



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

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

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(dehydrogenation 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 H-transfer 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 NH₄⁺-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% O₂ in He stream (83.3 cm³ g⁻¹ s⁻¹, Praxair) by heating to 818 K (at 0.025 K s⁻¹) and holding for 3 h to convert the NH₄⁺ to H⁺, and then cooled to 503 K. *n*-Butane (99.9%, Praxair), isobutane (99.9%, Praxair) or 2-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 × 0.32 mm × 1.05 μm 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 × 1 × 1 Monkhorst–Pack k-point mesh was used to sample the first Brillouin 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

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