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Experimental and theoretical assessment of the mechanism of hydrogen transfer in alkane-alkene coupling on solid acids



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ABSTRACT

Experimental and theoretical methods are used to probe the mechanism and site requirements for C-C bond formation and hydride transfer (HT) reactions of alkane-alkene mixtures on solid acids with diverse acid strength and confining voids. Such methods provide quantitative descriptors of reactivity in terms of the properties of molecules and solids for chemistries that enable the practice of alkylation and oligomerization catalysis. In these processes, chain growth is controlled by HT from alkanes to alkene-derived bound alkoxides formed via oligomerization or β-scission. Transition state (TS) treatments of the elementary steps that mediate these reactions show that HT rates depend on the energies required to desorb alkoxides as carbenium ions and to cleave the weakest C-H bond in gaseous alkanes. These energies serve as accurate molecular descriptors of hydride transfer reactivity and, taken together with the acid strength and van der Waals stabilization properties of catalytic solids, provide the kinetic details required to predict the relative rates at which alkoxides react with alkenes (to form C-C bonds and larger alkenes) or alkanes (to accept H-atoms and desorb as alkanes) for chains with a broad range of size and skeletal structure. Confinement effects reflect the size of the TS and its precursors for C-C coupling and HT relative to the dimensions of the confining voids, which determine how guest species form van der Waals contacts with the host without significant distortions. Smaller voids preferentially stabilize the smaller C-C bond formation TS over the larger structures that mediate HT. Acid strength, in turn, influences the stability of conjugate anions at the ion-pair TS: stronger acids lead to higher turnover rates for C-C coupling and HT, but to similar extents, because their TS structures contain fully-formed framework anions that benefit similarly from their more stable character in stronger acids.

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1. Introduction

The practice of catalytic alkylation upgrades small alkanes by incorporating them into alkene oligomerization cycles through the transfer of hydrogen to growing chains, typically using sulfuric or hydrofluoric liquid acids [1,2]. Solid Brønsted acids contain much lower densities of protons and exhibit faster deactivation than these liquid acids [3–8], but avoid the environmental risks of materials corrosion and toxicity upon release, characteristics that are ubiquitous in the case of liquid acids. The conversion of alkenes to larger chains, useful as chemicals and fuels, involves concurrent oligomerization, isomerization, β -scission, hydride transfer and cyclization reactions [9–11]. Hydride transfer from alkanes to alkoxide intermediates provides strategies for regulating chain growth via controlled termination as less reactive alkanes, while consuming typically unreactive alkanes and forming

* Corresponding author. E-mail address: iglesia@berkeley.edu (E. Iglesia). stable, larger alkanes as products [3,5,6,12–15]. Hydride transfer can also lead to the formation of dienes and trienes from H-donors; such species can act as precursors to cyclic and unsaturated molecules that ultimately form unreactive residues, thus rendering acid sites inaccessible in solid acid catalysts.

These oligomerization and H-transfer reactions, as well as most other reactions catalyzed by protons, involve full ion-pair transition states, which vary in size among the different routes. These size differences allow some control of reactivity and selectivity based on the size of confining voids, as a result of the preferential van der Waals stabilization of transition states of a certain size [16–18]. Turnover rates for each given reaction also depend on the chemical stability of the anion and the cation in the relevant ion-pair transition state. The stability of the conjugate anion is dictated by the strength of the solid acid, which is given, in turn, by the deprotonation energy of the acid [19,20]. The organic cationic moiety at the transition state becomes more stable as its proton affinity increases and, in the case of bimolecular hydride transfer, as the energy required to abstract a hydride from the donor species





JOURNAL OF CATALYSIS (dehydridation energy) decreases. The identity, structure, and energy of such cationic moieties are specific to the reactants involved; their properties become the molecular descriptors of reactivity and selectivity, as this study shows through a combination of theory and experiment for alkane-alkene reactions on solids that differ in acid strength and in the size and shape of the confining void structure.

Alkene oligomerization turnover rates are limited by the kinetically-relevant formation of a C-C bond between an alkoxide and an unbound alkene [16]. This study shows that the transfer of a H-atom from the alkane to an alkoxide limits alkane incorporation into alkene oligomerization cycles, leading to rates proportional to the pressure of the H-donor alkane and to the concentration of a given alkoxide. The formation rates of C₆ alkanes, through Htransfer from alkanes to bound hexoxides formed via propene dimerization, depend on the size and shape of the confining voids. H-transfer transition state structures are significantly larger than those for dimerization, leading to ratios of H-transfer to dimerization rate constants (i.e., selectivity) that also depend sensitively on the void size of the porous aluminosilicates. Both transition state structures are, however, fully formed ion-pairs. As a result, they benefit to the same extent from stronger acids; consequently, acid strength does not influence the relative rates of oligomerization and H-transfer for protons residing either within voids larger than the transition state structures (e.g., Keggin polyoxometalates dispersed on SiO₂ and mesoporous aluminosilicates) or within voids of similar size, which provide weak or similar van der Waals contacts, respectively.

Molecular descriptors of H-transfer reactivity must consider the stability of both the hydride acceptors (alkoxides) and the hydride donors (alkanes) as they rearrange the cationic charge at the transition state; descriptors must also consider the relative size of this transition state and its relevant precursors. Thus, measured kinetic rates for hydride transfer, which reflect energy differences between the transition state and its alkoxide precursor, decrease as the alkoxide becomes smaller. The skeletal structures of bound alkoxides also influence their properties as H-acceptors, as shown by the different rate constants for the formation of each skeletal hexane isomer from their respective bound and equilibrated hexoxide isomers. Similarly, the extent of substitution at the hydride donor increases hydride transfer rates for a given alkoxide, because they lead to more stable cations at the bimolecular transition states that mediate such reactions. The results, calculations, and concepts gleaned here through the use and benchmarking of experiment and theory have allowed the first accurate, quantitative assessment of the relative reactivity of the relevant molecules in alkane-alkene reactions. These assessments have led to molecular and catalyst descriptors, which taken together with previous studies [9,16], allow their reliable extrapolation to related reactions and processes catalyzed by solid acids and relevant to the practical upgrading and conversion of fuels, energy carriers, and chemical feedstocks.

2. Experimental methods

2.1. Materials and rate measurements

The properties and protocols used in the synthesis of the H⁺form of BEA, MFI, MOR, TON, and FAU zeolites, mesoporous silica-alumina and Keggin POM clusters dispersed on mesoporous colloidal silica [21] have been reported elsewhere [9,16] and in Table 1; these samples were pelleted, crushed, and sieved to retain 180–250 µm aggregates before use. The number of protons in each sample was determined from NH₃ evolution from NH₄⁴-exchanged samples for zeolitic acids (Supplemental Information (SI); Fig. S1) and from 2,6-di-tert-butylpyridine titration uptakes for mesoporous acids that allowed the diffusion of such large titrants, which selectively interact with protons without binding on Lewis acid sites. Samples (15–50 mg) were placed within a tubular reactor with plug-flow hydrodynamics (316 stainless steel; 12 mm I.D.) held within a three-zone resistively-heated furnace (Applied Test Systems Series 3210; Watlow controllers; 96 Series). The temperature was measured with a K-type thermocouple held within an internal concentric thermowell placed in the middle of the catalyst 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 species before reaction measurements. Aluminosilicates were treated before catalytic rate measurements in a 5% O_2 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-methylbutane (99.5% HPLC grade, Sigma-Aldrich) were mixed into a stream of propene (99.9%, Praxair, Praxair) in He. Liquid 2-methylbutane was evaporated into a flowing He stream (UHP Praxair) using a high-pressure syringe pump (Teledyne Isco Series D). The effluent was transferred through heated 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 \times 0.32 mm \times 1.05 μ m film). Reactant pressures were varied by dilution with He (99.999%, Praxair) at a system pressure held constant by a dome-loaded regulator (Tempresco). Molecular speciation was confirmed by the use of known compounds and by mass spectrometry after chromatographic separation.

Alkene conversion turnover rates (per proton) were measured in the absence co-fed alkanes to determine alkene oligomerization rates [16]. Hydride transfer turnover rates were determined from the rate of formation of alkanes and reported either as the total hydride transfer rate (the combined formation rates for all isomers with a given number of C-atoms) or as the rate of formation of a given skeletal isomer, which reflects the H-acceptor properties of the bound alkoxide with that specific skeleton. Selectivities are defined as the ratio of H-transfer and oligomerization rate constants and extracted from kinetic data for different acceptor alkoxides and H-donor alkanes.

2.2. Density functional theory methods

Periodic density functional theory, as implemented in the Vienna ab initio simulation package (VASP) [24–27], was used to optimize structures and energies for stable intermediate and transition states involved in the elementary steps for dimerization and hydride transfer. A periodic plane-wave basis-set expansion to a cutoff energy of 396 eV was used to represent the wavefunctions for valence electrons and projector-augmented wave (PAW) pseudopotentials were used to account for electron-core interactions [28,29]. Exchange and correlation energies were calculated using the generalized gradient approximation and the revised Perdew–Wang (PW91) functional [30]. A $1 \times 1 \times 1$ Monkhorst–Pack kpoint mesh was used to sample the first Brillioun zone [31].

Keggin POM clusters were described by placing full clusters (1.1 nm diameter) at the center of cubic unit cells (3 nm edge length) in order to prevent electronic interactions among neighboring cells [19,32]. Minimum energy paths were calculated using nudged elastic band (NEB) methods [33] with structures converged to 1×10^{-4} eV for energies and 0.3 eV Å⁻¹ for forces. NEB-derived transition state structures were then refined using the Dimer method [34] with more stringent convergence for energies and forces on each atom (10^{-6} eV and 0.05 eV Å⁻¹). The bridging O-atoms in the HPW POM clusters (H₃PW₁₂O₄₀) were used as the

	, 1			
	Sample	Source	Si/Al ratio ¹	H^{+}/T^{*} ratio
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	[22,23]	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 /SiO ₂	5	0.04	0.72

 Table 1

 Source, Si/Al ratios, and proton counts for solid acids used.

¹ Elemental analysis (ICP-OES).

² NH₃ evolution from NH₄⁺-exchanged samples.

³ 2,6-di-*tert*-Butylpyridine titration.

initial proton location for optimization of bound intermediates and transition states. The charge at each atom in optimized structures was determined by transforming converged wavefunctions into localized quasi-atomic orbitals (QUAMBO) [35–38].

3. Results and discussion

3.1. Hydride transfer rates from alkanes to alkoxides during oligomerization turnovers

Oligomerization turnovers on Brønsted acids involve the kinetically-relevant addition of gaseous alkenes to bound alkoxides (Scheme 1) that are present at near saturation coverages during catalysis, as shown by kinetic, spectroscopic, and theoretical studies [16,39]. Oligomerization rates for an alkene with *i* carbon atoms are given by:

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

where $k_{oligo,i}$ is the rate constant for the elementary reaction of a gaseous alkene (C_i) with a bound alkoxide (C_i^{alk}) present at cover-

ages in equilibrium with the corresponding gaseous alkene via an adsorption constant K_i . Mixtures of isomers with distinct points of attachment at the surface give $\langle K_i \rangle$ values averaged over all such binding configurations (*j*) or, in the case of oligomer-derived alkoxides, over all skeletal isomers, because of their formation as equilibrated mixtures [9,16].

The alkoxides can desorb via deprotonation to form all skeletal and double bond alkene isomers. These alkoxides can also desorb as the corresponding alkanes after hydride transfer (HT) when alkane co-reactants are present. This sequence of steps is illustrated for isobutane-propene reactant mixtures in Scheme 1. HT events introduce chain termination routes that can be exploited to control the number of oligomerization events that occur, which would depend otherwise only on the intrinsic dimerization reactivity and adsorption-desorption thermodynamics of each alkoxide structure. These HT processes also allow the incorporation of unreactive alkanes into oligomerization cycles at modest temperatures (400-500 K). HT replaces alkene-derived alkoxides with another alkoxide, formed from the alkane via ion-pair transition states that mediate the transfer of a H-atom. The primary and tertiary isobutoxides formed (in the case of isobutane) can desorb as isobutene, but also react with propene to form C7 alkoxides that can either



Scheme 1. Isobutane-propene reaction pathways on solid Brønsted acids. Equilibrated skeletal and regioisomers are indicated by [...].

deprotonate to form gaseous C_7 alkenes or accept a hydride from isobutane to form C_7 alkanes with the skeletal structure of the bound alkoxides.

The turnover rates (per H^+) for the formation of C₆ alkanes from isobutane-propene mixtures are proportional to isobutane pressure on all microporous and mesoporous acids (Fig. 1; 0–250 kPa isobutane; 9 kPa propene; 503 K). Such rates are consistent with a kinetically-relevant bimolecular step in which the isobutane donor transfers a H-atom to the alkoxide acceptors (e.g., C₆ alkoxides formed by propene dimerization) on surfaces nearly saturated with propene-derived alkoxides as in the case of propene dimerization reactions in the absence of H-donor alkanes [16]. The resulting rate equation for hydrogen transfer is:

$$r_{HT_{nij}} = \frac{k_{ij}[C_n^o][C_{ij}^{alk}]}{\langle K_3 \rangle [C_3]} = \frac{k_{ij}K_{ij}[C_n^o][C_{ij}]}{\langle K_3 \rangle [C_3]} = \frac{k_{ij}K_{ij}}{\langle K_3 \rangle} \frac{[C_{ij}]}{[C_3]} [C_n^o]$$
(2)

where k_{ij} is the rate constant for the elementary HT reaction from an alkane (C_n^0) with *n* C-atoms to an alkoxide isomer *j* (C_{ij}^{alk}) with *i* C-atoms, occurring on protons saturated with alkene-derived alkoxides [16,39] that are equilibrated with the gas-phase (C_{ij}) via K_{ij} . The total rate of HT for a pool of alkoxides with *i* C-atoms ($r_{HT_{art}}$) is:

$$r_{HT_{ni}} = \sum_{j} r_{HT_{nij}} \tag{3}$$

The measured rate constant $(k_{HT,nij}^{eff})$ represents a combination of the intrinsic HT rate constant and the thermodynamic constants for alkoxide formation and reflects, in turn, a free energy difference $(\Delta G_{n,ij})$ that is given by the difference between the transition state energy $(G_{HT,n,ij}^{\ddagger})$ and those for the gaseous alkane $(G_n^{(g)})$ and the alkoxide acceptor $(G_{ij}^{(g)})$ present on surfaces predominantly covered with propene-derived C₃ alkoxides:



Fig. 1. C₆ alkane formation rates during reactions of isobutane-propene mixtures as a function of isobutane pressure on aluminosilicates with different void dimensions but similar acid strengths (BEA (\blacktriangle), FAU (\diamondsuit), SiAl (\triangle), MOR (\bigcirc), MFI (\diamondsuit), TON (\blacksquare)) [9 kPa propene, 503 K, < 5% alkene and alkane conversions].

$$k_{HT,nij}^{eff} = \frac{k_{HT,nij}K_{ij}}{\langle K_3 \rangle} = \exp\left(-\Delta G_{nij}/RT\right)$$
(4)

$$\Delta G_{nij} = G_{HT,nij}^{\dagger} - G_n^{(g)} - G_{ij}^{(g)} - (\langle G_3^{alk} \rangle - G_3^{(g)})$$
(5)

The formation of C_7 alkenes and alkanes and the increase in the C_7/C_6 product ratios with increasing isobutane pressure (Fig. S2, S1) indicate that isobutane-derived alkoxides can also react with propene in subsequent oligomerization steps. HT from isobutane to the predominant bound propoxide species also occurs, albeit at rates lower than those for larger alkoxides; such rates are also proportional to the prevalent isobutane pressure (Fig. 2; BEA (a) and HPW (b)).

C–C bond cleavage (β -scission) occurs concurrently with C–C bond formation (via its microscopic reverse) to form alkoxides and alkenes with intermediate carbon numbers (i.e., not multiples of *i*, the number of carbons in the monomer) [9]; these smaller alkoxides can also undergo HT to form the corresponding alkanes. The linear dependence of the rates of formation of these alkanes (e.g. pentanes, Fig. 2; BEA (a) and HPW (b)) is also proportional to isobutane pressure, indicative of a common HT mechanism for alkoxide acceptors of different size. HT turnover rates, however, depend on the identity of both the alkoxide acceptor and the alkane donor and also on the acid strength and confinement properties of the solid acids, as discussed in the sections that follow.

3.2. Effects of confinement and acid strength on hydride transfer rates and rate constants

The slope of the rate data in Fig. 1 reflects the combination of kinetic and thermodynamic constants and of the $[C_i]$ and $[C_3]$ concentrations, as they appear in Eq. (2). These slopes vary among solid acids, even among aluminosilicates with different void structures, but containing acid sites of similar strength [40]. These linear relations indicate that the concentrations of hexenes and their equilibrated isomeric hexoxides are unaffected by the presence or pressure of isobutane, which does not perturb the alkenealkoxide equilibrium or the dimerization rates. Also, C₆ alkanes represent a small fraction of the total C₆ products formed, even at the highest isobutane pressure, because hexoxide depletion via HT is much slower than the formation and desorption of hexenes via dimerization events. Thus, the concentrations of hexenes and propene remain unaffected by the isobutane pressure and represent the kinetic driving forces in the slopes extracted from the rate data in Fig. 1 because they determine, in turn, the surface coverages of the corresponding alkoxides. The resulting kinetic constants, after accounting for the alkene pressures, solely reflect the kinetic and thermodynamic constants present in Eq. (4).

These effective HT rate constants for isobutane reactions with the lumped hexoxide or propoxide isomer pools are shown in Fig. 3 for hexoxides $(k_{HT,4,6}^{eff})$ (Fig. 3a) and proposides $(k_{HT,4,3}^{eff})$ (Fig. 3b) as a function of the void diameter in the microporous and mesoporous aluminosilicate hosts. Such diameters, as used in Fig. 3, have been defined using a purely geometric descriptor consisting of the largest diameter sphere that either (i) can be inscribed within the void space or (ii) can traverse throughout the void structure unimpeded by smaller apertures [41,42]. The HT rate constants for both hexoxide and propoxide acceptors increased as the void size decreased and then reached a maximum value. The initial increase in reactivity with decreasing void size reflects the preferential stabilization of the larger bimolecular transition state involved in these reactions over the smaller alkoxide precursor via van der Waals interactions with the lattice oxygens in the aluminosilicate frameworks, as given by the chemical identity of the rate and equilibrium constants contained in Eq. (4).



Fig. 2. C₆, C₅, and C₃ alkane formation rates from hexoxides (▲), pentoxides (●), and propoxides (♦), respectively, present as a mixture of equilibrated isomers measured during reactions of isobutane-propene mixtures as a function of isobutane pressure on (a) BEA and (b) HPW [9 kPa propene, 503 K, <5% alkene and alkane conversion].



Fig. 3. First-order rate constant for reaction of isobutane with (a) hexoxide pool and (b) propoxide pool as a function of void diameter [503 K, <5% alkene and alkane conversion].

The void size corresponding to the largest HT rate constants, however, is slightly larger for hexoxides (BEA; Fig. 3a) than for propoxides (MOR; Fig. 3b). This difference reflects the size of their respective transition state structures and their consequently different ability to form van der Waals contacts with the void walls. The size of the DFT-derived structures for these transition states is defined here as the diameter of the sphere of equivalent volume determined from a Connolly surface of the organic moiety optimized on HPW POM clusters. The relative sizes of transition states do not vary significantly when optimized on such Keggin clusters or in zeolites, as previously shown for propene dimerization on HPW and TON [16]. The transition state for hydride transfer from isobutane to hexoxides contains ten C-atoms; its diameter for the specific case of the tertiary-2-methylpentoxide on HPW clusters (Fig. 4; right) is 0.73 nm. In contrast, there are seven C-atoms in the transition state for HT to *sec*-propoxides, leading to a smaller mean diameter (0.66 nm) for this transition state than for that involved in isobutane HT to hexoxide acceptors. Consequently, the transition state for HT to propoxides becomes most stable on MOR channels (0.64 nm); these channels are slightly smaller than the BEA channels (0.67 nm) that exhibit the largest HT rate constants for isobutane reactions with hexoxides.

The matching of voids with transition state structures in size and shape leads to optimal van der Waals contacts, while avoiding



Fig. 4. DFT-derived transition state structures for oligomerization (C–C bond formation between secondary propoxide and propene) and hydride transfer from isobutane to tertiary 2-methylpentoxide on HPW [PW91; PAW]. Axes for a and b are shown, with c into the page. The dimensions for oligomerization are [0.63, 0.26, 0.43] and are [0.78, 0.53, 0.81] for hydride transfer. Charges from QUAMBO (Section 2.2) and diameters of spheres with equivalent volume $\langle d \rangle$ are also included.

steric effects that can cause an increase in energy by requiring significant geometric distortions of the organic guest or the inorganic host. The heuristic geometric descriptors based on spherical constructs (and used in Figs. 3 and 4) lead to mean diameters <d> that cannot capture the most effective "fit" because neither host nor guest structures are spherical in shape. For instance, alkyl chains in alkoxides benefit from cylindrical voids, but may require significant disruptions from their most stable configurations to benefit from van der Waals contacts with cage-like hosts. Here, mean diameters are used as approximate descriptors of size for transition states and bound species. They are appropriate and sufficient for the comparisons intended, which involve structures that differ significantly in size for the chemical transformations of interest. The refinement of such an analysis, when so required for specific predictive purposes, can be carried out using the averaging of van der Waals interaction energies for a given organic moiety through each specific void structure using methods developed and applied in previous studies of alkene coupling [16], alkoxide stability [39], and acetone condensation [43] within confining environments.

The transition state for isobutane HT to *tert*-2-methylpentoxide (0.73 nm) is significantly larger than that for the dimerization of propene with *sec*-propoxide (0.62 nm) (Fig. 4). The ratio of the rate constants for isobutane HT to C₆ alkoxides (Eq. (2)) to those for propene dimerization (Eq. (1)) is given by:

$$\gamma = \frac{k_{HT,46}K_6}{k_{oligo,3}K_3} = \exp(-\Delta G_{\gamma/RT})$$
(6)

a measure of the probability of terminating chains before further growth. This ratio is not affected by void size for larger voids (BEA, FAU, SiAl), but decreases sharply for protons residing within smaller voids (TON, MFI, MOR) (Fig. 5), as a result of a larger HT transition state that becomes less stable compared with a smaller dimerization transition state as the size of voids approaches that of the HT transition state. The effects of van der Waals interactions on this ratio of rate constants (γ), using the void diameter as a proxy of size and van der Waals contacts, depends solely on the difference in free energy between the two relevant transition states:

$$\Delta G_{\gamma} = G_{HT,46}^{\dagger} - G_{oligo,3}^{\dagger} - G_4^{(g)} - G_6^{(g)} + 2G_3^{(g)}$$
(7)

where $G_{HT,46}^{\dagger}$ and $G_{oligo,3}^{\dagger}$ are the respective free energies of the HT and C–C bond formation transition states. The other terms in Eq. (7) represent properties of the gaseous alkanes and alkenes, which do not depend on stabilization by binding or confinement and thus



Fig. 5. Rate constant ratio of hydride transfer between isobutane and equilibrated hexoxide pool to oligomerization of propene as a function of void diameter [503 K, <5% alkene and alkane conversion].

do not sense any property of the host. As a consequence, the trends evident in Fig. 5 must reflect either (i) an increase in $G^{\dagger}_{HT,46}$ through steric destabilization of the HT transition state or (ii) a decrease in $G^{\dagger}_{oligo,3}$ as a result of the more effective van der Waals contacts of the dimerization transition state with the smaller voids.

Measured rate constants for hydrogen transfer (and for oligomerization [16]) also depend on acid strength, because of its inherent role in determining the stability of the conjugate anion at ion-pair transition states. Indeed, HT rate constants on HPW, a strong acid with a deprotonation energy (DPE; [32,40]) of 1085 kJ mol⁻¹, are about 100-fold larger than on weaker mesoporous SiAl acids (1220 kJ mol⁻¹ DPE [40]) for isobutane reactions with both hexoxides (Fig. 3a) and propoxides (Fig. 3b). Stronger acids, with more stable conjugate anions, lead to ion-pair transition states of lower energy, because the charge in the organic and inorganic moieties are much larger than in the essentially neutral (covalentlybound) alkoxide precursors (Eq. (4)). These DFT-derived charges are ±0.96 for the isobutane-tert-2-methylpentoxide HT transition states and ±0.90 for isobutane-sec-propoxide HT transition states, but only ±0.30 for the sec-propoxide precursor in the latter reaction.

Similarly, the isobutane *tert*-2-methylpentoxide HT transition state and the propene-*sec*-propoxide dimerization transition state are ion-pairs of similar charge (±0.96 and ±0.94, respectively; Fig. 4). As a result, mesoporous HPW (on SiO₂) and SiAl, two solid acids of very different acid strength and containing voids much larger than either of these transition states, give similar ratios of HT and dimerization rate constants (γ ; Eq. (5)), because the stability of the conjugate anions influence the $G_{HT,ni}^{\dagger}$ and $G_{oligo,3}^{\dagger}$ terms in Eq. (7) to similar extents. We conclude that HT and oligomerization rate constants depend similarly on acid strength when protons are located either within large mesoporous voids or within voids of similar dimension and shape, thus rendering acid strength inconsequential in the control of chain length via systematic changes

in the relative rates of HT and oligomerization in isobutane-alkene alkylation processes.

3.3. Effects of chain length and substitution in alkoxide acceptors on hydride transfer rates

In the kinetic treatments and discussion above, HT rates are reported for a lumped pool of bound alkoxides (hexoxides, propoxides) consisting of isomers different in skeleton and surface attachment point. Such treatments exploit the equilibrated nature of all regioisomers and skeletal isomers of alkoxides and alkenes of a given chain length [9]. This lumping of bound alkoxide acceptors based on chain length is undone here as a strategy to determine the reactivity of each skeletal isomer within this equilibrated pool with isobutane (and with *n*-butane and 2-methylbutane in Section 3.5). Such speciation is made possible because the specific skeletal alkane isomers formed from each alkoxide skeleton via HT can be detected in the gaseous products.

Approach to equilibrium values for all hexene isomers formed from propene dimerization with respect to a given isomer (2methyl-2-pentene; 2M2P) on TON, MFI, BEA, SiAl, and HPW are near unity [9] even at very low propene conversions (<0.1%; Table 2; approach to equilibrium for C_5 in Fig. S3). These isomers are grouped in Table 2 according to their skeletal backbone: 2methylpentenes (2-MP), 3-methylpentenes (3-MP), linear hexenes (n-H), and 2,3-dimethylbutenes (23-DMB). Each skeletal lump contains all double bond and stereoisomers. Only 23-DMB isomers in TON are slightly below equilibrium values, a consequence of the slow diffusion of the bulkiest C₆ skeleton through the smallest channels, but approach unity with increasing conversion. The equilibration of 23-DMB isomers within zeolite crystals was demonstrated by the fast intramolecular scrambling of all products formed from singly-labeled propene [9]. The 2,2-dimethylbutenes (22-DMB) were not detected either because of the difficulty in forming quaternary C atoms via skeletal isomerization or because of its diffusion-enhanced secondary interconversion via subsequent isomerization or β -scission.

Bound alkoxides with different skeletal structures undergo hydride transfer from isobutane (Scheme 2) to form 2methylpentane (2MP), 3-methylpentane (3MP), 2,3dimethylbutane (23DMB), and *n*-hexane (nH) at rates proportional to the prevalent isobutane pressure (Fig. 6; BEA) but with rates and rate constants that differ among these backbones. Equilibrated pentoxides, formed via β -scission of larger oligomers, lead to the formation of 2-methylbutane (2MB) and n-pentane (nP) at rates also proportional to the H-donor pressure. The rate constants for

Table 2

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 HPW (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 hexenes (*n*-H), and 2,3-dimethylbutene (2,3-DMB).

Backbone	Approach to equilibrium (w.r.t. 2M2P)	TON	MFI	BEA	SiAl	HPW
2-MP	2M2P	1	1	1	1	1
	4M1P	0.96	0.93	0.93	1.09	0.82
	c-4M2P	1.00	1.21	1.33	1.00	1.05
	t-4M2P	0.96	0.96	0.97	1.05	0.87
	2M1P/1-H	0.93	0.91	0.91	0.96	0.90
3-MP	3M1P	0.79	0.76	0.76	1.09	0.67
	2E1B	0.87	0.75	0.65	0.92	0.63
	c-3M2P	0.92	0.82	0.67	0.97	0.67
	t-3M2P	0.93	0.84	0.68	1.00	0.68
n-H	c/t-3-H	1.06	0.87	0.87	0.97	1.00
	с-2-Н	1.03	0.86	0.86	0.98	1.00
	t-2-H	1.04	0.85	0.85	0.99	1.01
2,3-DMB	2,3-DM1B	0.35	1.40	1.14	1.00	0.92
	2,3-DM2B	0.35	1.13	1.13	1.01	0.92

hydride transfer from isobutane to each isomer j ($k_{HT,4ij}^{eff}$) are grouped in Fig. 7 according to the number of carbon atoms in the bound alkoxide acceptor, which acts here as the initial surrogate for their relative size. Such kinetic constants combine the effects of chain length and extent of substitution on alkoxide reactivity.

The rate constants for each of the alkoxide acceptors are larger on HPW than on SiAl (Fig. 7), consistent with HT transition states that benefit from a more stable conjugate anion to a greater extent than the bound alkoxide precursors. Isobutane HT rate constants for each alkoxide are larger on BEA than on SiAl (Fig. 7), indicative of the more effective van der Waals contacts between the HT transition state and the smaller channels in BEA, in spite of the similar acid strength previously demonstrated for aluminosilicates of different framework structure and crystallinity [16,39]. The diversity of activity and selectivity of zeolite catalysts has previously been inaccurately attributed to differences in acid strength among different frameworks, a consequence of the inappropriate use of the adsorption energy or evolution temperature of bound titrants. Such properties are not direct descriptors of acid strength because they also reflect the stabilization of bound species by electrostatic and van der Waals interactions that are unrelated to acid strength.

Alkoxides with different backbone structures differ in reactivity because of the effects of substitution in the stability of the protonated organic moiety that forms at the HT transition state. These reactivity trends with alkoxide structure remain mostly unchanged, however, with changes in acid strength or confining voids (Fig. S4), apparently because the differences in charge and size between the HT transition state and its alkoxide precursor depend only slightly on the skeletal structure of the bound alkoxide acceptors, a concept that we examine in more detail through DFT treatments below.

3.4. Density functional theory treatments of hydride transfer transition states on HPW POM clusters

The elementary steps of hydride transfer between isobutane and various alkoxides were investigated on HPW POM clusters (described in Section 2.2) as an illustrative example of an unconstrained solid acid. Fig. 8 shows the HT reaction coordinate, defined in terms of the C–H bond length in the donor that transfers the Hatom to the bound alkoxide, for isobutane reactions with secondary *n*-hexoxides or tertiary 2-methyl-pentoxides. The optimized structures of the transition states indicate that the highest energy saddle point occurs at different C–H bond lengths for these two alkoxide acceptors (Fig. 8). In forming 2MP from 2-methyl



Scheme 2. Alkane incorporation into equilibrated alkoxide isomer pools. Illustrated here is the hexoxide pool that forms 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane (*n*H), or 2,3-dimethylbutane (2,3DMB) after hydride transfer from isobutane.





Fig. 6. Formation rates of 2-methylpentane (2MP; \blacksquare), 3-methylpentane (3MP; \blacktriangle), 2,3-dimethylbutane (23DMB; \blacklozenge), and *n*-hexane (nH; \bigcirc) measured during reactions of isobutane-propene mixtures as a function of isobutane pressure on BEA [9 kPa propene, 503 K, <5% alkene and alkane conversion].

pentoxides, the H-atom has already fully transferred at the transition state, while the transition state structure is formed before hydride transfer for *n*-hexoxide acceptors. The energy barrier for HT to the tertiary 2-methyl-pentoxide is $16 \text{ kJ} \text{ mol}^{-1}$ smaller than for HT to the secondary *n*-hexoxide, consistent with the more stable nature of tertiary carbenium ions relative to those secondary carbenium ions and with the location of the transition state along the hydride transfer reaction coordinate.

The activation energy ($\Delta E_{HT,nij}$) for HT transfer from donor *n* to acceptor *i,j* can be dissected into individual components for hypothetical connecting paths between precursors and transition states

Fig. 7. First-order rate constant for alkane formation via hydride transfer between isobutane and propoxide, pentoxide, or hexoxide isomer pools on BEA (▲), HPW (■), and SiAl (♦) [9 kPa propene, 503 K, <5% alkene and alkane conversion].

via Born-Haber thermochemical cycles (Scheme 3). In such cycles, alkoxides first desorb as their respective protonated gaseous analogs at an energy cost given by the carbenium-ion detachment energy (CDE). A gaseous isobutane (the donor n) then transfers a hydride to these species to form a *tert*-butyl gaseous cation and a gaseous alkene, with a reaction energy given by the gaseous hydride transfer energy (HTE). The gaseous *tert*-butyl cation is then brought closer to the conjugate anion in order to recover an interaction energy (IE) with electrostatic and charge reorganization components [44]. The transition state structure for nH formation from *sec*-hexoxide (Fig. 8) shows that the H-atom to be transferred



Fig. 8. DFT-derived electronic energies for hydride transfer from isobutane to secondary hexoxide (--) or tertiary 2-methylpentoxide (--) relative to alkoxide and gas phase isobutane as a function of C-H bond length in the donor (isobutane) [PW91, PAW].



Scheme 3. Thermochemical cycle for hydride transfer between an alkane donor (*i*) and an alkoxide acceptor (*ij*) (here, isobutane and tertiary 2-methylpentoxide), in terms of carbenium-ion detachment energy (CDE), hydride transfer energy (HTE), and interaction energy (IE).

remains with the isobutane donor, indicating that the barrier to form this transition state predominantly reflects that required to form the secondary carbenium-ion from the sec-hexoxide (CDE). The hydride has been transferred to the acceptor in forming 2MP from 2-methyl pentoxide bound through its tertiary C-atom (Fig. 8). These results indicate that substitution at hydride acceptors affects the transition state energy, leading to the observed differences in measured rates for HT to alkoxides with different skeletons from isobutane (Fig. 7). The extent to which the formation of the carbenium ion (CDE) from the alkoxide acceptor or the detachment and reattachment of the H-atom being transferred (HTE) contribute to this transition state energy reflects their relative magnitudes, with the formation of the carbenium ion becoming the sole determinant of transition state stability as the carbenium ions derived from the bound alkoxides become increasingly unstable.

Measured rate constants for hydride transfer from isobutane to different alkoxide acceptors reflect the energies of their transition states relative to their different respective precursors. These transition states differ in their size and numbers of C-atoms (Section 3.2). Their van der Waals volumes, surface areas, and equivalent sphere diameters (Section 3.2) are shown in Table 3 for HT reactions on HPW using isobutane as the H-donor and each of the C₆, C₅, and C₃ skeletally-distinct alkoxides with the attachment locations listed (optimized structures in Fig. S5). The measured HT rate constants on HPW, BEA, and SiAl increased as the DFT-derived size of the respective transition state structures (on HPW) increased (Fig. 9), even though TS structures with the same number of C-atoms differ only slightly in size. On mesoporous acids (HPW and SiAl), such an increase predominately reflects the greater stability of the cationic moiety as the electrondonating alkyl chains become longer, since van der Waals interactions change less sensitively with transition state size over flat and concave unconfined surfaces than over the smaller concave domains prevalent within zeotypes.

Transition states of similar size by the metrics used here can exhibit different rate constants when the degree of substitution at the center of charge in the organic moiety varies (e.g. nP vs. 2 MB formation; $\langle d \rangle = 0.712$ and 0.714 nm and $k_{HT,A5j}^{eff} = 33.9$ and 61.3 µmol (H⁺-s-kPa)⁻¹, respectively), because of the different stability of their respective alkoxide-derived carbenium ions at the transition state. For each type of backbone (e.g., linear alkoxides; Fig. 9, open symbols), HT rate constants for the formation of propane, *n*-pentane and *n*-hexane increased monotonically with chain length on both HPW and SiAl. In contrast, such chain length effects became weaker for larger chains on BEA, as steric effects require distortions in the framework and the organic moiety and impose energetic penalties that ultimately offset the more effective van der Waals contacts between voids and larger transition states, as discussed earlier (Section 3.2).

3.5. Effects of hydride donor chain length and substitution on hydride transfer rates

Hydride transfer rates also depend on the size and substitution in the donor alkanes. The rate of formation of C_6 alkanes from all combined isomers of bound hexoxides on BEA are proportional to the pressure of 2-methylbutane, isobutane, and *n*-butane (Fig. 10). The first-order rate constants for the formation of each C_3 , C_4 , C_5 , and C_6 alkane isomers from HT with *n*-butane, isobutane, 296

DFT-derived van der Waals volumes (V _{vdw}), surface areas (SA _{vdw}), and diameters ((d)) of hydride transfer transition state structures for the given donor and acceptor on HPW. The
diameters are calculated assuming a sphere of equivalent volume.

H-donor (n)	H-acceptor C-atoms (i)	H-acceptor isomer (j)	attachment	V _{vdW} [nm ³]	SA _{vdW} [nm ²]	$\langle d \rangle$ [nm]
n-Butane	6	2MP	tertiary	0.211	2.18	0.739
Isobutane	6	2MP 23DMB	tertiary tertiary	0.203	2.06 1.95	0.730
		3MP	tertiary	0.202	1.95	0.728
	5	nH 2MB	secondary tertiary	0.208 0.191	2.18 1.85	0.736 0.714
	3	nP prop	secondary secondary	0.189 0.151	1.97 1.68	0.712 0.661
2-Methylbutane	6 3	2MP prop	tertiary secondary	0.222 0.169	2.13 1.85	0.751 0.686

and 2-methylbutane on BEA are shown in Fig. 11. Measured rates and rate constants all increased as the length and substitution of the H-donors increased for all alkoxide acceptors. These trends are consistent with the different dehydridation energies of these alkanes (Eq. (8); Fig. S6), which is calculated here as the energy required to remove the secondary H-atom from *n*-butane and the tertiary H-atom from isobutane and 2-methylbutane as a gaseous hydride ion:

Dehydridation Energy =
$$E_n - (E_{n-H^+} + E_{H^-})$$
 (8)

Here, E_n is the energy of the gaseous alkane, E_{n-H^+} is the energy of the cation formed upon hydride removal, and E_{H^-} is the energy of the hydride anion in its gaseous form. Eq. (8) illustrates the effects of the stability of the alkane-derived cation on hydride transfer energies (HTE) and on the energy of the HT transition state. Such effects become stronger for more stable alkoxide acceptors, for which the hydride has already been transferred at the transition state structures for hydride transfer from *n*-butane or isobutane to

tertiary 2-methylpentoxides on HPW (Fig. 12) indicate that the C–H bond length is similar for the two donors and that the hydride has been nearly fully transferred at the transition state. Their different measured rate constants on BEA (2.6 versus 6.9 µmol (H⁺-s-kPa)⁻¹ for *n*-butane and isobutane, respectively) thus reflect the different stabilities of the donor alkane as a cationic moiety, given that the alkoxide acceptor and the extent to which the H-atoms have been transferred are the same in HT reactions with these two H-donor alkanes.

The presence of an additional methyl group when isobutane is replaced with 2-methylbutane as the H-donor leads to an additional increase in hydride transfer rate constants on BEA (6.9 and 62μ mol (H⁺-s-kPa)⁻¹ for isobutane and 2-methylbutane, respectively; Fig. 11). Such an increase with chain length is larger than that observed upon changing the skeleton of C₄ alkanes (*n*-butane vs. isobutane). These differences reflect the combined effects of cation stability and of the larger size of the 2-methylpentane HT transition state, which can more effectively interact with BEA channels. Indeed, the transition state for 2-methylbutane HT to



Fig. 9. First-order rate constant for alkane formation via hydride transfer from isobutane and to propoxide, pentoxide or hexoxide isomer pools on BEA (\blacktriangle , \bigtriangleup), HPW (\blacksquare , \Box), and SiAl (\blacklozenge , \diamondsuit) as a function of estimated transition state diameter (<d>) from Table 3. Open symbols indicate hydride transfer to linear alkoxides, while closed symbols indicate hydride transfer to branched alkoxides.



Fig. 10. C_6 alkane formation rates from hydride transfer between hexoxide pool and 2-methylbutane (\blacktriangle), isobutane (\blacklozenge), or *n*-butane (\blacklozenge) measured when fed with propene as a function of alkane pressure on BEA [9 kPa propene, 503 K, <5% alkene and alkane conversion].



Fig. 11. First-order rate constant for alkane formation from hydride transfer between 2-methylbutane (\blacktriangle), isobutane (\blacklozenge), or *n*-butane (\blacklozenge) and proposide or butoxide, pentoxide or hexoxide pools on BEA [9 kPa propene, 503 K, <5% alkene and alkane conversion].



Fig. 12. DFT-derived transition state structures for hydride transfer between *n*-butane (left) or isobutane (right) and tertiary 2-methylpentoxide on HPW [PW91; PAW].

tertiary 2-methylpentoxides is larger (0.751 nm) than with *n*-butane (0.739 nm) or isobutane (0.730 nm) (Table 3) donors.

4. Conclusions

The evidence presented here based on theoretical and experimental assessments of the dynamics of hydride transfer processes show how the size and charge of the relevant transition states (and their precursors) determine the effects of confinement and acid strength on the relative rates of C–C bond formation and H-transfer in alkane-alkene reactions on solid acids. The results presented also assign such reactivity and selectivity characteristics to molecular descriptors of the properties of the alkoxide H-acceptors and the alkane H-donors. In doing so, this study provides a quantitative and previously unavailable framework for estimates of reactivity and selectivity for other alkanes and alkenes and their mixtures, with relevant consequences for kinetic predictions in the practice of oligomerization and alkylation catalysis.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.08.002.

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