

Effects of Charge, Size, and Shape of Transition States, Bound Intermediates, and Confining Voids in Reactions of Alkenes on Solid Acids

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Solid acids with sites varying in acid strength and in confining environments are used here to examine, through kinetic experiments and theory, how size and shape of organic guests and inorganic hosts at ion-pair transition states (TS) influence reactivity. Reactions of C_2 – C_4 alkene mixtures serve as the illustrative example; they involve kinetically-relevant C–C coupling between alkenes and bound alkoxides that saturate the surface on microporous (TON) and mesoporous (SiAI) aluminosilicates of similar acid strength and on stronger heteropolytungstic acids (HPW). Rate constants (per H⁺) increase with increasing TS size (number of C-atoms) because of the combined effects of size/substitution on proton affinities of coupling products and on van der Waals (vdW) contacts between carbocations and

voids. When the voids and organic moieties are similar in dimension, these contacts require framework distortions, leading to dispersive interactions that are compensated in part by enthalpic penalties associated with the distortions, which are quantified here with DFT-derived atomic displacements and distortion energies. DFT-derived proton affinities of the coupling products and vdW interaction energies between the TS and voids represent the most accurate and complete descriptors of reactivity, as the size and shape of TS structures vary in C–C coupling steps and more generally in acid-catalyzed transformations, and can be used in designing voids for stabilizing specific host-guest pairs.

Introduction

Porous solids containing Brønsted acid sites catalyze the formation of C–C bonds in alkene oligomerization processes,^[1-4] which are mediated by ion-pair transition states that differ in size and charge from their relevant kinetic precursors, thus leading to strong effects of confinement and of acid strength on the intrinsic reactivity of the active protons. These reactions are limited by the C-C bond formation elementary step, in which an alkene reacts with an essentially uncharged alkenederived bound precursor. The energy of the relevant transition states (TS) depends on the respective stabilities of the organic cation and the inorganic anion; the latter is determined by the acid strength of the solid, but also on TS-anion electrostatic interactions that reflect the ability of the two ions to delocalize their respective charges as the TS ion-pair forms along the reaction coordinate.^[5,6] Transition state stability, and thus reactivity, also depends on host-guest van der Waals contacts when protons, bound precursors, and transition states reside within voids of molecular dimensions.^[7-9] These confinement effects depend sensitively on the size and shape of the TS structures, their precursor species, and the confining voids. The stability of the cationic moiety at the TS depends on its size because larger and more substituted carbenium ions (i) deloc-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201800401 alize protons more effectively and (ii) make more effective van der Waals contacts. As a result, reactivity varies systematically with changes in the size and the skeletal structure of the alkene reactants.

These trends are systematically examined here for aluminosilicates with different framework structure but similar acid strength and also for solid acids with either voids of similar size or of size significantly larger than the molecular species involved, but with very different acid strength. These solids are used specifically for the dimerization and cross-dimerization of ethene, propene, and isobutene over a very broad pressure range (10-500 kPa). Their TS structures and stabilities are inferred from theory and experiment on a set of solid acids, specifically TON zeolites (10-membered ring), amorphous colloidal silica-alumina (SiAl), and Keggin polyoxometalate clusters dispersed on mesoporous colloidal silica (H₃PW₁₂O₄₀/ SiO₂; HPW). These reactions occur on acid sites that are essentially saturated with bound alkene-derived monomers in equilibrium with gaseous alkenes and involve the kineticallyrelevant addition of an alkene to such bound alkoxides, as evident from kinetic, spectroscopic and density functional theory (DFT) results.^[1,10,11]

Measured rate constants and activation energies for these alkenes and their mixtures reflect differences in size among their TS structures, which influence, in turn, their van der Waals contacts with the surfaces of the confining voids. Rate constants increase and activation free energies decrease as the TS structures become larger, because of the combined effects of more stable carbenium ions and of more effective van der Waals contacts with void surfaces. Optimal van der Waals interactions require host and guest structures to distort as the



TS approaches the size of the confining voids, leading to significant enthalpy penalties; as a result, voids of intermediate size lead to lower activation free energies and, thus, higher turnover rates. The respective contributions of intrinsic carbenium ion stability and van der Waals contacts on the free energies of TS ion-pairs are dissected here through mechanistic assessments of the effects of TS size on reactivity for acids that are able to establish strong (10-MR channels; TON) or weak (mesoporous SiAl, HPW) van der Waals interactions with the TS structures. The carbenium ion stability of transition states different in size are shown to depend on the DFT-derived proton affinity of the gaseous alkene products formed via each given TS. DFT functionals that account for dispersion effects are used here to benchmark and interpret the experimentally observed trends. DFT-derived transition state structures show that effective van der Waals contacts require distortions of the TS and framework structures, described in this study for the illustrative case of TON but evident in all framework and which become more significant for larger TS structures. The ability of these frameworks to distort has been discussed previously in the context of a flexibility window^[12-14] and of theoretical constructs useful in heuristic treatments of diffusive separations,^[15,16] but their role in TS formation and their consequences for reactivity have not been previously addressed. This restructuring of the inorganic host in order to optimize interactions with the organic guest plays even more significant roles in transformations of reactants larger than those examined here. Such structural distortions require enthalpy penalties that are recovered through more effective van der Waals contacts, while also balancing the entropy losses associated with tighter confinement in minimizing the free energies of transition states. Here, the systematic variation of charge, size and shape of transition states and voids makes these distortion effects separable from the effects of proton affinity (or for the specific case of acid catalysis, from acid strength). Such details must be rigorously and quantitatively considered in the design and optimization of host-guest pairs in order to achieve the preferential stabilization of specific transition states and the desired reactivity and selectivity targets for other reactions and catalyst systems.

Experimental Methods

Alkene coupling turnover rates were measured based at 503 K using a given alkene or binary mixtures of ethene (99.9%, Praxair) or isobutene (99.9%, Praxair) with propene (99.9%, Praxair) as reactants on TON (Si/Al=39), amorphous silica alumina (SiAl; Sigma-Aldrich) and $H_3PW_{12}O_{40}/SiO_2$ using a reactor and analytical system previously described.^[11] The number of accessible protons was measured for each sample from the amount of NH₃ evolved during thermal treatment of NH₄⁺-exchanged TON and from the number of 2,6-di-tert-butylpyridine titrants required to fully suppress oligomerization rates on mesoporous samples;^[11] values are found in SI Table S1. Solid acids (180–250- μ m aggregates; 15–100 mg) were held within a tubular reactor (316 stainless steel, 12-mm i.d.) for catalytic rate measurements. Before kinetic measurements, TON and SiAl were treated in 5% O₂/He (83.3 cm³g⁻¹s⁻¹; Praxair) by heating to 818 K (at 0.025 K s⁻¹; 3-h hold) and cooling to

reaction temperature. HPW was treated in He ($50 \text{ cm}^3 \text{g}^{-1} \text{s}^{-1}$; 99.999%; Praxair) by heating (at 0.083 K s⁻¹) to 503 K in order to remove any adsorbed ambient moisture, while avoiding changes in their Keggin structure. Reactant and product concentrations were measured using flame ionization detection (Agilent 6890 GC) after chromatographic separation (methyl silicone capillary column; HP-1 column; 50 m×0.32 mm×1.05-µm film).

The rates of formation (normalized per number of accessible protons) of each coupling product for a given alkene or binary mixture (e.g. C4, C5, C6 for ethene-propene reactants) were fit to an Eley-Rideal rate expression [Eq. (1)] for data collected while the relative concentrations of alkenes were varied systematically. This rate expression does not include the presence of free protons in the denominator because at the pressures utilized in our study, the protons are saturated with reactant alkenes. These coupling species made up the majority of the products, as (i) the low conversion suppressed trimer formation, and (ii) the catalysts used were previously shown to inhibit secondary reactions such as β scission.^[17] Further, these turnover rates were shown to be devoid of mass transfer limitations because rates were independent of acid site density.^[1] The measured formation rates were fit to Equation (1) by minimizing the sum of squared residuals to generate a secondorder rate constant, which reflects carbon-carbon bond formation transition states, and equilibrium constants, which reflect alkoxide formation from each of the reactant alkenes.

Periodic plane-wave density functional theory methods (Vienna ab initio Simulation Package; (VASP))[18-21] were used to determine optimized structures and energies for all stable intermediate and transition states with projector-augmented wave (PAW5) pseudopotentials and their cut-off energy of 396 eV (taken from O-atoms value).^[22,23] Exchange and correlation energies were calculated within the generalized gradient approximation using revised Perdew–Burke–Ernzerhof (RPBE) functionals^[24-26] with dispersive energies and forces calculated by DFT-D3 algorithms during each energy minimization step,^[27,28] which have been used previously in these systems to benchmark against experiment.^[1,29] A $1 \times 1 \times 1$ Monkhorst-Pack k-point mesh was used to sample the first Brillouin zone. $^{\scriptscriptstyle [30]}$ TON was described using a supercell with the dimensions of 1.4105×1.7842×2.1024 nm³, comprised of five unit cells (one unit cell defined in^[31]), and the Al3-O4(H) site (as numbered by convention^[31]) was chosen as the location for alkene adsorption to form alkoxides. Reaction paths of minimum energy were calculated using nudged elastic band (NEB) methods^[32] with structures converged to energies within 1×10^{-4} eV and forces to within 0.3 eVÅ⁻¹ to identify the starting TS structures, which were then refined using Dimer calculations^[33] with convergence criteria of 1×10^{-6} eV for energies and 0.05 eVÅ⁻¹ for the forces on each atom. All energies are referenced to the H-form of the catalyst and the gaseous alkene reactants for each given C-C coupling TS. The accurate determination of charges in intermediates, transition states, and solid catalyst structures remains a challenging task, which we have chosen to address here through a Löwdin population analysis on the individual atoms in optimized structures by transforming the converged wavefunctions into a set of localized guasi-atomic orbitals (QUAMBO).[34-37] Frequency calculations were performed on all optimized structures to determine zero-point vibrational energies (ZPVE), vibrational enthalpies and free energies, and, in the case of gaseous molecules, translational and rotational enthalpies and free energies. The low-frequency modes (<150 cm¹) for weakly-bound intermediates and transition states contribute significant errors to vibrational free energies. As a result, these modes were assumed to retain a fraction (0.70) of the translational and rotational entropies of their gaseous analogs, as suggested by measured entropies of adsorption on oxide surfaces.[38]

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Results and Discussion

Turnover rates for homodimerization (r_{i+i}) and cross-dimerization (r_{i+n}) reactions of alkenes with *i* or *n* C-atoms and their mixtures are given by:

$$\mathbf{r}_{i+n} = \frac{\left(\langle k_{i,n} K_i \rangle + \langle k_{n,i} K_n \rangle\right)^* [C_i] [C_n]}{\langle K_i \rangle [C_i] + \langle K_n \rangle [C_n]} \tag{1}$$

when protons are saturated with mixtures of alkene-derived bound alkoxides, an assumption consistent with measured rates and confirmed by infrared spectra during reaction and by adsorption energies derived from density functional theory (DFT).^[1,10] The homodimerization rates (r_{i+i}) are given by Equation (1) for the case of i=n. C_i and C_n are the concentrations of the extracrystalline gaseous alkenes (with i or n Catoms), which determine equilibrium alkoxide coverages through an adsorption constant $(\langle K_i \rangle, \langle K_n \rangle)$ that represents an average over all of its *j* alkoxide surface attachment modes,^[10] these adsorption constants lump the effects of physisorption into the voids and binding onto the inorganic frameworks, a formalism allowed because the equilibrium among extracrystalline, intracrystalline, and bound (alkoxide) forms of the alkene renders all species to be present at the same chemical potential. This equilibrium holds with the assumption that pore filling is low during catalysis. Adsorption data of light alkanes in Silicalite-1 at 473 K indicated that ethane and propane molecules do not reach saturation coverages until pressures well beyond 400 kPa.^[39] While isobutane did reach saturation at lower pressures (150-200 kPa), it is still below the pressures of isobutene in our studies. Here, alkanes are used as proxies for alkenes because their physisorption characteristics are nearly identical and physisorption data for alkenes is unavailable at 473 K because of their reactivity at such temperatures. Low pore-filling is also consistent with turnover rates during single component reactions that did not deviate from first-order for pressures up to 500 kPa, $^{\scriptscriptstyle [1]}$ as saturation would have resulted in a zero-order regime.

The first grouping of parameters in the numerator in Equation (1) $(\langle k_{i,n}K_i \rangle)$ accounts for the addition of an alkene with *n* C-atoms to an alkoxide with *i* C-atoms, while the second term $(\langle k_{n,i}K_n \rangle)$ represents the reaction of the alkene with *i* C-atoms to an alkoxide with *n* C-atoms. The $k_{i,n}$ and $k_{n,i}$ terms denote intrinsic rate constants for the coupling of alkenes with *i* and *n* carbons (again, the first subscript denotes the alkene that forms the alkoxide). These second-order constants $(\langle k_{i,n}K_i \rangle, \langle k_{n,i}K_n \rangle)$ reflect the ensemble averaging over all steps that add a given alkene with *n* C-atoms to all attachment isomers of an alkoxide derived from an alkene containing *i* C-atoms.

The second-order rate constants $(\langle k_{i,n}K_i \rangle + \langle k_{n,i}K_n \rangle)$ obtained by regressing the rate data (illustrative example for TON shown in Figure 1) for each alkene mixture (C₂–C₂, C₃–C₂, C₃–C₃, C₃–iC₄, iC₄–iC₄) to the functional form of Equation (1) are shown in Figure 2a for TON, SiAI, and HPW acids. Additional rates for different conditions and catalysts are not included because they have been reported in previous reports.^[1,10] The cross-coupling rate constants (i.e. propene with either ethene or isobutene) are extracted from Equation (1) and from the rates, expressed as the sum of the two possible C–C bond formation configurations (i.e. $\langle k_{i,n}K_i \rangle$ and $\langle k_{n,i}K_n \rangle$). The measured second-order rate constants reflect energy differences (in terms of Gibbs free energy; Equation (2) between the kinetically relevant C–C bond formation transition state and the gaseous reactant alkenes:

$$\Delta G_{i,n} = G_{i,n}^{\dagger} - G_{i}^{g} - G_{n}^{g} - G_{H}$$

$$\tag{2}$$

where \ddagger and g denote Gibbs free energies of the transition state (for the alkene with n C-atoms adding to an alkoxide with i C-atoms) and gaseous alkenes with i and n C-atoms, respectively. G_H is the Gibbs free energy of the catalyst. This



Figure 1. Formation rates of dimers and co-dimers from ethene and propene (a) and isobutene and propene (b) mixtures on H-TON [503 K; < 5% alkene conversion]. Dashed lines indicate regression fit from Equation (1).



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Figure 2. Measured rate constants from alkene coupling reactions of alkene mixtures (ethene + propene) and (propene + isobutene) on TON (\bigcirc), SiAI (\blacklozenge) and HPW (\blacksquare) as a function of (a) number of carbon atoms in the transition state (TS) and (b) diameter of a sphere with equivalent DFT-derived volume on TON. Ratios of rate constants relative to SiAI are given for TON (\bigcirc ; a) and HPW (\square ; a) [503 K; < 5% alkene conversion; dashed lines connect data points to guide the eye]. Proton affinities (\blacktriangle ; b) for the product alkenes (Figure 5) are given as a function of the equivalent TS diameter.

Gibbs free energy difference is related to the measured secondorder rate constants by Equation (3):

$$k_{i,n}K_i = \frac{k_BT}{h} \exp\left(-\Delta G_{i,n}/RT\right)$$
(3)

The magnitude of the measured rate constants increase as the number of C-atoms at the C-C coupling TS increases on all acids (Figure 2a (closed symbols)). These rate constants are larger on the stronger acid sites in HPW than on the weaker acid sites present in SiAl for all TS structures, where the acid strength is given by the respective deprotonation energies (DPE) of these solid acids (1090 kJ/mol,^[40] HPW; 1,190–1,222 kJ/ mol,^[6,41] aluminosilicates). This finding is consistent with previous work that showed first-order propene coupling rate constants decreased exponentially with increasing DPE for both a series of unconfined protons (Keggin structure with different central atoms) as well as a series of confined protons (Al, Fe, Ga, B isomorphously-substituted MFI).^[1] Figure 3 depicts the DFTderived TS structures for the five alkene coupling reactions on Al3-OH site on TON zeolites. The electronic energies are shown (referenced to two gaseous alkene molecules) along the reaction coordinate for the addition of a gaseous alkene to a bound alkoxide for all alkene combinations in the SI (Figure S1). All dimerization TS structures are more highly-charged (DFT partial charges: $+/-0.86-0.93 e^-$; Figure S3) than their covalently-bound alkoxide precursors (DFT: $+/-0.31\text{--}0.35~\text{e}^{-})^{[10]}$ and the uncharged gaseous alkene reactants. These charges are localized near the AI atom for both the alkoxide and the TS structures (shown for propene-propene coupling in Figure S4). As a result, the ion-pair TS benefits from the more stable conjugate anion in stronger acids preferentially over its less charged precursors, leading to a lower energy barrier (in terms of Gibbs free energy; Equation (2)), and thus a larger rate constant. The mechanistic interpretations of measured rates and their trends with TS size are in fact unaffected by whether the reactant alkene-derived bound precursors consist of alkoxides, H-bonded alkenes, or carbenium ions, because they lead to TS structures of similar size and shape, and rate constants are insensitive to the free energy of the bound precursor (Equation 2). A carbenium ion precursor would lead to a different charge than a covalently bound alkoxide, but measured equilibrium constants of alkene adsorption do not depend on acid strength,^[10] suggesting the precursor species is uncharged. Further, evidence from infrared spectroscopy and DFT in our previous studies have shown that alkoxides are the prevalent bound precursors for these reactants and catalysts at these conditions,^[1,10] leading us to consider them for these specific examples.

The large voids in HPW and SiAl acids interact with bound species through van der Waals contacts, but ones that are limited in comparison to microporous materials. Their void surfaces are essentially flat at the scale of molecular dimensions, thus leading to similar stabilization of the species through van der Waals contacts on both acids. The ratios of dimerization rate constants on HPW and SiAl are indeed similar for all TS sizes and much larger than unity (Figure 2a (open symbols)), because of the similar extent to which TS structures (irrespective of size) benefit from the more stable conjugate anion at such ion-pair transition states relative to their gaseous precursors. Consequently, the increase in rate constants with TS size must reflect cationic TS moieties that become more stable primarily because of their greater proton affinity and secondarily because of their more effective van der Waals contacts with the nearly flat surfaces of HPW/SiO₂ and SiAl solid acids.

The guest species size is redefined with a diameter $\langle d \rangle$ instead of by the number of C-atoms. The TS diameter ($\langle d \rangle$) is defined as that of the sphere with equivalent volume (V_{vdW}) to





Figure 3. DFT-derived TS structures for alkene coupling reactions on TON [AI3–OH site] for different chain lengths and substitution of the alkene precursors [RPBE-D3BJ], where (i + n) indicates the number of carbon atoms in the alkoxide and alkene, respectively.

that obtained for the DFT-derived transition state (Figure 4a for propene + secondary-propoxide TS) using solvent-excluded (Connolly^[42]) surfaces using a sphere (of solvent) with a radius of 0.05 nm (Figure 4b). These V_{vdW} and $\langle d \rangle$, as well as the surface area (SA_{vdW}), values are shown in Table 1 for all TS structures on TON; the effects of $\langle d \rangle$ on measured rate constants are depicted in Figure 2b (closed symbols). The use of $\langle d \rangle$ replaces the number of atoms with a more accurate description of TS size; such descriptions remain incomplete, however, because they account for the mean size, but ignore the shape, of the organic TS moieties. Transition states that are fairly spherical, like these small alkene-coupling TS, will have their characteristic size accurately approximated using this method, but this approximation will be less exact for TS that are more ellipsoidal in shape.

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Figure 4. (a) DFT-derived TS structure of propene addition to secondary propoxide on TON [Al3 site] with van der Waals radii and (b) equivalent van der Waals volume (V_{vdW}) calculated from enclosed volume of a Connolly surface.

Table 1. DFT-derived van der Waals volumes (V_{vdW}), surface areas (SA_{vdW}) and diameters ($\langle d \rangle$) of alkene coupling transition state structures for a given alkoxide and alkene measured on TON. The diameters are calculated assuming a sphere of equivalent volume.

Number of C- Atoms in TS	Alkoxide	Alkene	V _{vdW} [nm³]	SA _{vdW} [nm²]	$\langle d angle$ [nm]
4 5 6	p-ethoxide p-ethoxide s-propoxide s-propoxide	ethene propene ethene propene	0.077 0.101 0.102 0.118	1.07 1.23 1.20 1.38	0.528 0.578 0.579 0.609
7 8	s-propoxide t-butoxide t-butoxide	isobutene propene isobutene	0.135 0.136 0.153	1.54 1.58 1.71	0.636 0.638 0.664

To determine an energetic descriptor for the difference in TS stability, the DFT-derived proton affinities for the isomer of the gaseous alkene that forms in the C-C coupling step with the lowest energy barrier for each of the five alkene coupling reactions calculated. These are used here as proxies for the stability of the carbenium ions at the TS structures that form each of them. The molecular structure of each of these products and their respective carbenium ions are shown in Figure 5. The energy required to form the most stable cation for each molecule from a gaseous proton and a given gaseous alkene product is shown as a function of the diameter of the relevant TS in Figure 2b (open symbols). The proton affinity is calculated for this one isomer, because DFT-derived barriers for the formation of other isomers are much smaller for this specific path than for all others that lead to homodimerization reactions.^[1] Rapid secondary H-shifts and methyl-shifts lead to equilibrated mixtures of product isomers,^[17] thus precluding experimental verification of the identity of the specific isomer that preferentially forms as the first product of the C-C coupling step. The increase in proton affinity with TS size parallels the concomitant increase in measured rate constants as the number of C-atoms in the TS increase on these mesoporous acids (Figure 2b (open symbols) and Figure S2 (rate constants for TON, SiAl, and HPW as a function of proton affinity directly), consistent with such proton affinities as the appropriate descriptors of the stability of the organic cation at the TS. When van der Waals interactions with the inorganic surface are weak, as in mesoporous solid acids, the TS size appears to influence reactivity largely through its concomitant



Figure 5. Structures for the product alkenes from C–C bond formation reactions and their respective carbenium ions formed after protonation. These proton affinities, or the energy required to protonate at the specified position, are used as proxies for the stability of the corresponding carbenium ions at the C–C bond formation transition states.

effects on proton affinity. This descriptor, however, does not account for the effects of size on activation entropies, caused by the entropy loss upon formation of the TS, and for the consequences of entropy in Gibbs free energies. It also excludes the inevitable effects of size on van der Waals interactions even on nearly flat surfaces; the latter effects become much stronger on the curved surfaces present in zeolitic acids and account for the different trends in rate constants with TS proton affinity on TON, shown directly in Figure S2. These effects of TS size on van der Waals contacts are separated and addressed in detail next in the context of microporous solid acids.

The protons present in AI-TON and SiAI solids, and more generally on other aluminosilicate frameworks, show a similar range of acid strengths, as a result of their similar composition and thus the similar stability of their respective conjugate anions (DPE values: 1190–1222 kJ/mol^[41]). The small channels in TON (0.57 nm diameter^[31,43]) can provide significant van der Waals contacts with guest species; these interactions are much stronger than on large SiAl mesopores containing sites of similar acid strength. As a result, TON channels preferentially stabilize dimerization TS over gaseous alkenes through dispersive forces, especially as the TS size approaches that of the TON channels. TON indeed shows larger dimerization rate constants than SiAl (Figure 2a; ratios of TON to SiAl rate constants (open symbols) larger than unity). These rate enhancements conferred by TON channels, however, weaken as the TS structures become larger (e.g. enhancement ratios of 18.2 and 1.55 for $C_3 \! - \! C_3$ and $iC_4 \! - \! iC_4$, respectively; Figure 2a). These trends reflect enthalpic and entropic penalties imposed by the lattice and guest distortions that must occur for effective van der Waals contacts as confinement becomes tighter and the required orientations require more precision and specificity for larger TS structures when voids closely match their size and shape. The rate enhancement upon confinement is weaker for the bulkiest TS (iC_4 - iC_4) on TON than in SiAl; these differences do not reflect a distinct mechanism or the emergence of dimer desorption or diffusion with TS size since such effects are not observed in the experimental rate data or on the larger voids prevalent in the other solid acids.

DFT-derived free energy barriers for C–C coupling of alkenes on TON decrease with increasing TS size (Figure 6; electronic energy barriers Figure S1), as also shown by meas-



Figure 6. DFT-derived dispersive interaction energy on TON of the TS [Eq. (4); (\bigcirc)] and the energy barrier with respect to gas-phase alkenes in terms of either Gibbs free energy [Eq. (2); \blacksquare] or total electronic energy (\blacktriangle).

ured second order rate constants $\langle k_{i,n}K_i \rangle$ that increase with the number of C-atoms at the TS (Figure 2a). The RPBE-D3BJ functionals used here include dispersive contributions that can be separated from the quantum mechanical component of DFT-derived estimates of total energies. The van der Waals interaction energies between the TS and the zeolite framework (E_{vdW}^{+}) are obtained by subtracting the dispersive component of the protonated framework energy (E_{Z-H}) and the two gaseous alkenes that form the TS (E_{i}^{g}, E_{n}^{g}) from the dispersive component of the total electronic TS energies $(E_{i,n})$ [Eq. (4)]:

$$E_{vdW}^{\ \ } = E_{i,n}^{\ast} - E_{i}^{g} - E_{n}^{g} - E_{Z-H}^{g}$$
(4)

Such treatments consider all dispersive interactions among the atoms in the inorganic host and organic guest species, but



 E_{vdW}^{\dagger} retains only those energies associated with their interactions with each other (and not those among atoms within each moiety itself). These van der Waals contributions lead to energies that become monotonically more negative as the TS size increases, as expected from the more effective contacts inherent in the consequent tighter fits (Figure 6). These monotonic effects are not consistent, however, with the smaller isobutene dimerization rate constants on TON relative to those on SiAl (Figure 2a; open symbols), suggesting that an energetic penalty must act in a manner that compensates these stronger van der Waals interactions as the TS approaches the size of the confining voids. The calculated van der Waals energies account for the attractive part of these interactions and do not include any repulsion terms that prevail as electron clouds start to overlap. These repulsive interactions are included, however, in the quantum mechanical components of the total energies; consequently, the optimized structures using these functionals represent those with the minimum overall total energy for the system at the transition state.

Such compensating energy penalties reflect framework distortions that are quantified here using DFT-derived structures and the displacement of Si, O, and AI atoms in the host framework as the TS replaced the proton along the reaction coordinate. These distortions have been discussed previously during adsorption processes in the context of a flexibility window^[12-14] and empirical treatments of diffusive separations,^[15,16] but their specific impact on chemical reactivity has not been explored. The TS structures (Figure 3) for alkene coupling are fully-formed ion-pairs with the covalent C–O bond in alkoxide precursors fully cleaved at the TS (bond distances for the organic atoms and coordinates for all atoms are in Tables S2 and S3 for all five coupling TS). The center of mass of the carbenium ion moiety moves slightly towards the channel centerline as the alkene reacts with the alkoxide to form the TS.

Such displacement allows the organic moiety to interact with the largest number of framework atoms at channel walls. The framework atoms move slightly in a concerted manner towards the channel centerline, so as to shorten the distance and increase the van der Waals contacts with the organic moiety.

These displacements are described here using the TON channel centerline as the x and y origin with the z-direction aligned along the TON channel (Figure 7a). Each lattice atom *m* described by its coordinates, denoted as $[(x_{i,n}^{,+}, y_{i,n}^{,+}, z_{i,n}^{,+})_m]$ when it interacts with the TS formed from *i* and *n* alkenes and as $[(x^{H}, \theta^{H}, z^{H})_m]$ in the protonated framework, which is the same for all TS studied here. The total displacement of each lattice atom *m* in the TS form relative to the proton form is given by $\Delta p_{i,n_m}$ [Eq. (5)]:

$$(\Delta p_{i,n_m})^{2} = \left(x_{i,n_m}^{+} - x_{m}^{H}\right)^{2} + \left(y_{i,n_m}^{+} - y_{m}^{H}\right)^{2} + \left(z_{i,n_m}^{+} - z_{m}^{H}\right)^{2}$$
(5)

and the root mean square average displacement for all the M atoms in each transition state is given by [Eq. (6)]:

$$\langle p_{i,n} \rangle = \frac{1}{M} \sum_{m}^{M} p_{i,n_m} \tag{6}$$

Figure 7b shows $\Delta p_{i,n_m}$ values for individual atoms as a function of their location in the z-direction in TON (grouped as 0.2 nm bins) for the propene and isobutene homodimerization TS structures. The maximum $\Delta p_{i,n_m}$ occurs for lattice atoms *m* at the longitudinal position along the channel corresponding to the location of the Al-atom, which is consistent for all other TS structures (SI; Figure S5). The widths at half-maximum for $\Delta p_{i,n_m}$ values are similar to the TS diameter ($\langle d_{i+n} \rangle$), indicative of distortions that remain localized near the TS. The O-atoms within circles in Figure 8 are those in the TS for isobutene



Figure 7. Coordinate system for TON zeolite (left) and squared displacements $[(\Delta p)^2; Eq. (5); binned every 0.2 nm; right]$ of lattice oxygen between TS and H-form or C₈ and C₆ formation on TON as a function of Z (down the channel), where (i + n) indicates the number of carbon atoms in the alkoxide and alkene, respectively. Z_{Al} is the location of the Al and $< d_8 >$ and $< d_6 >$ are the respective TS diameters, which are similar to the breadth of the distortions.



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Figure 8. Location of distortions from C₈ TS on TON as viewed from the top and the side. O-atoms highlighted in circles (and in green) have displacements [Δp ; Equation (5)] that are more than one standard deviation from mean [$<\Delta p$ >; Eq. (6)].

homodimerization with $\Delta p_{i,n_m}$ displacements larger than a standard deviation from the mean displacements. These distortions are again strongest at locations nearest the TS structure (all TS structures in Figure S6, SI) for the smaller TS, but extend over somewhat longer distances for larger TS structures.

The directionality of the displacements towards the channel centerline for a C–C bond formation TS between *i* and *n* alkenes is given by the value of $\langle \Delta r_{i,n} \rangle$ [Eqs. (7)-(9)].

$$(r_{i,n-m}^{j})^{2} = (\mathbf{x}_{i,n-m}^{j})^{2} + (\mathbf{y}_{i,n-m}^{j})^{2} \quad (\mathbf{j} = \mathbf{H}, \ \pm)$$
 (7)

$$\Delta \mathbf{r}_{i,n_m} = \mathbf{r}_{i,n_m}^{+} - \mathbf{r}_{i,n_m}^{H} \tag{8}$$

$$\langle \Delta \mathbf{r}_{i,n} \rangle = \frac{1}{M} \sum_{m}^{M} \Delta \mathbf{r}_{i,n_m}$$
⁽⁹⁾

For the O-atoms within the first shell at the channel wall, the values of $\langle \Delta r_{i,n} \rangle$ in Figure 9a for the smaller TS structures (e.g., ethene-ethene, ethene-propene coupling) are negative, which indicates that the O-atoms move towards the channel centerline. For larger TS structures, $\langle \Delta r_{i,n} \rangle$ values are positive, which indicates the O-atoms in the first shell from away from the channel centerline (and the TS) so as to minimize the electron cloud overlap and Pauli repulsion contributions to the quantum mechanical energy component. The magnitude of these outward displacements is most significant for the bulkiest transition states ($\langle \Delta r \rangle = +0.33$ pm for isobutene vs. +0.055 pm for propene homodimerization), while the inwards displacements are most evident for the smaller transition states ($\langle \Delta r \rangle = -0.21$ for ethene homodimerization vs. -0.063 for ethene-propene coupling). Figure 9a provides compelling evidence for the distortions required to reach the minimum overall TS energy through a compromise between stronger van der Waals contacts and the energy penalties incurred in the framework distortion required to achieve such contacts. Such compromises are inherently ignored by theoretical treatments that neglect attractive dispersion forces, which reflect induced dipole non-covalent effects neglected in quantum mechanical treatments.

These energy penalties from framework distortions are given by the differences in total energy between the protonated framework (E_2) and that contain a TS formed by the proton transfer of the proton to an organic moiety containing the two alkene reactants (E_{Z^*}).

$$\Delta E_{distortion} = |E_{Z}^{*} - E_{Z}| = \left| \left(E_{Z}^{*} - E_{organic} \right) - \left(E_{Z-H} - E_{H} \right) \right|$$
(10)

Here, the $E_{Z^{*+}}$ and E_{Z-H} terms are the D3BJ (attractive) interaction energies for the optimized transition state and proton structures (Si, Al, O, C, and H atoms), respectively; $E_{organic}$ and E_{H} represent the dispersive energies of the organic

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Figure 9. (a) Mean oxygen displacement $[<\Delta r>$; [pm]; Eqs. (7)–(9)] between H-form and TS of lattice oxygen in the first shell of the pore network in TON as a function of equivalent TS diameter (<*d*>) and (b) Distortion energies [Eq. (10)] for TS on TON relative to the H-form.

transition state and the proton (C and H atoms only), respectively. These energies thus exclude the effect of the distortions associated with atomic displacements in the organic moieties, so as to isolate the energy costs required for these framework distortions (Si, Al, and O atoms). Figure 9b shows the values of $\Delta E_{distortion}$ [Eq. (10)] as a function of the diameter of the transition state organic moieties lead to more costly distortions in order to gain the van der Waals contacts that lead to minimum total energies for the relevant transition states. Such effects are undoubtedly more consequential for larger transition states than those for which we have shown their significant relevance in this study.

Conclusions

C-C bond formation during coupling reactions of ethene, propene, and isobutene using microporous and mesoporous acids with different acid strength and void size was investigated experimentally and using density functional theory (DFT). Measured second order rate constants of alkene coupling reactions, which reflect free energy differences between C-C bond formation transition states (TS) and gaseous reactant alkenes, increase with increasing TS size irrespective of acid strength or confinement due to combined effects of size and substitution on the proton affinity of the alkene products and on van der Waals contacts between carbocations and void surfaces. This measured increase on mesoporous acids (SiAl and HPW) is predominately due to increased stability of the carbocation, consistent with DFT-derived proton affinities of the product alkenes. The second order rate constants also increase with increasing TS size on TON zeolite has additional effects of more effective van der Waals contacts with the microporous void surfaces. However, selectivity to transition states that are

near the size of the pores in which they are formed is decreased in TON relative to mesoporous acids without pores of molecular dimension. The local environment around the organic moieties distorts to increase the van der Waals interactions with the lattice oxygen and the organic atoms as examined from DFT treatments that rigorously account for van der Waals interactions pertinent in microporous materials. Distortions are quantified here in terms of O-atom displacement and dispersive interaction energy of inorganic atoms, both of which indicate that distortions increase with increasing chain length and substitution of the TS. However, these structural distortions recover the concomitant enthalpy penalties through more effective van der Waals contacts between the inorganic framework and the organic moiety, while also balancing the associated entropy losses of tighter confinements. This study utilizes reactants and catalysts that vary in size, shape, and charge systematically so that such details (proton affinity, van der Waals interactions, acid strength, and distortions) become separable. The results indicate that these are the important descriptors that must be considered in the design and optimization of host-guest pairs that leads to the preferential stabilization of specific transition states and to reach desired reactivity and selectivity for other reactions and catalyst systems.

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Conflict of Interest

The authors declare no conflict of interest.

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