Mechanism of Isobutanal–Isobutene Prins Condensation Reactions on Solid Brønsted Acids

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Supporting Information

ABSTRACT: The selectivity to 2,5-dimethyl-hexadiene isomers (2,5-DMH) via acid-catalyzed isobutanal−isobutene Prins condensation is limited by isobutene oligomerization reactions (to 2,4,4-trimethyl-pentene isomers) and by skeletal isomerization and cyclization of the primary 2,5-DMH products of Prins condensation. Experiment and theory are used here to assess and interpret acid strength effects on the reactivity and selectivity for isobutanal−isobutene Prins condensation routes to 2,5-DMH, useful as precursors to p-xylene. Non-coordinating 2,6-di-tert-butylpyridine titrants fully suppress reactivity on Keggin heteropolyacids, niobic acid, and mesoporous and microporous aluminosilicates, indicating that Prins condensation, parallel isobutene oligomerization, and secondary skeletal isomerization and cyclization of primary 2,5-DMH products occur exclusively on Brønsted acid sites. The number of titrants required to suppress rates allows site counts for active protons, a requirement for comparing reactivity among solid acids as turnover rates, as well as for the rigorous benchmarking of mechanistic proposals by theory and experiment. Kinetic and theoretical treatments show that both reactions involve kinetically relevant C−C bond formation elementary steps mediated by cationic C−C coupling transition states. Transition state charges increase with increasing acid strength for Prins condensation, becoming full carbenium-ions only on the stronger acids. Oligomerization transition state structures, in contrast, remain full ion-pairs, irrespective of acid strength. Turnover rates for both reactions increase with acid strength, but oligomerization transition states preferentially benefit from the greater stability of the conjugate anions in the stronger acids, leading to higher 2,5-DMH selectivities on weaker acids (niobic acid, aluminosilicates). These trends and findings are consistent with theoretical estimates of activation free energies for Prins condensation and oligomerization elementary steps on aluminosilicate slab and Keggin heteropolyacid cluster models. High 2,5-DMH selectivities require weak acids, which do not form a full ion-pair at transition states and thus benefit from significant stabilization by residual covalency. These trends demonstrate the previously unrecognized consequences of incomplete proton transfer at oxygen-containing transition states in dampening the effects of acid strength, which contrast the full ion-pair transition states and stronger acid strength effects in hydrocarbon rearrangements on solids acids of catalytic relevance. These mechanistic conclusions and the specific example used to illustrate them led us to conclude that reaction routes involving O-containing molecules become prevalent over hydrocarbon rearrangements on weak acids when parallel routes are accessible in mixtures of oxygenate and hydrocarbon reactants.

KEYWORDS: isobutene, isobutanal, Prins reaction, oligomerization, 2,5-dimethyl-hexadienes, solid acid, acid strength, density functional theory

1. INTRODUCTION

The acid-catalyzed electrophilic addition of alkanals to alkenes, known as the Prins reaction, selectively forms C−C bonds between the terminal C atoms in the two reactants to form specific Cₙ skeletal structures (n > 4); these backbone structures are not accessible via C−C bond formations in aldol condensation nor oligomerization reactions. For isobutanal−isobutene mixtures, which can be derived from isobutanol, Prins condensation reactions form 2,5-dimethyl-hexadiene (2,5-DMH) molecules that are convenient precursors to p-xylene (Scheme 1), a chemical precursor to terephthalic acid. Isobutanol can be formed from carbohydrates via fermentation, from ethanol−methanol mixtures via aldol condensation, or from CO–H₂ mixtures via sequential hydrogenation and condensation reactions on bifunctional catalysts (e.g., Cu/MgCeOₓ, Cu/ZnO/Cr₂O₃, and Pd/ZrO₂/ZnO/MnOₓ). The successful deployment of active, selective, and stable Prins condensation catalysts would create alternate routes to p-xylene and its derivatives and could do so entirely from renewable resources.

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Solid acids, such as Nb$_2$O$_5$·nH$_2$O,$^{6,7,18}$ WO$_3$/TiO$_2$, 7
heterosilicates, $^{6,9,19,20}$ and zirconium and niobium phosphates,$^{21}$ catalyze alkanal–alkene Prins condensation in parallel with alken e oligomerization$^{22}$ and isomerization, cyclization, and β-scission of the primary products formed via Prins condensation reactions.$^{2,3,24}$ Formaldehyde–isobutylen e condensation to isoprene occurs more selectively on H-B-MFI than on stronger acids (i.e., H-Al-FAU and H-Al-MFI),$^{19}$ indicating that these undesired reactions may be suppressed relative to condensation reactions on weaker acids. Previous studies, however, have remained silent about the number or type of catalytically relevant acid sites, and their reactivity has not been rigorously reported as turnover rates.$^6$–$^9$ Such details are required for benchmarking density functional theory (DFT) and experiments based on activation free energies. Such benchmarking allows, in turn, rigorous assessments of the benchmarking allows, in turn, rigorous assessments of the fundamental underpinnings for the e xploratory work, whereas the Lewis acid sites and the 5
respectively (Table S1, SI). Niobic acid (Nb$_2$O$_5$·nH$_2$O; Nb$_2$O$_5$/H$_2$O 5.1 molar, 118 m$^2$ g$^{-1}$) was obtained from CBMM (Companhia Brasileira de Metallurgia e Minação). The H$_3$PW$_12$O$_{40}$/SiO$_2$ catalyst (5% wt. POM, 0.04 POM nm$^{-2}$) was prepared by incipient wetness impregnation of SiO$_2$ (Cab-O-Sil HS-S, 310 m$^2$ g$^{-1}$) with an ethanol solution of H$_3$PW$_12$O$_{40}$ (Sigma-Aldrich, reagent grade).$^3$

H-Al-MCM-41, H-ASA, and H-CD-FAU were treated in flowing dry air (Praxair, 99.999%, 1.67 cm$^3$ g$^{-1}$ s$^{-1}$) by heating to 823 K (at 0.025 K s$^{-1}$) and holding for 5 h; Nb$_2$O$_5$·nH$_2$O and 5% wt. H$_3$PW$_12$O$_{40}$/SiO$_2$ were treated similarly but at lower temperatures (573 K) in order to prevent structural degradation. All catalyst samples were then pressed, crushed, and sieved to retain 106–180 μm aggregates. X-ray diffraction (XRD) measurements (Bruker D8 Advance; Cu Kα radiation, λ = 0.15418 nm, 40 kV, 40 mA) were used to confirm their respective crystal structures; diffractograms were measured in the 5–60° range of 2θ using a scan rate of 0.033° s$^{-1}$ and finely ground powders held onto quartz slides.

2.2. Catalytic Rates and Selectivities. Steady-state rates of isobutanal–isobutene reactions were measured in a tubular quartz reactor with plug-flow hydrodynamics at 453–633 K. Samples (0.020–0.6 g) were held as a packed-bed and treated in flowing air (Praxair, 99.999%, 1.67 cm$^3$ g$^{-1}$ s$^{-1}$) by heating to the required reaction temperature (at 0.0833 K s$^{-1}$) and holding for 4 h before rate measurements. Temperatures were controlled using a resistively heated furnace and a temperature controller (Watlow, Series 988) and measured using a K-type thermocouple (0.05 cm diameter, 16 cm length, Omega) held against the outer reactor wall at the location of the catalyst bed.

Isobutanal (Sigma-Aldrich, ≥ 99%) was fed using a syringe pump (Cole Parmer, 74900 series) into isobutene (Praxair, 99%) and He (Praxair, 99.999%) flows that were metered by mass flow controllers (Porter, Model 201). Transfer lines after the liquid injection point were held at 433 K using heating tape (Omega) to prevent condensation of reactants or products. The concentrations of reactants and products were measured by online gas chromatography (Agilent 6890) using a methyl silicone capillary column (Agilent HP-1, 50 m, 0.32 mm ID; 1.05 μm film) and flame ionization detection. Known standards and speciation by mass spectrometry after chromatographic

Scheme 1. Proposed Pathways for p-Xylene Synthesis from Isobutanol

- [Scheme 1](#)

- [Scheme 1](#)
separations (HP 5972 GC/MS) using a similar column and similar heating protocols were applied to confirm the identity and to determine the detector response factors for all species present in effluent streams. Isomers with different C=C bond positions (i.e., alkenes and alkadienes) were separable by chromatographic retention time but could not be individually identified because of their identical mass spectra; these isomers were lumped together in reporting rates and selectivities. All reported rates were measured at differential reactant conversions (<5%) and corrected for any intervening deactivation by rates periodically measured at a reference condition (1.0 kPa isobutene, 2.0 kPa isobutanal, 473 K).

2.3. Selective Titrations of Brønsted Acid Sites by 2,6-Di-tert-butylpyridine during Catalysis. Protons on H-Al-MCM-41, H-ASA, Nb2O5·nH2O, and H3PW12O40/SiO2 were titrated using 2,6-di-tert-butylpyridine (DTBP; Aldrich, > 97%) during reactions of isobutanal–isobutene reactant mixtures (1.0 kPa isobutene, 2.0 kPa isobutanal, 473 K). In these experiments, Prins condensation and alkene oligomerization rates were measured for about 1 h before the introduction of DTBP, and the reactant mixture was then replaced with one containing DTBP in the liquid isobutanal component of the isobutanal–isobutene reactants (isobutanal/DTBP = 200–1000 molar) to give a DTBP pressure of 2–10 Pa. The concentrations of the reactants, products, and titrant were measured using the chromatographic protocols described above. The number of accessible protons in each sample was determined from titrant uptakes required to fully suppress isobutanal–isobutene reactions (assuming a 1:1 DTBP/H+ adsorption stoichiometry). The proton density of H-CD-FAU (0.37 H+/Al) was measured from the DTBP titration during CH3OH dehydration (0.5 kPa CH3OH, 0.1 kPa DTBP, 433 K) using methods described elsewhere.

2.4. Density Functional Theory Methods. The energetics of the elementary steps involved in acid-catalyzed isobutanal–isobutene Prins condensation and isobutene oligomerization reactions were examined using periodic plane-wave DFT as implemented in the Vienna ab initio simulation package (VASP). All calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and projector augmented-wave (PAW) pseudopotentials (energy cutoff 396 eV). Convergence criteria were 1 × 10−6 eV for energies and 0.05 eV Å−1 for forces on all atoms. The van der Waals interactions between atoms were taken into account by including Grimme’s D3BJ dispersion corrections after each step in the energy minimization algorithm. DFT calculations were carried out using model solids consisting of amorphous aluminosilicate slabs and Keggin POM clusters. The aluminosilicate slabs were built based on reported pure Si MCM-41 silanol-terminated surfaces. These model surfaces exhibit isolated silanols with vibrational

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frequencies around 3740 cm⁻¹ and a range of diverse H-bonded silanols with vibrational frequencies centered at 3550 cm⁻¹, these DFT estimates are consistent with those observed on pure silica MCM-41 materials (3745 and 3536 cm⁻¹, respectively). A four-layer silicate slab of 1.2 nm thickness (Si₉₀O₁₂₄H₄ per unit cell; Scheme 2) was extracted from the channel wall of the Si MCM-41 model (0.24 surface silanol nm⁻²); the lateral dimensions of the cell are 1.3 nm × 1.3 nm (Scheme 2), which are large enough to avoid repulsive lateral interactions between reactants or transition states in vicinal cells (the distance between organic moieties in vicinal cells above 0.9 nm; an example of the Prins condensation C–C coupling TS is shown in Figure S1, SI). A Si atom on the top surface was then replaced by an Al atom, and an extra H atom was attached to one of the O atoms bound to the Al atom to maintain charge neutrality (Si₅₉AlO₁₂₄H₄ per unit cell; Scheme 3a). Periodic images of this aluminosilicate slab were separated by a 4.0 nm vacuum region in the z-direction; dipole and quadrupole interactions between images along this direction were corrected during each geometric optimization step. A 2 × 2 × 1 Monkhorst–Pack k-point mesh was used to sample the first Brillouin zone for simulations using this aluminosilicate slab.

Full Keggin clusters (H₂₈₋ₓXₓWₓO₁₄₋ₓ₋₂₋ₓ₋₄₋ₓ₋₈₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₋x₋₁₀, 1204 kJ mol⁻¹; RPBE) and those reported for microporous aluminosilicates (1201 ± 11 kJ mol⁻¹, RPBE) are consistent with the lack of any effects of the local structure/coordination on DPE values for aluminosilicates and Keggin polyoxometalates (POM) and also indicates that this construct of the aluminosilicate slab provides a practical and computationally tractable model to examine the acid strength and reactivity of unconfined aluminosilicate protons. DFT-derived DPE values were 1073–1204 kJ mol⁻¹ (PBE; Table 1) for the Keggin clusters and aluminosilicate slab models; their broad range allows the systematic examination of the effects of acid strength on reactivity for isobutanal–isobutene Prins condensation and isobutene oligomerization reactions.

Transition state (TS) structures for all elementary steps were first optimized using the nudged elastic band (NEB) method with convergence criteria of 1 × 10⁻⁵ eV for energies and of 0.2 eV Å⁻¹ for the forces on each atom. Converged TS structures were then optimized using the dimer method with more stringent convergence criteria for electronic energies (1 × 10⁻⁶ eV) and forces (0.05 eV Å⁻¹). A frequency analysis (calculation parameters described below) was used to confirm that the TS structure exhibited a single imaginary frequency, characteristic of the molecular vibration along the reaction coordinate. Löwdin population analyses were performed to examine the charge distribution in all reactants and TS structures.

Table 1. DFT-Derived Deprotonation Energies (DPE) for the Aluminosilicate Slab and Keggin W Polyoxometalate Cluster Models

<table>
<thead>
<tr>
<th>Cluster Model</th>
<th>PBE</th>
<th>RPBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminosilicate slab</td>
<td>1204</td>
<td>1212</td>
</tr>
<tr>
<td>H₂AW₁₂O₄₀</td>
<td>1123</td>
<td>1137</td>
</tr>
<tr>
<td>H₂SW₁₂O₄₀</td>
<td>1109</td>
<td>1121</td>
</tr>
<tr>
<td>H₂PW₁₂O₄₀</td>
<td>1087</td>
<td>1101</td>
</tr>
<tr>
<td>H₂SW₁₂O₄₀</td>
<td>1073</td>
<td>1089</td>
</tr>
</tbody>
</table>

*Unit: kJ mol⁻¹; protons involved in the calculations are indicated in Scheme 3.*
Equilibrium constants between regioisomers involved in isobutanal–isobutene Prins condensation and isobutene oligomerization products (i.e., C₈ dienes and alkenes) were estimated from DFT-derived free energies of formation for these unsaturated C₈ hydrocarbons. Such free energies of formation were calculated using the G4MP2 composite theoretical method implemented in the Gaussian 09 program to reach accuracy within 4 kJ mol⁻¹.

3. RESULTS AND DISCUSSION

3.1. Effects of Acid Strength on the Selectivities of Isobutanal–Isobutene Reactions on Solid Acids.

The Prins condensation reactions of isobutanal–isobutene mixtures led to 2,5-dimethyl-hexa-1,3-diene (2,5-DMH) reformed; consisting of isomers with different C=C bond positions, e.g., 2,5-dimethyl-hexa-2,4-diene and cis/trans-2,5-dimethyl-hexa-1,3-dienes on all solid acid catalysts (Keggin H₃PW₁₂O₄₀/SiO₂, H-Al-MCM-41, H-ASA, H-CD-FAU, and Nb₂O₅·nH₂O). Isobutene oligomerization products, predominantly consisting of 2,4,4-trimethyl-pentene positional isomers (2,4,4-TMP), skeletal isomerization products of 2,5-DMH to dienes with different skeletal backbones (2,4,4-DMH and 3,4-DMH), and cyclization products of 2,5-DMH to 1,4-dimethyl-cyclohexene (1,4-DMCH) (Scheme 4) were also detected. As in the case of 2,5-DMH, the skeletal isomerization and cyclization reactions of the other products (e.g., 2,4,4-TMP, 2,4,4-DMH, and 3,4-DMH) were also observed but at rates that were 10-fold smaller than those for the other reactions. These products are lumped as the combined formation rates of 2,5-DMH and the products of 2,5-DMH to 1,4-dimethyl-cyclohexene (1,4-DMCH) (Scheme 4) were also detected. As in the case of 2,5-DMH, the skeletal isomerization and cyclization reactions here-are the sum of 2,5-DMH positional isomers and its skeletal and cyclization isomers, to 2,4,4-TMP products did not depend on conversion (3.3 ± 0.2; Figure 1a), consistent with the primary nature of both Prins condensation and oligomerization reactions of isobutanal–isobutene reactants. Similar selectivity trends were also observed on aluminosilicates (H-Al-MCM-41 20 ± 1, Figure 1b; H-CD-FAU 18 ± 1, Figure 1c; H-ASA 19 ± 1, section S5, SI) and on Nb₂O₅·nH₂O (9.6 ± 0.5, Figure 1d), indicative of a similar reaction network on all solid acids. Condensation/oligomerization selectivity ratios are significantly higher on the weaker aluminosilicate acids (DPE 1204 kJ mol⁻¹; Table 1) than on H₃PW₁₂O₄₀ acids (1087 kJ mol⁻¹); these effects of acid strength are discussed based on the elementary steps and transition states involved in section 3.6. They appear to indicate that the strength of the acid sites in Nb₂O₅·nH₂O is intermediate between those of the acid sites present in aluminosilicates and H₃PW₁₂O₄₀ an inference that cannot be confirmed by DFT methods because the uncertain structure of the conjugate anion in Nb₂O₅·nH₂O solids precludes any reliable structural models on which to estimate DPE values. Selectivities to products of skeletal isomerization and cyclization reactions of 2,5-DMH on aluminosilicates and Nb₂O₅·nH₂O (<15% and 2% at 8–10% isobutene conversion, respectively; Figure 1b–d) were also much lower than on H₃PW₁₂O₄₀/SiO₂ (54% and 3%, respectively, Figure 1a), indicative of the stronger dependence on acid strength of these reactions relative to the Prins condensation steps that form 2,5-DMH. These data show that the rates of all reactions decrease with increasing DPE values of solid acids but that Prins condensation reactions are more weakly affected than oligomerization or secondary reactions, leading to a preference for 2,5-DMH Prins condensation products over those of oligomerization, skeletal isomerization, and cyclization on weaker acids.

3.2. Site Titrations during Isobutanal–Isobutene Reactions on Solid Acids.

Non-coordinating 2,6-di-tert-butylpyridine (DTBP) titrants were introduced during isobutanal–isobutene reactions to determine the number and type of acid sites responsible for the products observed. DTBP is irreversibly protonated on Bronsted acids but cannot coordinate with Lewis acid centers because of the significant steric hindrance at its N atom. Titration with DTBP fully suppressed rates for Prins condensation reactions (rPrins, defined as the combined formation rates of 2,5-DMH and the products of its skeletal isomerization and cyclization reactions here-inforth) and for oligomerization reactions (rOligo) in a concurrent manner on all solid acids (e.g., H₃PW₁₂O₄₀/SiO₂ and H-Al-MCM-41 in Figure 2; H-ASA and Nb₂O₅·nH₂O in section S6, SI). These data show that both reactions occur exclusively on the same Bronsted acid sites present on each solid acid. The number of these active protons is given by the amount of DTBP required to fully suppress each of two rates. These proton counts are reported in Table 2 for each sample and are used to calculate turnover rates, a measure of the
Figure 1. Selectivities of 2,5-DMH (●) and the respective skeletal (□) and cyclized (△) isomers and 2,4,4-TMP (◊) as a function of isobutene conversion on (a) H₃PW₁₂O₄₀/SiO₂, (b) H-Al-MCM-41, (c) H-CD-FAU, and (d) Nb₂O₅·nH₂O (473 K; 2.0 kPa isobutanal; 1.0 kPa isobutene). The dashed curves indicate trends.

Figure 2. Isobutanal—isobutene Prins condensation (rₚrins) and isobutene oligomerization (rₜₚₜₚ) rates as a function of cumulative 2,6-di-tert-butylpyridine (DTBP) uptakes on (a) H₃PW₁₂O₄₀/SiO₂ and (b) H-Al-MCM-41 (473 K; 2.0 kPa isobutanal; 1.0 kPa isobutene; DTBP 2.0 Pa for H₃PW₁₂O₄₀/SiO₂ and 2.5 Pa for H-Al-MCM-41). The dashed lines represent linear regression fits.
Table 2. Proton Densities, Turnover Rates for Isobutanal Oligomerization ($r_{\text{oligo}}$) and for Isobutanal–Isobutene Prins Condensation ($r_{\text{prins}}$), and Ratios of the Two Rates on Solid Acid Catalysts$^{a}$

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$H_3PW_{12}O_{40}$/SiO$_2$</th>
<th>Nb$_2$O$_5$·nH$_2$O</th>
<th>H-CD-FAU</th>
<th>H-Al-MCM-41</th>
<th>H-ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$ density (mmol g$^{-1}$)</td>
<td>0.049</td>
<td>0.017</td>
<td>1.4</td>
<td>0.15</td>
<td>0.064</td>
</tr>
<tr>
<td>$r_{\text{oligo}}$</td>
<td>11.2</td>
<td>2.3</td>
<td>1.0</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$r_{\text{prins}}$</td>
<td>35.6</td>
<td>20.6</td>
<td>18.1</td>
<td>14.8</td>
<td>14.3</td>
</tr>
<tr>
<td>$r_{\text{skeletal}}$</td>
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<td>19.2</td>
<td>16.9</td>
<td>14.1</td>
<td>13.5</td>
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<tr>
<td>$r_{\text{cyclization}}$</td>
<td>11.6</td>
<td>1.1</td>
<td>1.0</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$r_{\text{prins}}/r_{\text{oligo}}$</td>
<td>3.2</td>
<td>9.0</td>
<td>18</td>
<td>20</td>
<td>19</td>
</tr>
</tbody>
</table>

$^a$473 K, 2.0 kPa isobutanal, 1.0 kPa isobutene, 3% isobutene conversion; $r_{\text{prins}}$ is the sum of formation rates of 2,5-DMH ($r_{2,5-DMH}$) and the products of its skeletal isomerization ($r_{\text{skeletal}}$) and cyclization ($r_{\text{cyclization}}$).

intrinsic reactivity of the Brønsted acid sites in each sample. The accurate assessment of turnover rates allows, in turn, rigorous comparisons among catalyst samples and also between measured rates and those derived from DFT treatments of plausible elementary steps for Prins condensation and oligomerization catalytic sequences (section 3.6).

3.3. Turnover rates of Isobutanal–Isobutene Reactions on Solid Acids. Both isobutanal–isobutene Prins condensation and isobutene oligomerization rates ($r_{\text{prins}}$, $r_{\text{oligo}}$) on solid acids decreased with time on stream ($H_3PW_{12}O_{40}$/SiO$_2$ and H-Al-MCM-41 as illustrative examples shown in section S7, SI), but the $r_{\text{prins}}/r_{\text{oligo}}$ ratios remained essentially unchanged throughout (3.5 ± 0.2 for $H_3PW_{12}O_{40}$/SiO$_2$; 21 ± 2 for H-Al-MCM-41; section S7, SI), consistent with the involvement of the same Brønsted acid sites in both reactions (section 3.2) and with deactivation processes that merely remove sites instead of changing their reactive properties. $H_3PW_{12}O_{40}$/SiO$_2$ and H-Al-MCM-41 showed similar deactivation rate constants (0.12 vs 0.16 ks$^{-1}$, section S7, SI) but distinct selectivities to Prins condensation and oligomerization products ($r_{\text{prins}}/r_{\text{oligo}}$ 3.5 ± 0.2 vs 21 ± 2), indicating that the deactivation rates do not depend sensitively on the prevalent concentration of any specific products but are likely to reflect instead intrinsic side reactions from common precursors involved in Prins condensation and oligomerization pathways.

All rate data reported herein were corrected for deactivation by periodically returning to standard conditions as described in section 2.2 when measuring Prins condensation and oligomerization rates at different reactant pressures or temperatures. Table 2 depicts turnover rates for isobutanal–isobutene Prins condensation and isobutene oligomerization reactions on all solid acid catalysts examined in this study (473 K; 2.0 kPa isobutanal; 1.0 kPa isobutene). The turnover rates for both reactions were higher on $H_3PW_{12}O_{40}$/SiO$_2$ than on weaker acids (Nb$_2$O$_5$·nH$_2$O, H-CD-FAU, H-Al-MCM-41, and H-ASA), indicating that both reactions are mediated by cationic TS, which contain conjugate anionic moieties that become more stable with increasing acid strength.$^{41}$ In contrast, $r_{\text{prins}}$, $r_{\text{oligo}}$ ratios were larger on weaker acids (Table 1), as also evident in their selectivities at all isobutene conversions (0–15%; Figure 1). These trends indicate that the charge difference between the cationic transition states for Prins condensation ($TS_{\text{prins}}$) and oligomerization ($TS_{\text{oligo}}$) is larger on the weaker acids. DFT treatments show that the extent of protonation of the isobutanal-derived moiety involved in $TS_{\text{prins}}$ increases as the acid becomes stronger, leading to a concomitant increase in the charge of the $TS_{\text{prins}}$ structure with increasing acid strength (+0.73 on aluminosilicates; +0.94 on $H_3PW_{12}O_{40}$; section 3.6); in contrast, fully formed carbenium ions are present at $TS_{\text{oligo}}$ structures, irrespective of the acid strength, leading to charges of $TS_{\text{oligo}}$ structures close to unity on all acid catalysts, as also observed in previous studies.$^{3,22}$ As a result, $TS_{\text{oligo}}$ benefits

![Figure 3](https://example.com/figure3.png)

Figure 3. Effects of temperature on the (a) rates of isobutanal–isobutene Prins condensation ($r_{\text{prins}}$) and isobutene oligomerization ($r_{\text{oligo}}$) and (b) selectivities of isobutanal–isobutene reactant mixtures at 10% isobutene conversion (H-Al-MCM-41; 20 kPa isobutanal; 20 kPa isobutene). The dashed curves indicate trends. Solid lines represent exponential regression fits. Activation enthalpies ($\Delta H^\ddagger$) for Prins condensation and oligomerization reactions at 473 K were calculated from the exponential regression fits according to the Arrhenius equation ($E_a = -R \frac{d \ln(r)}{d(1/T)}$, where $E_a$ is the activation energy, $r$ is the reaction rate; $\Delta H^\ddagger = E_a + RT$) and were shown beside the respective rate data.
more significantly from the stability conferred by the more stable conjugate anions of the stronger acids than TS\textsubscript{Prins}, causing the selectivity to Prins reaction products to increase as acid sites weaken. Such effects of acid strength ultimately weaken for stronger acids because both TS\textsubscript{Prins} and TS\textsubscript{oligo} structures become full ion-pairs and similarly sensitive to the stability of the conjugate anions at the TS. Fully formed carbenium ions are also involved in the transition states that mediate secondary isomerization and cyclization reactions of primary 2,5-DMH products\textsuperscript{3} stronger acids thus favor these transition states over the less charged TS structures that mediate the primary formation of the 2,5-DMH Prins reaction products (Table 1). These effects of acid strength on reactivity and selectivity are confirmed in section 3.6 using density functional theory (DFT) calculations.

The strength of Bronsted acid sites in aluminosilicates is essentially independent of the framework structure and similar in crystalline and amorphous solids (section 2.4).\textsuperscript{42,46–48} The higher $r_{\text{Prins}}$ and $r_{\text{oligo}}$ values observed on microporous H-CD-FAU relative to mesoporous H-Al-MCM-41 and H-ASA samples (Table 2), taken together with their similar $r_{\text{Prins}}/r_{\text{oligo}}$ ratios (18–20, Table 2), indicate that the van der Waals stabilization conferred by the confining voids in these samples is similar for Prins condensation and oligomerization transition states. We note that alternate proposals that would implicate differences in acid strength to account for the different reactivities on H-CD-FAU, H-Al-MCM-41, and H-ASA would be inconsistent with their similar $r_{\text{Prins}}/r_{\text{oligo}}$ ratios.

Isobutanal–isobutene reaction rates and selectivities were measured over a broad range of temperature (473–633 K) and at higher reactant pressures (20 kPa isobutanal; 20 kPa isobutene) on H-Al-MCM-41 to explore the effects of the higher reactant conversions and temperatures envisioned in practice. The data in Figure 3a show that $r_{\text{Prins}}$ and $r_{\text{oligo}}$ both exhibit Arrhenius-type temperature dependences with a slightly lower activation enthalpy for the isobutanal–isobutene Prins condensation than for isobutene oligomerization (36 ± 1, 43 ± 2 kJ mol\textsuperscript{-1}; Figure 3a). These small differences led to a slight
decrease in $r_{\text{prins}}/r_{\text{oligo}}$ ratios from 10.6 (at 473 K) to 7.4 (at 633 K) with increasing temperature (Figure 3a). Higher temperatures also favored the formation of skeletal isomers and cyclic products via secondary reactions of the 2,5-DMH primary products of Prins condensation (Figure 3b), but the sum of the selectivities to these products remains below 20% (at 10% isobutene conversion) on these weaker acids at temperatures below 600 K.

3.4. Effects of Isobutene and Isobutanal Pressures on Prins Condensation and Oligomerization Turnover Rates. The rate of Prins condensation reactions ($r_{\text{prins}}$) of isobutanal–isobutene mixtures on H-Al-MCM-41 increased monotonically with isobutene and isobutanal pressures (Figure 4), but such linear increases at low pressures became weaker as pressure increased. These prevalent effects of the pressures of both reactants on $r_{\text{prins}}$ are consistent with the formation of 2,5-DMH products via kinetically relevant C–C bond coupling between isobutene and isobutanal on proton sites, which become increasingly covered by adsorbed species derived from one or both reactants as their respective pressures increase. In contrast, isobutanol oligomerization rates ($r_{\text{oligo}}$) showed a stronger than linear dependence on isobutene pressure (Figure 5a), and these rates decreased with increasing isobutanol pressure (Figure 5b). These trends indicate that the formation rate of 2,4,4-TMP is limited by steps that are mediated by bimolecular transition states involving two isobutene molecules on protons partially occupied by isobutanal-derived bound species. The proportional dependence of $r_{\text{prins}}/r_{\text{oligo}}$ on isobutanol/isobutene reactant ratios (Figure 6) indicates that the rate equations for both reactions share a common denominator term, which reflects the relative coverages of various species at protons and the common involvement of protons of uniform acid strength as the active sites for both reactions.

The observed effects of isobutene and isobutanol pressures on Prins condensation and oligomerization rates on H$_3$PW$_{12}$O$_{40}$/SiO$_2$ (Figures 7 and 8) and H-CD-FAU resemble those observed on H-Al-MCM-41 (Figures 4 and 5), indicative of Prins condensation and oligomerization elementary steps that are similar on all acids, irrespective of the number or acid strength of their active protons (Tables 1 and 2). The ratio of Prins condensation and oligomerization rates on H$_3$PW$_{12}$O$_{40}$/SiO$_2$ and H-CD-FAU is also strictly proportional to isobutanal/isobutene reactant ratios (Figure 6), confirming that both reactions occur on the same proton sites, as also found on H-Al-MCM-41. The slopes of these linear trends reflect the intrinsic selectivities of Prins condensation and oligomerization reactions. Such intrinsic selectivities depend on acid strength, as discussed in section 3.3 and as interpreted mechanistically by DFT treatments of the proposed elementary steps in section 3.6.

Scheme 5 depicts a plausible sequence of elementary steps for Prins condensation and oligomerization reactions using isobutanol and isobutene as illustrative coreactants on Bronsted acid sites. These elementary steps are consistent with the observed effects of isobutene and isobutanol pressures on Prins condensation and oligomerization rates (Figures 4–8) and with the DFT-derived free energies described in section 3.6. In these steps, isobutene first binds to protons via H-bonding between its carbonyl O atom or via H-transfer to form 1-hydroxy-isobutoxides (steps 1–2, Scheme 5a). Isobutene, in contrast, binds by forming a π-complex, an iso-butoxide, or a tert-butoxide at Bronsted acid sites (steps 1′–2′, Scheme 5b). Each bound species can react with either isobutanol or isobutene to form the respective dimers (steps 3–4, Scheme 5a; steps 4′–5′, Scheme 5b). Some of these dimer species could be present at kinetically relevant coverages on catalysts that contain protons within voids of molecular dimensions (e.g., H-MFI, H-BEA), which preferentially stabilize these dimers over monomer species via van der Waals stabilization, because of their larger size and more effective contacts with the void walls.

The C–C bond formation in Prins condensation reactions occurs via nucleophilic attack by the terminal C atom in the C=C bond of a gaseous isobutene molecule at the carbonyl C atom of a H-bonded isobutene molecule to form γ-hydroxy-C$_8$ alkoxides (step 5, Scheme 5a). These alkoxides subsequently undergo concerted elimination and deprotonation (step 6, Scheme 5a) and dehydration (step 7, Scheme 5a) to form 2,5-DMH. Oligomerization reactions form C=C bonds via nucleophilic attack by the same terminal C atom in a gaseous isobutene molecule at the tertiary C atom of tert-butoxides (step 6′, Scheme 5b) to form C$_9$ alkoxides that subsequently deprotonate to form 2,4,4-TMP (step 7′, Scheme 5b).

These elementary steps (Scheme 5), taken together with the assumption that all bound monomer and dimer species derived from isobutanol–isobutene reactants may exist at kinetically significant coverages, led to rate equations for isobutanol–isobutene Prins condensation ($r_{\text{prins}}$) and isobutene oligomerization ($r_{\text{oligo}}$):

\[
r_{\text{prins}} = \frac{k_{\text{prins}} P_{\text{isobutene}} P_{\text{al}}}{1 + K_{P_{\text{al}} P_{\text{al}}} + K_{P_{\text{al}} P_{\text{ene}}} + K_{P_{\text{ene}} P_{\text{ene}}} + K_{P_{\text{al}} P_{\text{ene}}}^{\prime} + K_{P_{\text{ene}} P_{\text{ene}}}^{\prime}}
\]

\[
r_{\text{oligo}} = \frac{k_{\text{oligo}} P_{\text{al}}^{\prime 2}}{1 + K_{P_{\text{al}} P_{\text{al}}} + K_{P_{\text{al}} P_{\text{ene}}} + K_{P_{\text{al}} P_{\text{ene}}}^{\prime} + K_{P_{\text{ene}} P_{\text{ene}}}^{\prime}}
\]

These two rates share a common denominator. The $k_{\text{prins}}$ and $k_{\text{oligo}}$ parameters denote the respective second-order rate constants for Prins condensation and oligomerization, and $P_{\text{al}}$ and $P_{\text{ene}}$ are the isobutanol and isobutene pressures; the $K_{P_{\text{al}}}$
$K_{\text{ene}}, K_{\text{al-ene}}, K_{\text{al-al}},$ and $K_{\text{ene-ene}}$ parameters represent the lumped adsorption equilibrium constants; the lumping strategy is meant to account for all distinct adsorbed configurations that can form as bound monomers or dimers upon adsorption of isobutanal, isobutene, isobutanal–isobutene pairs, isobutanal–isobutanal pairs, and isobutene–isobutene pairs on protons.

The parity plots of predicted and measured rates (section S8, SI; using the regressed parameters in Table 3) show that equations 1 and 2 accurately describe all Prins condensation and oligomerization rate data on H-Al-MCM-41 (Figures 4 and 5) and H$_3$PW$_{12}$O$_{40}$/SiO$_2$ (Figures 7 and 8) over a broad range of conditions. These equations also describe the observed effects of isobutanal/isobutene reactant ratios on $r_{\text{prins}}/r_{\text{oligo}}$ ratios (Figure 6):

$$\frac{r_{\text{prins}}}{r_{\text{oligo}}} = \frac{k_{\text{prins}}p_{\text{al}}}{k_{\text{oligo}}p_{\text{ene}}}$$

The slope for the data shown in Figure 6 reflects the ratio of the second-order rate constants ($k_{\text{prins}}/k_{\text{oligo}}$) and thus the intrinsic selectivities for Prins condensation and oligomerization on protons present in a given solid acid. Such mechanistic interpretations of the reactivity and selectivity of isobutanal–isobutene reactants allow a rigorous assessment of the validity of this proposal and of the implications of this mechanistic proposal for the consequences of acid strength and confinement using DFT methods (section 3.6).

### 3.5. Effects of Acid Strength on Prins Condensation and Oligomerization Turnover Rates

The second-order Prins condensation rate constant ($k_{\text{prins}}$; eq 2) depends on the activation free energy ($\Delta G_{\text{prins}}^\ddagger$) for the kinetically relevant elementary step:

$$k_{\text{prins}} = \frac{k_B T}{h} \exp(-\Delta G_{\text{prins}}^\ddagger/RT)$$

The value of $\Delta G_{\text{prins}}^\ddagger$ is the free energy of the C–C coupling TS ($G_{\text{prins}}^\ddagger$) referenced to those of gaseous reactants and a bare

---

**Figure 7.** Effects of (a) isobutene pressure and (b) isobutanal pressure on isobutanal–isobutene Prins condensation rates (5% wt. H$_3$PW$_{12}$O$_{40}$/SiO$_2$; 473 K; 0–5 kPa isobutanal; 0–5 kPa isobutene). The dashed lines represent regressed fits to the functional form of eq 2.

**Figure 8.** Effects of (a) isobutene pressure and (b) isobutanal pressure on isobutene oligomerization rates (5% wt. H$_3$PW$_{12}$O$_{40}$/SiO$_2$; 473 K; 0–5 kPa isobutanal; 0–5 kPa isobutene). The dashed lines represent regressed fits to the functional form of eq 3.
Surface site; in this case, such species are one gaseous isobutanal molecule ($G_{\text{al}}$), one gaseous isobutene molecule ($G_{\text{ene}}$), and a proton ($G_{\text{H}}$), as inferred from the schematic reaction coordinate diagram for Prins condensation elementary steps (Scheme 6):

$$
\Delta G^\ddagger_{\text{prins}} = G^\ddagger_{\text{prins}} - G_{\text{al}} - G_{\text{ene}} - G_{\text{H}}
$$

(6)

The value of the oligomerization rate constant ($k_{\text{oligo}}$) reflects its corresponding activation free energy ($\Delta G^\ddagger_{\text{oligo}}$; eq 3):

$$
k_{\text{oligo}} = \frac{k_\text{B}T}{h} \exp(-\Delta G^\ddagger_{\text{oligo}}/RT)
$$

(7)

The value of $\Delta G^\ddagger_{\text{oligo}}$ is given by the free energy difference between the oligomerization C–C coupling TS ($G^\ddagger_{\text{oligo}}$) and two gaseous isobutene reactants ($G_{\text{ene}}$) and a bare proton ($G_{\text{H}}$) as illustrated in Scheme 6:

$$
\Delta G^\ddagger_{\text{oligo}} = G^\ddagger_{\text{oligo}} - 2G_{\text{ene}} - G_{\text{H}}
$$

(8)

Measured $\Delta G^\ddagger_{\text{prins}}$ and $\Delta G^\ddagger_{\text{oligo}}$ values on H-Al-MCM-41 were 107 ± 1 and 116 ± 1 kJ mol$^{-1}$ (473 K; Table 4, 1 bar reference state), respectively, in agreement with their respective

### Table 3. Rate Constants and Adsorption Constants Obtained from Regression Fits of Prins Condensation and Oligomerization Rate Data (at 473 K) to the Respective Functional Forms of Eqs 2 and 3 for H-Al-MCM-41 and SiO$_2$-Supported H$_3$PW$_{12}$O$_{40}$

| catalyst          | H-Al-MCM-41$^a$ | H$_3$PW$_{12}$O$_{40}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{prins}}$ (ks$^{-1}$ kPa$^{-2}$ per H$^+$)</td>
<td>12 ± 2</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>$k_{\text{oligo}}$ (ks$^{-1}$ kPa$^{-2}$ per H$^+$)</td>
<td>1.2 ± 0.3</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>$k_{\text{al}}$ (kPa$^{-1}$)</td>
<td>0.3 ± 0.1</td>
<td>0.12 ± 0.02</td>
</tr>
<tr>
<td>$K_{\text{ene}}$ (kPa$^{-1}$)</td>
<td>0.3 ± 0.1</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>$K_{\text{al-ene}}$ (kPa$^{-1}$)</td>
<td>0.17 ± 0.02</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>$K_{\text{al-al}}$ (kPa$^{-1}$)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>$K_{\text{ene-ene}}$ (kPa$^{-1}$)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

$^a$From data in Figures 4 and 5. $^b$From data in Figures 7 and 8.
Theoretical Treatments of Adsorbed Species and Elementary Steps and Their Kinetic Relevance in Prins Condensation and Oligomerization Catalytic Sequences. DFT methods are used in this section to confirm the mechanistic details inferred from measured rates and selectivities and to interpret the effects of acid strength on reactivity and selectivity for Prins condensation and oligomerization reactions. These calculations were carried out on model aluminosilicate slabs and POM clusters with W addenda atoms and S, P, Si, or Al central atoms (section 2.4). These materials provide a broad range of DPE values (1204 kJ mol\(^{-1}\)) for the aluminosilicate slab; 1073–1123 kJ mol\(^{-1}\) for W-based POM clusters; Table 1) appropriate to probe the effects of acid strength on reactivity and selectivity.

The structure and binding energy of monomeric adsorbed species derived from isobutanal (H-bonded isobutanal and 1-hydroxy-iso-butoxide; steps 1 and 2, Scheme 5a) and isobutene (\(\pi\)-complex, iso-butoxide and tert-butoxide; steps 1′–3′, Scheme 5b) via interactions with protons were first examined on aluminosilicate slab surfaces. The regressed adsorption constants obtained from rate data on H-Al-MCM-41 (eq 2; Table 3) show that monomeric species derived from isobutanal and isobutene are present at higher coverages than for the various dimer species derived from isobutanal–isobutene reactants, indicating that such monomeric species are the most abundant adsorbed intermediates during catalysis. DFT treatments allow assessments about the prevalent forms of the isobutanal and isobutene gaseous reactants, which reflect catalyst-independent properties of the gaseous reactants (eq 10). Measured \(\Delta G_{\text{prins-oligo}}^\ddagger\) values for H-Al-MCM-41 and H\(_3\)PW\(_{12}\)O\(_{40}\) indicate that the stability of the oligomerization C–C coupling TS depends more sensitively on acid strength than for the Prins condensation C–C coupling TS. Such different sensitivities reflect, in turn, differences in the partial charge at these two cationic TS structures, a conclusion confirmed by DFT-derived energies and TS structures for the elementary steps that mediate oligomerization and Prins condensation catalytic sequences (section 3.6).

Table 4. Measured Free Energy Activation Barriers for Isobutanal–Isobutene Prins Condensation (\(\Delta G_{\text{prins}}^\ddagger\)) and Isobutene Oligomerization (\(\Delta G_{\text{oligo}}^\ddagger\)) and Adsorption Energies for Isobutanal (\(\Delta G_{\text{ads,al}}\)) and Isobutene (\(\Delta G_{\text{ads,ene}}\)) on H-Al-MCM-41 and SiO\(_2\)-Supported H\(_3\)PW\(_{12}\)O\(_{40}\)\(\ddagger\) (473 K; Table 4), respectively, in agreement with the trends derived from DFT treatments (−15 and −4 kJ mol\(^{-1}\); section 3.6). The different \(\Delta G_{\text{prins-oligo}}^\ddagger\) values on H-Al-MCM-41 and H\(_3\)PW\(_{12}\)O\(_{40}\) indicate that the stability of the oligomerization C–C coupling TS depends more sensitively on acid strength than for the Prins condensation C–C coupling TS. Such different sensitivities reflect, in turn, differences in the partial charge at these two cationic TS structures, a conclusion confirmed by DFT-derived energies and TS structures for the elementary steps that mediate oligomerization and Prins condensation catalytic sequences (section 3.6).

DFT treatments using model aluminosilicate slab surfaces (109 and 124 kJ mol\(^{-1}\); section 3.6). Measured \(\Delta G_{\text{prins}}^\ddagger\) and \(\Delta G_{\text{oligo}}^\ddagger\) values on H\(_3\)PW\(_{12}\)O\(_{40}\)/SiO\(_2\) (104 ± 1 and 107 ± 1 kJ mol\(^{-1}\); 473 K; Table 4) were lower than their respective values on H-Al-MCM-41, as a result of the smaller DPE values of POM clusters compared with H-Al-MCM-41 (1087 and 1204 kJ mol\(^{-1}\); Table 1). Such effects of acid strength are consistent with those determined from DFT-derived free energies on aluminosilicate slab and H\(_3\)PW\(_{12}\)O\(_{40}\) cluster models (section 3.6). These data confirm that the C–C coupling transition states involved in Prins condensation and oligomerization reactions both become more stable with increasing acid strength as a result of the more stable conjugate anions prevalent in stronger acids.\(^{41}\)

The ratio of the \(k_{\text{prins}}/k_{\text{oligo}}\) parameters reflects the difference between \(\Delta G_{\text{prins}}^\ddagger\) and \(\Delta G_{\text{oligo}}^\ddagger\) values (\(\Delta \Delta G_{\text{prins-oligo}}^\ddagger\)) (Scheme 6):

\[
\frac{k_{\text{prins}}}{k_{\text{oligo}}} = \exp (-\Delta \Delta G_{\text{prins-oligo}}^\ddagger / RT)
\]

\[
= \exp (- (\Delta G_{\text{prins}}^\ddagger - \Delta G_{\text{oligo}}^\ddagger) / RT) \quad (9)
\]

\[
\Delta \Delta G_{\text{prins-oligo}}^\ddagger = G_{\text{prins}}^\ddagger - G_{\text{oligo}}^\ddagger - G_{\text{al}} + G_{\text{ene}} \quad (10)
\]

These ratios are thus determined by the free energy differences between the two C–C coupling transition states, which depend on the identity of the solid acids, specifically on their acid strength and on any relevant effects of confinement imposed by voids of molecular dimensions,\(^{7}\) and between their respective
monomers derived from either isobutanal or isobutene and about the involvement of their stable and unstable forms in subsequent reactions that lead to the kinetically relevant transition states for Prins condensation and oligomerization reactions; the relative stabilities and involvement of these distinct forms of each monomer or dimer species, differing in structure and reactivity, but not in stoichiometry, cannot be discerned from experiments.

Isobutanal can bind at a proton site via its O atom to form H-bonded species with O–H distances of 0.155 nm (Scheme 7a). H-transfer can form 1-hydroxy-iso-butoxides with the carbonyl C atom bound to a lattice O atom (dC–O = 0.154 nm, Scheme 7b) and the proton residing at the carbonyl O atom (dH–O = 0.098 nm, Scheme 7b). H-bonded isobutanal and 1-hydroxy-iso-butoxide show similar adsorption enthalpies (ΔH_ads; −68 and −8 kJ mol⁻¹, Scheme 7; 473 K henceforth), but the slight enthalpic preference for H-bonded species becomes much more consequential for its prevalence when its greater entropy is taken into account, which leads to free energies that make H-bonded isobutanal the most abundant isobutanal-derived adsorbed species (ΔG_ads −8 vs +20 kJ mol⁻¹). Such entropy differences reflect the suppression of free rotations upon formation of the strong covalent bond between the carbonyl C atom and the framework O atom in 1-hydroxy-iso-butoxide, leading to a preference for H-bonded isobutanal that becomes even stronger at higher temperatures because of the pre-eminence of entropy as the determinant of Gibbs free energies at higher temperatures. Such differences in stability lead to a coverage ratio of 1200 between H-bonded isobutanal and 1-hydroxy-iso-butoxide at 473 K on aluminosilicate slab surfaces. The predominant presence of H-bonded species on such surfaces is also consistent with measured ΔG_ads values (−13 ± 2 kJ mol⁻¹, Table 4) that resemble DFT-derived values for H-bonded isobutanal (−8 kJ mol⁻¹, Scheme 7a) but differ significantly from those calculated for 1-hydroxy-iso-butoxide species (+20 kJ mol⁻¹, Scheme 7b).

The DFT-derived structure of the π-complex of adsorbed isobutene shows the proton aligned with the π orbital at the C=C bond at 0.195 and 0.233 nm from the primary and tertiary C atoms in isobutene, respectively (Scheme 7c). H-transfer to the tertiary C atom forms an iso-butoxide (Scheme 7d), while transfer to the primary C atom forms a tert-butoxide (Scheme 7e). The C–O bond is longer in the tert-butoxide than in the terminal iso-butoxide (0.155 vs 0.149 nm, Schemes 7d,e), indicative of steric hindrance at the tertiary C atom. DFT-derived ΔH_ads and ΔG_ads for tert-butoxide (−81 and −10 kJ mol⁻¹, Scheme 7e) were more negative than the respective values for π-complexes (−64 and −4 kJ mol⁻¹, Scheme 7c) or iso-butoxides (−72 and 0 kJ mol⁻¹, Scheme 7d), reflecting the prevalence of tert-butoxides among isobutene-derived monomer species. As in the case of isobutanal-derived species, these DFT-derived ΔG_ads values for tert-butoxides (−10 kJ mol⁻¹, Scheme 7e) agree with those measured from the denominator term corresponding to isobutene-derived monomers in eq 2 (−13 ± 2 kJ mol⁻¹, Table 4), which are significantly more negative than DFT estimates for iso-butoxides or π-complexes of isobutene. Such benchmarking of theoretical and experimental ΔG_ads estimates provides confirmatory evidence for the adequacy of the aluminosilicate slab models used in describing the binding properties of the active protons in H-Al-MCM-41.

Scheme 7. DFT-Optimized Structures of Adsorbed Species Formed from Isobutanal ((a) H-Bonded Isobutanal and (b) 1-Hydroxy-iso-butoxide) and Isobutene ((c) π-Complex, (d) Iso-butoxide, and (e) tert-Butoxide) on Proton Sites and Their Respective Adsorption Enthalpies (ΔH_ads) and Adsorption Free Energies (ΔG_ads).^a

^aAluminosilicate (Si₅₉AlO₁₂₄H₉) slabs, PBE+D3BJ; 473 K, 1 bar; relative to a bare surface and respective gaseous reactants.
The structure and stability of the monomeric adsorbed species derived from isobutanal and isobutene reactants (steps 1, 2 and steps 1′−3′, Scheme 5) were also examined on H3PW12O40 clusters. Specifically, the adsorption constant regressed from measured rates (eq 2; Table 3) indicate that isobutanal-derived monomers are the most abundant adsorbed intermediates and that isobutene-derived monomers are present at much lower coverages on H3PW12O40 (Kal 0.12 ± 0.02 kPa, Kene < 0.01 kPa, Table 3). DFT-optimized structures for H-bonded isobutanal are similar to those on aluminosilicate slabs, but proton distances from the carbonyl O atom are slightly shorter on H3PW12O40 than on aluminosilicates (0.150 and 0.155 nm, Schemes 7a and 8a), as expected from their di
terence in acid strength (Table 1). In contrast, the C−O bond between 1-hydroxy-iso-butoxides and framework O atoms is longer on H3PW12O40 than on aluminosilicates (0.160 vs 0.155 nm, Schemes 7b and 8b), reflecting the more ionic character of this bond on stronger acids. These trends with acid strength are also observed for the monomeric species derived from isobutene (i.e., π-complex, iso-butoxide, and tert-butoxide; Scheme 8). The π-complexes reside closer to the protons on H3PW12O40 clusters than on aluminosilicates, with the proton located 0.189 nm (Scheme 8c) and 0.195 nm (Scheme 7c) away from the terminal C atom in isobutene, respectively. In contrast, iso-butoxides and tert-butoxides bind to the conjugate anions of H3PW12O40 clusters with slightly longer C−O bonds (0.150 and 0.158 nm, Scheme 8d,e) than to aluminosilicates (0.149 and 0.155 nm, Scheme 7d,e).

As in the case of isobutanal interactions with aluminosilicate slabs, H-bonded isobutanal is more stable than 1-hydroxy-iso-butoxide on H3PW12O40 clusters (ΔGads −12 vs +27 kJ mol−1, Scheme 8a,b) and their ΔGads values agree with those regressed from rate data (−10 ± 1 kJ mol−1, Table 4). DFT-derived ΔGads values for π-complexes, iso-butoxides, and tert-butoxides on H3PW12O40 clusters were −1, +17, and +41 kJ mol−1, respectively, indicating that these species are less stable than isobutanal-derived monomers, as also concluded from the regression of all rate data to the functional form of eq 2 (ΔGads > 0 kJ mol−1, Table 4). The different stability of tert-butoxides on aluminosilicate slabs and H3PW12O40 clusters (ΔGads −10 vs +41 kJ mol−1, Schemes 7e and 8e) predominantly reflects enthalpic effects (ΔHads −81 vs −47 kJ mol−1, Schemes 7e and 8e) resulting from steric hindrance imposed by the two terminal lattice O atoms adjacent to the bound tert-butoxides on H3PW12O40 clusters. This enthalpic difference is much smaller for protonated isobutene bound through its less substituted primary C atom (to from iso-butoxide species) on both aluminosilicate slabs and H3PW12O40 clusters (ΔHads −72 vs −65 kJ mol−1, Schemes 7d and 8d), consistent with the pre-eminence of steric effects as descriptors of stability for bound alkoxydes. DFT-derived binding energies show that H-bonded isobutanals are also the predominant adsorbed species on other POM clusters (H5AlW12O40, H4SiW12O40, and H2SW12O40; section S9, SI); their stability increases slightly as the DPE values of the POM clusters decrease (e.g., H5AlW12O40 −9 kJ mol−1, H4SiW12O40 −13 kJ mol−1, section S9, SI).

Nucleophilic attack by gaseous isobutene molecules at the carbonyl C atom in H-bonded isobutanal leads to C−C bond
Scheme 9. DFT-Derived Structures of Reactants, Transition States, and Products Involved in the C−C Bond Formation Elementary Steps for (a) Isobutanal−Isobutene Prins Condensation (Step 5, Scheme 5a) and (b) Isobutene Oligomerization (Step 6', Scheme 5b)

formation (step 5, Scheme 5a). DFT treatments of this step on aluminosilicate slabs show that the H-bonded isobutanal becomes partially protonated as the primary C atom in isobutene approaches the carbonyl C atom to form an incipient C−C bond at the TS (Scheme 9a). Such charge transfer is evident from the distance between the proton and the carbonyl O atom, which is much shorter at the Prins TS (TSPrins, 0.109 nm, Scheme 9a) than in H-bonded isobutanal (0.153 nm, Scheme 9a) but slightly longer than that in the O−H bond at the product state (0.099 nm, Scheme 9a). The extent of charge transfer at the TSPrins was probed using the QUAMBO method (section 2.4), which estimates the most likely Lewis electronic structures for periodic systems and combines the electron densities within the structures to calculate charges. The estimated charge of the cationic TSPrins structure was +0.73 (Scheme 10a), confirming its cationic character but without the full protonation of the isobutanal moiety at the TS on aluminosilicates. In contrast, the DFT-derived TS structure that mediates C−C bond formation in isobutene oligomerization (TSoligo) on aluminosilicates involves a tert-butoxide species that forms a full carbenium ion as the terminal C atom in the C≡C bond in a gaseous isobutene molecule attacks the tertiary
Figure 9. DFT-derived reaction free energy diagrams of (a) isobutanal−isobutene Prins condensation and (b) isobutene oligomerization pathways (aluminosilicate (Si₅₉AlO₁₂₄H₉) slabs, PBE+D3BJ; 473 K, 1 bar). TSj and Pj represent the respective transition state and product of Step j in Scheme 5; AL and ENE represent gaseous isobutanal and isobutene, respectively. Energies are relative to a bare surface and respective gaseous reactants.

Scheme 11. DFT-Derived Structures of Reactants, Transition States, and Products Involved in the C−C Bond Formation Elementary Steps for (a) Isobutanal−Isobutene Prins Condensation (Step 5, Scheme 5a) and (b) Isobutene Oligomerization (Step 6', Scheme 5b)⁴

⁴H₃PW₁₂O₄₀ clusters were used for the DFT calculations (PBE+D3BJ); distances are reported in nm.
C atom in tert-butoxide (step 6', Scheme 5b). The formation of a full carbenium ion at TS_{oligo} is also evident from the distances between the tertiary C atom and the framework O site in tert-butoxides (0.155 nm, Scheme 9b) and in TS_{oligo} (0.333 nm, Scheme 9b). The estimated partial charge at the cationic TS_{oligo} structure was +0.92 (Scheme 10b), consistent with these conclusions; such fully formed carbenium ions are typical of the cationic transition states that mediate acid-catalyzed oligomerization, isomerization, and β-scission reactions of hydrocarbons and alkenes and contrast the less pronounced charge (+0.73, Scheme 10a) separation at the oxygen-containing transition states that mediate C–C bond formation in Prins condensation reactions on aluminosilicates.

The C–C bond formation steps involved in Prins condensation lead to γ-hydroxy-C₈ alkoxydes (Step 5, Scheme 5a) that convert to 2,5-DMH via concerted elimination reactions. The isobutene-isobutene TS_{oligo} indicative of transition states that occur later along the reaction coordinate on aluminosilicates (0.183 vs 0.196 nm, Schemes 9a and 11a), condensation reactions on aluminosilicates. The isobutene C coupling transition states that mediate C–C bond formation in Prins condensation reactions on aluminosilicates.

Figure 10. DFT-derived electronic charges for C–C coupling transition states involved in isobutanol–isobutene Prins condensation (TS_{prins}) and isobutene oligomerization (TS_{oligo}) as a function of deprotonation energy of solid acids (PBE+D3BJ). The solid lines represent trends.

C2H5OH + C2H5OH $\rightarrow$ C2H5OCH2CH2OCH2CH3 + H2O

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Figure 10. DFT-derived electronic charges for C–C coupling transition states involved in isobutanol–isobutene Prins condensation (TS_{prins}) and isobutene oligomerization (TS_{oligo}) as a function of deprotonation energy of solid acids (PBE+D3BJ). The solid lines represent trends.

Figure 10. DFT-derived electronic charges for C–C coupling transition states involved in isobutanol–isobutene Prins condensation (TS_{prins}) and isobutene oligomerization (TS_{oligo}) as a function of deprotonation energy of solid acids (PBE+D3BJ). The solid lines represent trends.
TSprins and TSoligo structures are enthalpically more stable than the respective referenced gaseous reactants, which are imparted by the stable conjugate anions of strong acids as also observed for H2SW12O40, H4SiW12O40, and H5AlW12O40 clusters (Figure 11b).

DFT-derived $\Delta G^{\dagger}_{\text{prins}}$ and $\Delta G^{\dagger}_{\text{oligo}}$ for POM clusters both increase monotonically as the DPE values increase with changes in the central atom (Figure 11a), consistent with the lower stability of the conjugate anions in weaker acids and with the cationic character of both C–C coupling transition states, which contain the conjugate anion interacting with the organic cation. Linear trends are also evident between the activation enthalpies ($\Delta H^{\dagger}_{\text{prins}}, \Delta H^{\dagger}_{\text{oligo}}$) and the DPE value of each acid (Figure 11b). These relationships highlight the predominant role of enthalpic stabilization in the higher reactivity conferred upon stronger acids by their more stable conjugate anions. Such stabilization becomes more consequently as the cation and anion at the TS acquire a more significant charge. The TSprins and TSoligo structures on the stronger acids, illustrated here by the POM clusters, have similar charges (+0.92–+0.94, Figure 10); their $\Delta G^{\dagger}_{\text{prins}}$ and $\Delta G^{\dagger}_{\text{oligo}}$ values thus lie along similar trend lines as a function of DPE values (Figure 11a). Selectivity, in this case reflected in the $k_{\text{prins}}/k_{\text{oligo}}$ ratios (eq 9), therefore becomes independent of acid strength, as previously shown for other catalytic reactions in which parallel routes are mediated by TS structures of similar charge.

$\Delta G^{\dagger}_{\text{prins}}$ and $\Delta G^{\dagger}_{\text{oligo}}$ for aluminosilicate slab models deviate from their linear trends with DPE values on the stronger POM acids (Figure 11a). The deviation for $\Delta G^{\dagger}_{\text{oligo}}$ values arises mainly from the entropy component in $\Delta G^{\dagger}_{\text{oligo}}$; weaker acids lead to TSoligo structures with higher entropy because the fully formed tert-butyl carbocation and gaseous isobutene species

Figure 11. DFT-derived (a) activation free energies ($\Delta G^{\dagger}_{\text{prins}}$ and $\Delta G^{\dagger}_{\text{oligo}}$) and (b) their enthalpy components for isobutanal–isobutene C–C coupling steps involved in Prins condensation (●) and isobutene-isobutene C–C coupling steps involved in isobutene oligomerization (○) as a function of the deprotonation energy of solid acids (PBE+D3BJ; referenced to a bare proton site and respective gaseous reactants; 473 K, 1 bar). The solid lines represent trends.

Figure 12. DFT-derived (a) $\Delta \Delta G^{\dagger}_{\text{prins}-\text{oligo}}$ and (b) respective enthalpy components ($\Delta \Delta H^{\dagger}_{\text{prins}-\text{oligo}}$) as a function of deprotonation energy of solid acids (PBE+D3BJ; referenced to a bare proton site and respective gaseous reactants; 473 K, 1 bar). The solid lines represent trends.
are more tightly bound at the later TS_{oligo} on weaker acids (Scheme 9) than the respective moieties at the earlier TS_{oligo} on stronger acids (Scheme 11). Figure 11b shows that ΔH^f_{oligo} values for the aluminosilicate slab lie along the linear trend of ΔH^f_{oligo} with DPE values set by the POM acids, as expected from the full ion-pair character of TS_{oligo} structures on both aluminosilicate slab and POM cluster models (+0.92-+0.94, Figure 10), thus confirming that entropic effects account for the lower than predicted ΔG^f_{oligo} values for aluminosilicates.

The ΔH^r_{prins} values on aluminosilicate slabs (~52 kJ mol⁻¹, Figure 11b), however, are much lower than expected from the ΔH^r_{prins}-DPE trends given by the POM clusters (~3 kJ mol⁻¹, Figure 11b). These differences account for the lower ΔG^r_{prins} values on aluminosilicate slabs, which also lie below these linear trends (109 kJ mol⁻¹ (calculated) vs 148 kJ mol⁻¹ (expected), Figure 11b). These more negative ΔH^r_{prins} values reflect, in part, TS_{prins} structures that are less sensitive to the less stable nature of the conjugate anions as acids weaken because of their lower charges on aluminosilicates than on POM clusters (+0.72 vs +0.94, Figure 10); they also reflect the additional stabilization imparted by the partially covalent O–H bond that remains at the solid acid moiety because of the incomplete transfer of the proton at the TS_{prins} on aluminosilicate slabs (O–H distance 0.139 nm (at TS) vs 0.104 nm (in the TS precursor), Scheme 9a).

On stronger acids (H₄X₅⁺X⁺W₁₂O₄₀, X⁻ = S⁶⁺, P⁶⁺, Si⁶⁺, and Al¹⁺ POM), TS_{prins} and TS_{oligo} are both fully protonated as discussed above (+0.92-+0.94, Figure 10); Prins condensation and oligomerization reactions thus depend similarly on acid strength, as evident from the similar differences between ΔG^r_{prins} and ΔG^r_{oligo} values on these solid acids (ΔΔG^r_{prins-oligo} = −2 to −7 kJ mol⁻¹, Figure 12a) over a broad range of DPE values (1073–1123 kJ mol⁻¹, Table 1). On weaker acids, such as aluminosilicates (DPE 1204 kJ mol⁻¹, Table 1), TS_{prins} and TS_{oligo} differ significantly (+0.72 vs +0.92, Figure 10) because of the incomplete proton transfer at TS_{prins}; as a result, the TS_{prins} structures are less destabilized by greater instability of the conjugate anions and the greater residual covalency as acids weaken. Such trends lead, in turn, to more negative ΔΔG^r_{prins-oligo} values (~15 kJ mol⁻¹, Figure 12a) on aluminosilicates than on stronger POM acids and thus to the observed preference for the formation of 2,5-DMH over isobutene oligomers or products of secondary isomerization of 2,5-DMH; the latter also involve full ions-pairs at their TS structures on all solid acids. The pre-eminence of enthalpic stabilization in determining the selectivity to 2,5-DMH is evident from DFT-derived ΔΔH^f_{prins-oligo} components that show similar trends with DPE values as ΔΔG^f_{prins-oligo} estimates (Figure 12b).

DFT-derived entropy contributions (TDΔS^f) in the free energies of Prins condensation and oligomerization transition states (TS_{prins} and TS_{oligo}) are shown in section S12 of the SI. These entropy components are similar for the TS_{prins} and TS_{oligo} structures on the POM clusters and the TS_{oligo} structure on the aluminosilicate slab (~131 to ~142 kJ mol⁻¹, Figure S10a, SI), which consist of full ions-pairs at the TS, but more negative for the TS_{prins} structure on the aluminosilicate slab (~161 kJ mol⁻¹, Figure S10a, SI), because of the residual covalent bond that exists between the TS_{prins} and the conjugate anion of the proton site as discussed above. The differences in the entropy components between the TS_{prins} and TS_{oligo} structures (TDΔS^f_{prins-oligo}) reflect the entropy contributions to the free energy difference between these two transition states, which determine Prins condensation to oligomerization rate ratios. The ΔΔΔG^f_{prins-oligo} values for the POM clusters (~2 to ~3 kJ mol⁻¹, Figure S10b, SI) and the aluminosilicate slab (~30 kJ mol⁻¹, Figure S10b, SI) were all less negative than the respective ΔΔH^f_{prins-oligo} values (Figure 12b), further confirming that the Prins condensation and oligomerization selectivities for a proton site are predominately determined by the different enthalpies of their TS structures.

Finally, we examine the expectations for how confinement within voids of molecular dimensions is likely to influence reactivity and selectivity in alkanal–alkene reactions on solid acids. The van der Waals volumes for TS_{prins} and TS_{oligo} structures (calculated from solvent-excluded surfaces using a sphere (of solvent) with a radius of 0.14 nm) on aluminosilicate slabs were 0.153 nm³ and 0.144 nm³, respectively (Scheme 10). These transition state structures are expected to become stable relative to their respective H-bonded isobutanal and bound alkoxydes when the conforming voids are of similar volume and dimensions, as observed experimentally from the higher turnover rates on microporous H-CD-FAU relative to mesoporous H-Al-MCM-41 of similar acid strengths (r_{prins} 18.1 vs 14.8 ks⁻¹ per H⁺; r_{oligo} 1.0 vs 0.8 ks⁻¹ per H⁺; Table 2). The similar size of the TS_{prins} and TS_{oligo} Structures makes k_{prins}/k_{oligo} ratios (ΔΔΔG^f_{prins-oligo}; eq 10) essentially independent of the void size in aluminosilicates (k_{prins}/k_{oligo} = 9.7 ± 0.3 (H-CD-FAU) vs 10.3 ± 0.2 (H-Al-MCM-41); 473 K; Figure 6) because both TS structures are stabilized to the same extent by van der Waals contacts with the walls of the confining voids. Such confinement effects on reactivity and selectivity are consistent with measurements on microporous aluminosilicates with smaller voids (e.g., H-BEA, H-MOR, H-TON, and H-FER) as will be shown in a later report that focuses on the appropriate descriptor of size and reactivity for protons confined within voids of molecular dimensions.

These mechanistic interpretations, underpinned by consistent experimental and theoretical evidence, illustrate how the incompleteness of charge separation at transition states on weak acids can be used for significant selectivity benefits in reactions, in which oxygenates act as electrophiles in the presence of hydrocarbons as coreactants or products. In practice, these findings provide guidance in the design of solids with acid strength that leads to optimal selectivities for such general families of useful catalytic reactions.

4. CONCLUSIONS

Isobutanol and isobutene form 2,5-dimethyl-hexadienes (2,5-DMH) via Prins condensation reactions on Bronsted solid acids (Keggin heteropolyacids, Nb₂O₅·nH₂O and mesoporous and microporous aluminosilicates). The selectivity to 2,5-DMH, a precursor to p-xylene, is limited by parallel isobutene isomerization reactions, in which oxoesters act as electrophiles in the presence of hydrocarbons as coreactants or products. In practice, these findings provide guidance in the design of solids with acid strength that leads to optimal selectivities for such general families of useful catalytic reactions.
slightly lower than that for isobutene oligomerization (36 ± 1 vs 43 ± 2 kJ mol⁻¹), consistent with a minor decrease in \( r_{\text{prins}}/r_{\text{oligo}} \) ratios (10.6–7.4) with increasing temperature (473–633 K).

Kinetic and theoretical assessment showed that (i) Prins condensation and oligomerization reactions are mediated by the respective C–C bond formation steps of gaseous isobutene with partly or fully protonated isobutanal and tert-butyl carbenium ions formed from protonation of isobutene; (ii) active proton sites present on the solid acids have uniform acid strength and are predominantly covered by H-bonded isobutanal and isobutene in the form of tert-butoxide (for mesoporous aluminosilicates) or by H-bonded isobutanal solely (for H₃PW₁₂O₄₀/SiO₂). Measured free energy barriers for these C–C bond formation steps involved in Prins condensation (\( \Delta G^f_{\text{prins}} \)) and oligomerization (\( \Delta G^f_{\text{oligo}} \)) reactions were both higher on mesoporous aluminosilicates (107 ± 1 and 116 ± 1 kJ mol⁻¹; 523 K) than on H₃PW₁₂O₄₀/SiO₂ (104 ± 1 and 107 ± 1 kJ mol⁻¹; 523 K), whereas the difference between \( \Delta G^f_{\text{prins}} \) and \( \Delta G^f_{\text{oligo}} \) (\( \Delta\Delta G^f_{\text{prins-oligo}} \)), which determines the intrinsic selectivities to the Prins condensation and oligomerization products, was more negative on mesoporous aluminosilicates (−9 ± 2 kJ mol⁻¹; 523 K) than on H₃PW₁₂O₄₀/SiO₂ (−3 ± 2; 523 K); these data are consistent with theoretical estimates using aluminosilicate slab and Keggin H₃PW₁₂O₄₀ cluster models and confirm that mesoporous aluminosilicates with the acid strength weaker than for H₃PW₁₂O₄₀ are less reactive but more selective to the Prins condensation products.

Theoretical treatments unveiled that the C–C bond formation transition states for Prins condensation (TS_{prins}) and oligomerization (TS_{oligo}) reactions are both cationic and have similar charges on stronger acids (+0.94 vs +0.93; on H₃PW₁₂O₄₀), while the charge of the TS_{prins} is lower than that for TS_{oligo} on weaker acids (+0.73 vs +0.92; on aluminosilicates), as a result of the incomplete protonation of isobutanal at the TS_{prins}. The cationic nature of TS_{prins} and TS_{oligo} leads to the decrease of their stability with increasing deprotonation energies (DPE) for solid acids, as acid sites weaken and their conjugate anions become less stable, but the stability of the TS_{prins} depends less sensitively on acid strength than for the TS_{oligo} because of the concomitant decrease of the TS_{prins} charge with decreasing acid strength. Such different dependences of the TS stability on DPE values, taken together with an additional stabilization for TS_{prins} on weaker acids imparted by the partially covalent O–H bond remained in the solid acid as a result of the incomplete proton transfer at the TS_{prins} account for the preferential stabilization of TS_{prins} over TS_{oligo} on weaker acids, which allows to mediate \( r_{\text{prins}}/r_{\text{oligo}} \) ratios for alkane–alkene reactant pairs by choosing solid acids with the proper acid strength. The TS_{prins} and TS_{oligo} structures on aluminosilicates have similar sizes (0.153 and 0.144 nm³), which makes these structures stabilized similarly by van der Waals contacts with the walls of confining voids differing in size but containing protons of similar acid strength, in consistency with the observed similar \( r_{\text{prins}}/r_{\text{oligo}} \) ratios for mesoporous and microporous aluminosilicates.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02171.

Number of proton and Lewis acid sites on aluminosilicate samples; top views of aluminosilicate slabs; structure of aluminosilicate clusters; effects of space velocity on selectivities to regioisomers of diene/alkene products; conversion-selectivity relations on H-ASA; site titrations of H-ASA and Nb₂O₅·nH₂O during catalysis; deactivation of solid acids during catalysis; parity plots of predicted and measured rates; and summary of DFT-derived enthalpies, entropies, and free energies for intermediates and transition states involved in Prins condensation and oligomerization elementary steps on aluminosilicates and POM clusters (PDF)

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**Notes**

The authors declare no competing financial interest.

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