilfree graphite gear micropump (GA V23, Micropump). Gas samples were extracted from the recirculating stream using a sampling valve and transferred through heated lines (>373 K) into a gas chromatograph equipped with flame ionization and mass spectrometric detectors (Agilent, Models 7890 A and 5975C), each connected to a capillary column (HP-1, methyl silicone, 50 m × 0.32 mm × 1.05 μ m film) to determine the chemical and isotopic composition of the reactor contents.

¹³C-labeled propene (2-¹³C-propene, 99 at. % ¹³C, Sigma-Aldrich) was used as the reactant with helium as the balance (99.999%, Praxair). Catalysts (TON, MFI, SiAl, and HSiW) were treated as described in Section 2.1 before exposure to 2-13Cpropene. 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 the expression

$$[l^{13}C_i]_j = \left[\chi_j U_j + (1-\chi_j) \left(\frac{l!}{(l-i)!i!} (\langle f_{13_C} \rangle)^i (1-\langle f_{13_C} \rangle)^{l-i} \right)\right]$$
(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 ¹³C in the species *j* (e.g., two labels for any C₆ isomer) and $\langle f^{i_3}_C \rangle$ is the mean ¹³C fraction in species *j*, as calculated by eq 4:

$$\langle f_{^{13}\mathrm{C}}\rangle_{j} = \frac{\left[l^{13}\mathrm{C}_{j}\right]_{j}}{l} \tag{4}$$

The value of χ_j was determined by regressing the measured isotopologue distribution to the functional form of eq 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_i 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 ¹³C, because cyclopropyl carbenium ion transition states mediate methyl shifts that result in both isomerization and intramolecular exchange among C atoms. The amount of ¹³C 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 ¹³C fraction at each C-position, as prescribed by eq 4. An isotopic scrambling conversion (σ) is defined here in eq 5 as a residual sum of squares:

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

where f_k is the measured ¹³C fraction at position k, f_{expected} is the ¹³C fraction at each position expected without intramolecular scrambling for each distinct chemical isomer, and $\langle f_{^{13}\text{C}} \rangle$ is the ¹³C 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 2-¹³C-propene oligomerization would lead to ¹³C atoms at the 2 and 4 positions and ¹²C 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 analogues, formed via dehydrogenation of 1^{-13} C-hexane on Pt/Al₂O₃ into the spectrometer chamber. The Pt/Al₂O₃ sample (1.5 wt %)¹³ 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).

2.4. Thermodynamics of Hexene Isomer Interconversions. The approach to equilibrium (η) for the formation of each C₆ chemical isomer (j) from 2-methyl-2-pentene (2M2P), chosen here as reference, is given by

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

Here, $K_{2M2P\leftrightarrow j}$ is the equilibrium constant for 2-methyl-2pentene conversion to the hexene isomer *j*, 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.

3. RESULTS AND DISCUSSION

3.1. Hydride and Methyl Shifts Reactions in Alkoxides Formed Via C₃H₆ 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: 2methylpentenes (2-MP), 3-methylpentenes (3-MP), linear hexenes (n-H) and 2,3-dimethylbutenes (2,3-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.¹³ The concentrations of each chemical isomer (relative to 2methyl-2-pentene (2M2P)) did not vary with C_3H_6 conversion as it changed with residence time (see Figure S1 in the Supporting Information (SI)), except for 2,3-DMB, which is one of the slowest diffusing skeletal isomers, in TON, which is the catalyst with the smallest channels; these concentration ratios also did not vary with changes in reactant pressure (25-400 kPa C_3H_6 in Figure S2 in the SI). However, these invariant approaches to equilibrium parameters $(\eta, eq 1)$ for all isomers

were neither 0 nor 1 (see Figure S3 in the SI) when estimated using reported thermodynamic data^{19,20} and the deviation from 1 did not improve systematically with temperature (over a range of 473–533 K, using data from ref 20; see Figure S4 in the 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 were tabulated from such data in Figure S15 in the SI; ΔG_{eq} values were tabulated from Figure S5 in the 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;¹³ this explanation is also at odds with the similar distributions observed on solid acids with very different acid strength and confining environments (see Figure S6 in the SI).

These arguments, taken together with the aforementioned inconsistencies among reported thermodynamic data, led us to reconsider the accuracy of tabulated free energies and, instead, use 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 (see Figure 1); these



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 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). Data for BEA and HSiW are found in Figure S2 in the SI).

 η values are near unity, even at propene fractional conversions of <0.05 and all temperatures, pressures, and conversions. We conclude from these data that hydride and methyl shifts are fast in C₆ oligomers and that the concentration of all isomers with a given carbon number is dependent only on their thermodynamics properties as gaseous species, even at very low conversions and modest temperatures (see Figure 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 Figure S7 in the SI) at all propene fractional conversions (0.02–0.8; Figure S8 in the SI) and all alkene

pressures (2–500 kPa C₃H₆); similar conclusions are reached for C₄ and C₅ chains, which is indicative of their significant isomerization after they form via secondary β -scission of primary (C₆) or secondary (C₉, C₁₂, ...) oligomerization products (for C₅, see Figures S9 and S10 in the SI).

Isomers with 2,3-DMB backbones are also present at nearequilibrium levels on all solid acids, except TON; this appears to reflect the small 1D 10-MR channels in TON (0.46 nm × 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 2methylhexane or 3-methylhexane in TON (10-fold larger diffusivities at 600 K).²³ These 2,3-DMB isomers approach their equilibrium concentrations on TON as the H⁺ densities increase (0.10 and 0.32 η values for 2,3-DM1B for 0.26 H⁺/u.c. (0.017 fractional conversion) and 0.36 $H^+/u.c.$ (0.011 fractional conversion), respectively) and as conversion increases with increasing residence time (0.22 to 0.93 for 0.01 and 0.42 fractional conversion on 0.36 H⁺/u.c. TON) (details are given in Figures S8 and S11 in the SI). These site density and conversion effects for 2,3-DMB isomers suggest that their lower η values are likely to reflect their local equilibration within TON crystals and 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 C_6 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.^{13,24} 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; Figure 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) (see Figure 3). The ¹³C-content in each C atom cannot be individually determined for some groupings of C atoms (denoted by the ovals in Figure 3), but the combined isotopic content in each grouping is consistent with fast intramolecular scrambling. Isotopic scrambling conversions $(\sigma, eq 5)$ 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; see Figure 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



Figure 2. ¹³C isotopologue distributions for the parent and the pentyl, butyl, and propyl fragment ions of 2M2P was formed on TON [0.08 C_3H_6 fractional conversion, 2 kPa 2-¹³C-propene, 503 K]. Average number of ¹³C atoms and fractional amount per carbon are shown in the brackets, respectively for each ion. The expected binomial distribution for the total ¹³C content of each ion is indicated by light gray bars.



Figure 3. ¹³C atom locations for the initial skeletal and regioisomers product formed (2M2P) and for a representative species formed from each type of isomerization event (trans-4M2P, trans-2-H, trans-3M2P, 23DM2B) on TON [0.08 C_3H_6 fractional conversion, 2 kPa 2-¹³C-propene, 503 K]. The two dots on 2M2P indicate the label positions if no scrambling had occurred. The dotted sections indicate fragments that cannot be distinguished because of symmetry and for which only their combined ¹³C content can be measured from the analysis of the mass fragmentation patterns.

also indicate that the observed deviations from chemical equilibrium for the bulkier 2,3-DMB isomers on TON (see Figures 1, as well as Figures S3 and S4) must reflect diffusional constraints instead of intrinsic kinetic hurdles.

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



Figure 4. Isotopic scrambling conversion (σ ; eq 6) for hexene isomers (\blacklozenge) 2M2P, (*) trans-4M2P, (\blacklozenge) trans-2-H, (\blacksquare) trans-3M2P, and (\blacktriangle) 2,3-DM2B on TON, SiAl, MFI, and HSiW [2 kPa 2-¹³C-propene, 503 K].

analogues (formed via dehydrogenation of 1^{-13} C-hexane on Pt/ Al₂O₃; 0.35 fractional conversion; 0.4 kPa 1^{-13} C-hexane; 573 K) led to pentyl and butyl fragments with isotopic contents consistent with unscrambled 1^{-13} C-hexane and 1^{-13} C-t-3-hexene molecules (0.51–0.56; see Table S1 in the SI), indicating that neither alkanes nor alkenes significantly 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 (see Figure S12 in the SI).

These data, taken together with the equilibrium isomer distributions derived from chemical speciation, are consistent with fast interconversions among isomers under 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 (see Figures 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 led 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 instead reflect 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.

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 ($l = m \cdot n$; $C_6^{=}$, $C_9^{=}$, $C_{12}^{=}$, ... for n = 3); these isomers can undergo secondary β -scission to form chains of intermediate chain length ($l \neq m \cdot n$; $C_4^{=}$, $C_5^{=}$, $C_7^{=}$, $C_8^{=}$, ... for n = 3) (see Scheme 1). Figure 5 shows the fraction of the C atoms in the

Scheme 1. C_3H_6 Oligomerization–Cracking Reaction Network on Solid Acids^{*a*}



 ${}^{a}C_{l}*$ represents alkoxides of *l* carbons that are equilibrated with their gas-phase concentrations by K_{b} and k_{oligo} is the rate constant for oligomerization.

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) (Figures 5a–d) and on BEA, MFI, and FAU (see Figures 5e–g). The products formed are predominantly alkenes, with only trace concentrations of small alkanes ($n \le 6$; < 2.5% C atoms), which form via H-transfer from larger alkenes to alkoxides (see Scheme 1) together with dienes and cycloalkenes coproducts that become detectable only at higher propene conversions (see Figure S13 in the SI; <0.2% C atoms of products).

The different carbon number distributions observed on different solid acids (Figure 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, which is consistent with the absence of ethene or methane in products (Figure 5) and the information provided by ref 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 a true oligomer $(l = m \cdot n)$. For example, the ratio of B-scission to formation rates for C₆ alkenes is given by

$$\frac{r_{\beta,6}}{r_{\text{oligo},6}} = \frac{k_{\beta,6}K_6P_6}{k_{\text{oligo},3}K_3(P_3)^2}$$
(7)

where K_l is the equilibrium constant for alkoxide formation with l C atoms, $k_{\text{oligo},3}$ is the rate constant for formation of C₆ oligomers, and P_l is the pressure of an alkene with l C atoms. In order to account for all products, eq 7 must be summed over all carbon numbers (eq 8):

$$\frac{r_{\beta}}{r_{\text{oligo}}} = \frac{\sum_{l=6} k_{\beta,l} K_l P_l}{\sum_{m=1} k_{\text{oligo},m} K_{3m} P_3 P_{3m}}$$
(8)



Figure 5. Carbon selectivities for chains in *l* number of carbon atoms formed in C_3H_6 oligomerization reactions (propene fractional conversions are 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].

where $k_{\text{oligo},m}$ 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 eq 8 by the expression

$$\chi = 1 - \frac{r_{\beta}}{r_{\text{oligo}}} \tag{9}$$

*

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 as the propene conversion increases (Figure 6).



Figure 6. True oligomer selectivity (χ ; eq 2) for C₃H₆ oligomerization as a function of propene fractional conversion for (a) zeolites ((\blacklozenge) TON, (\blacklozenge) MOR, (\blacksquare) BEA, (\blacklozenge) MFI and (*) FAU) and (b) mesoporous acids ((\blacksquare) MCM-41, (\blacklozenge) SiAl, (\blacklozenge) HPW, and (\blacktriangle) HSiW) [at 60 kPa, 503 K; dashed lines serve to guide the eye].

However, the χ values increase as the propene pressure increases for samples that do not have χ values of unity, consistent with eqs 7–9 (conversion range 0.02–0.04; see Figure S14 in the SI).

The formation of C4 and C5 products from propene (and others with $l \neq m$ ·3 C atoms) provide direct evidence of the occurrence of β -scission events. However, β -scission in larger species 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; see Figure 7). The contribution from this distribution is much greater in 3-D zeolites (MFI, BEA, FAU) than other acids (Figures 5 and 7) and it becomes increasingly binomial with increasing conversion, indicating that fewer of the observed oligomers are, in fact, "true oligomers". The use of 2-13C-propene can also rigorously quantify the fraction of "true oligomers" in the products. The intervening intramolecular ¹³C scrambling that occurs with oligomerization- β -scission events (Section 3.2) leads to a binomial distribution in the number of ¹³C atoms in a product formed from cleaving of a fully intramolecularly scrambled species. For example, each C₆ formed from 2-13C-propene dimerization contains two 13C atoms (Figure 8a; e.g., 2M2P on TON at low conversions (dark gray)). Isotopologues of C_6 isomers with more and less than two ¹³C atoms start to appear as conversion increases (for both TON and MFI; see light gray bars in Figures 8a and 8b). 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 (C₄⁼ and C₅⁼; see Figure S12).

The isotopologue distributions shown in Figure 8 indicate that the fraction of 2M2P isomers that leave before β -scission (χ_{2M2P} ; see eq 3) is smaller on MFI than TON. In fact, both chemical



Figure 7. Carbon selectivity for C_3H_6 oligomerization on MFI and TON at either low C_3H_6 fractional conversion (0.012 and 0.03, respectively; top) or high C_3H_6 fractional conversion (0.45 and 0.49, respectively; bottom) with nonoligomer products fit to a binomial distribution (dashed line) [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 (a) TON at low fractional conversion (0.03; dark gray) and high fractional conversion (0.49; light gray) and on (b) MFI at low (0.01; dark gray) and high fractional conversion (0.45; light gray) [2 kPa 2-¹³C-propene, 503 K].

speciation and isotopic labeling experiments show that MFI samples give smaller χ values and more binomial-like chain length distributions (see Figures 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.

3.4. Selectivity of Oligomerization to 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 aluminosilicate frameworks. The data in Figure 6 suggest that 1D zeolites, with channels of uniform cross section, and mesoporous solids, with channels significantly larger than the oligomers formed, lead to higher χ values than 3D zeolites at all conversions; 3D 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 framework²⁸ 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 (3D, 10-MR channels), FAU (3D cages with 12-MR windows), and BEA (3D, 12-MR channels); Figure 9). 1D



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

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 SiO₂ 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.

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 3D 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 cagelike 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 1D MOR zeolites (Figure 10) and on all mesoporous samples (Figure 6), despite their



Figure 10. True oligomer selectivity parameter (χ) for C₃H₆ oligomerization, as a function of pore limiting diameter/largest cavity diameter (PLD/LCD), for 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 serve to guide the eye].

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 3D zeolites (MFI, BEA, FAU; see Figure 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.

The lower selectivity to β -scission over oligomerization on 1D zeolites and mesoporous samples compared with that on 3D zeolites, irrespective of channel size, is consistent with the different extent to which the number of ¹³C atoms in oligomers formed from 2-¹³C-propene approaches binomial in these samples (see Figure 8). The randomization of the number of ¹³C atoms acts as a descriptor of the number of times the C atoms in such chains must traverse an oligomerization—cracking sequence. Figure 11 shows that χ_{2M2P} values decrease as the conversion increases, but are higher on 1D TON and mesoporous acids than on MFI. The higher χ_{2M2P} value and, then, macroscopic χ for the entire distribution value (Figure 10) on MFI at low conversions (0.87 versus 0.42, respectively),



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

indicate that the products have not gone through the cycle several times and the majority of β -scission results in C₄ and C₅ products, which is consistent with Figure 7.

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 (exhibiting deprotonation energies (DPE) of 1085 kJ mol⁻¹ for H₃PW₁₂O₄₀ vs 1190–1222 kJ mol⁻¹ for aluminosilicates).^{14,32} 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



Figure 12. True oligomer selectivity (χ) for C_3H_6 oligomerization, as a function of deprotonation energy (DPE)³² (given in units of kJ mol⁻¹) for mesoporous samples: HPW, HSiW, MCM-41 and SiAl at different fractional conversion: (\blacklozenge) 0.002–0.004, (\blacksquare) 0.009–0.01, and (\blacktriangle) 0.04–0.05 [503 K, 58 kPa C_3H_6].

transition states;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 (eqs 7–9).

Such effects can also be probed using X-MFI zeolites with different isomorphously substituted heteroatoms (X = Al³⁺, Ga³⁺, Fe³⁺, B³⁺). These samples provide a very diverse range of acid strengths 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:

$$\Phi^2 \propto \frac{k}{D_{\rm e}} \psi \tag{10}$$

where

$$\psi = [\mathrm{H}^+]L^2 \tag{11}$$

which is proportional to the site reactivity (k), the volumetric proton density $[H^+]$, and the square of the characteristic diffusion distance (in this case, the zeolite crystal radius (L)); it also is inversely dependent 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 $(0.36-4.5 \text{ H}^+/\text{unit cell})$ are plotted against Ψ in Figure 13, where



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].

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 eq 10 and also should affect the selectivity to the extent that stronger acids impose a larger diffusive barrier.³⁴ Therefore, the muddled effects in Figure 14 are indicative of the use of an incomplete descriptor of the catalyst properties that account for the magnitude of χ .

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 (C₆) and trimers (C₉) formed from

Table 2. Values of the Diffusion Parameters for MFI and TON Zeolites

$H^+/u.c.$	$\Psi \pmod{\operatorname{H}^{+}\operatorname{nm}^{-1}}$			
MFI Framework				
4.5	7484			
3.6	9595			
2.5	4593			
2.1	3721			
1.1	5431			
0.36	808			
TON Framework				
0.4	416			
0.36	622			
0.26	121			



Figure 14. True oligomer selectivity parameter (χ) for C₃H₆ oligomerization, as a function of proton density [[H⁺]/unit cell] for MFI samples with different heteroatoms: (**■**) Al, (**▲**) Fe, (**●**) Ga, and (**♦**) B [503 K, 58 kPa C₃H₆, 0.005–0.015 fractional conversion].

propene. These selectivities indicate that the larger oligomers do not form as much in the small channels of TON, compared to the intersection void in MFI (Figure 15). However, the trimers that are formed 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.

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 (eqs 7 and 8). Figure 16 shows that these distributions in the products formed from C₂H₄ (Figures 16a and 16b) and i-C4H8 (Figures 16c and 16d) reactants differ markedly on TON and MFI, as in the case of propene reactants (Figure 5). The 1D TON framework TON allows true oligomer products (C₄, C₆ and C₈ for C₂H₄; C₈ for i-C₄H₈) to egress without significant β -scission, thus leading to χ values near unity for both reactants (see Figures 17a and 17b). In contrast, such χ values are much smaller for C₂H₄ reactions on MFI than TON at all conversions. The chain length distribution is almost binomial (Figure 16b) for C_2H_4 , as in the case of C_3H_6 reactants (see Figures 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}



Figure 15. Larger oligomer selectivity (C_9/C_6) during C_3H_6 oligomerization for (\blacktriangle) MFI and (\blacksquare) 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, because of the large difference in zeolite crystal size of the samples.



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

Isobutene reactions also gave lower χ values on MFI than TON at all conversions (Figure 17c), but χ values were larger than for C₂H₄ (Figure 17a) or C₃H₆ reactants on MFI (Figure 17b). This is due to the fact that C₈ formation from i-C₄H₈ is more facile than C₆ formation from C₃H₆ (turnover rates of alkene consumption: 0.10 mol (H⁺-s)⁻¹ vs 0.02 mol (H⁺-s)⁻¹ at 60 kPa, respectively), because it involves a more-substituted carbenium ion in the C–C bond formation transition state. This higher reactivity appears in the denominator of the expression for



Figure 17. True oligomer selectivity (χ ; eq 2) for (a) C₂H₄ oligomerization and (b) *i*-C₄H₈ oligomerization, as a function of alkene fractional conversion for zeolites ((\blacklozenge) TON and (\blacktriangle) MFI) [60 kPa, 503 K].

 χ (see eqs 8 and 9), increasing the value of the selectivity parameter. Because β -scission is the reverse of oligomerization, just at a different C–C bond, β -scission of the initial C₈ product would also be faster than that for the C_6 product, but this step is far from equilibrium; rapid isomerization of the product skeletal backbone (Sections 3.1 and 3.2) results in C_8 isomers that would have to return via less-stable carbenium ions. In this case, isomerization preserves the chain length. 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 lessstable 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.

4. CONCLUSIONS

Selectivity

True Oligomer

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 at moderate temperature (473–533 K) and a wide range of alkene pressure (2–400 kPa). 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 under all conditions and on all solid acids. While the channel network does not influence the skeletal structure of the products, it does affect the 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 (1D) zeolites and mesoporous acids (both ordered 1D compounds and colloidal three-dimensional (3D) compounds) generated γ values close to unity, indicating the products that can egress via unobstructed diffusion, irrespective of channel size or acid strength. 3D 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 microporous and mesoporous frameworks (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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02128.

Detailed data for equilibrium of isomers as a function of conversion, pressure, site density, temperature, and catalyst, and compared to multiple tabulated sources, tabulated data from isotopic experiments using 1^{-13} C-hexane, true oligomer selectivity, as a function of pressure (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: iglesia@berkeley.edu.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Tabak, S. A.; Krambeck, F. J.; Garwood, W. E. AIChE J. 1986, 32, 1526–1531.

(2) Quann, R. J.; Green, L. A.; Tabak, S. A.; Krambeck, F. J. Ind. Eng. Chem. Res. 1988, 27, 565–570.

- (3) Norton, C. J. Ind. Eng. Chem. Process Des. Dev. 1964, 3, 230–236.
- (4) Johnson, O. J. Phys. Chem. 1955, 59, 827-831.
- (5) Occelli, M. L.; Hsu, J. T.; Galaya, L. G. J. Mol. Catal. 1985, 32, 377–390.

(6) Pines, H. The Chemistry of Catalytic Hydrocarbon Conversions; Academic Press: New York, 1981; pp 1–122.

- (7) Shephard, F. E.; Rooney, J. J.; Kemball, C. J. Catal. 1962, 1, 379-388.
- (8) Biscardi, J. A.; Iglesia, E. Catal. Today 1996, 31, 207-231.
- (9) Mlinar, A. N.; Zimmerman, P. M.; Celik, F. E.; Head-Gordon, M.; Bell, A. T. J. Catal. **2012**, 288, 65–73.

(10) Bandiera, J.; Ben Taarit, Y. Appl. Catal., A 1995, 132, 157-167.

(11) Corma, A. Chem. Rev. **1995**, 95, 559–614.

- (12) Jones, A. J.; Zones, S. I.; Iglesia, E. J. Phys. Chem. C 2014, 118, 17787-17800.
- (13) Knaeble, W.; Carr, R. T.; Iglesia, E. J. Catal. 2014, 319, 283-296.
- (14) Jones, A. J.; Carr, R. T.; Zones, S. I.; Iglesia, E. J. Catal. 2014, 312, 58–68.
- (15) White, C. M.; Hackett, J.; Anderson, R. R.; Kail, S.; Spock, P. S. J. High Resolut. Chromatogr. **1992**, *15*, 105–120.

(16) Soják, L.; Addová, G.; Kubinec, R.; Kraus, A.; Hu, G. J. Chromatogr. A 2002, 947, 103–117.

- (17) Biscardi, J. A.; Iglesia, E. J. Phys. Chem. B 1998, 102, 9284-9289.
- (18) Price, G. L.; Iglesia, E. Ind. Eng. Chem. Res. 1989, 28, 839-844.
- (19) Stull, D. R., Westrum, E. F., Sinke, G. C. The Chemical Thermodynamics of Organic Compounds; John Wiley and Sons: New York, 1969.

(20) Kilpatrick, J. E.; Prosen, E. J.; Pitzer, K. S.; Rossini, F. D. J. Res. Natl. Bur. Stand. (1934). 1946, 36, 559.

- (21) Cohen, N.; Benson, S. W. Chem. Rev. 1993, 93, 2419-2438.
- (22) Baerlocher, C.; McCusker, L. Database of Zeolite Structures; available via the Internet at: http://www.iza-structure.org/databases/.
- (23) Webb, E. B.; Grest, G. S.; Mondello, M. J. Phys. Chem. B 1999, 103, 4949-4959.
- (24) Rigby, A. M.; Kramer, G. J.; vanSanten, R. A. J. Catal. 1997, 170, 1–10.
- (25) Borchers, F.; Levsen, K.; Schwarz, H.; Wesdemiotis, C.; Winkler, H. U. J. Am. Chem. Soc. **1977**, 99, 6359–6365.
- (26) Chen, C. S. H.; Bridger, R. F. J. Catal. 1996, 161, 687-693.
- (27) Weitkamp, J.; Jacobs, P. A.; Martens, J. A. Appl. Catal. 1983, 8, 123-141.
- (28) First, E. L.; Gounaris, C. E.; Wei, J.; Floudas, C. A. Phys. Chem. Chem. Phys. 2011, 13, 17339–17358.

(29) Foster, M. D.; Rivin, I.; Treacy, M. M. J.; Delgado Friedrichs, O. *Microporous Mesoporous Mater.* **2006**, *90*, 32–38.

(30) Martens, J. A.; Verrelst, W. H.; Mathys, G. M.; Brown, S. H.; Jacobs, P. A. Angew. Chem., Int. Ed. 2005, 44, 5687-5690.

- (31) Jones, A. J.; Iglesia, E. ACS Catal. 2015, 5, 5741-5755.
- (32) Macht, J.; Carr, R. T.; Iglesia, E. J. Catal. 2009, 264, 54-66.
- (33) Mazar, M. N.; Al-Hashimi, S.; Cococcioni, M.; Bhan, A. J. Phys.
- Chem. C 2013, 117, 23609–23620.
- (34) Knaeble, W.; Iglesia, E. J. Catal. DOI: 10.1016/j.jcat.2016.08.007.
- (35) Garwood, W. E. ACS Symp. Ser. 1983, 218, 383-396.

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