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Consequences of metal-acid site proximity for alkane isomerization and β -scission mediated by bifunctional catalytic cascades

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ABSTRACT

Bifunctional isomerization and β -scission of alkanes involve kinetic cascades mediated by alkenes that form at a (de)hydrogenation function that resides within diffusion distances from the acid function at which alkenes react. Such distances matter for reactivity and selectivity, especially within voids of molecular dimensions, because of gradients in reactant and product concentrations within acid domains. Dispersing Pt nanoparticles within zeolite crystals places the two functions within nanometer distances, instead of the larger distances prevalent when the Pt function resides outside zeolite crystals. Such intimacy leads to higher n-heptane conversion turnover rates (per H⁺) and shifts selectivities towards primary isoalkanes, most evidently on medium-pore zeolites (MFI), because confinement effects lead to slower diffusion and higher intrinsic H⁺ reactivity than in larger-pore zeolites, and for shorter Pt-H⁺ distances. which define the dimensions of the acid domain. Intracrystalline Pt nanoparticles do not affect the number or intrinsic properties of the metal or acid functions or introduce reaction channels mediated by more reactive (but less abundant) diene intermediates, as demonstrated here by reactive probes of metal (CO oxidation) and acid (CH₃OH dehydration) functions, infrared spectra of OH groups and chemisorbed CO, kinetic effects of H₂ pressures, and transition state energies from density functional theory. Metal-acid distances influence the requisite kinetic cascades instead through the formation and scavenging of reactants and intermediates along the isomerization-scission sequence in the presence of significant gradients in their concentrations. Reaction-transport treatments show that such gradients weaken with increasing intracrystalline densities of Pt nanoparticles (and consequent smaller acid domains), thus circumventing isoalkene equilibration and local thermodynamic bottlenecks through hydrogenation of the primary isoalkene products. Such scavenging inhibits the formation of dimethylpentenes, which act as required precursors to β -scission products, leading to higher selectivities to isoalkanes as Pt-H⁺ distances decrease. These data and reaction-transport formalisms resolve persistent controversies about the chemical or diffusional origins of rate and selectivity consequences of the location of a metal function. They demonstrate the essential, but often neglected, need to determine the precise location of the metal function and to develop reaction-transport treatments to describe rates and selectivity in bifunctional metalacid catalysis.

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1. Introduction

Hydrocracking and hydroisomerization processes are used in practice to convert alkane feedstocks to smaller and more highlybranched molecules, leading to marketable products with useful rheological or combustion properties [1]. These reactions involve bifunctional catalytic cascades, with alkanes first forming alkenes on a metal function, alkenes undergoing skeletal isomerization or

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C—C bond cleavage on an acid function, and their products hydrogenating at the metal function to form their less-reactive saturated analogs [2-4]. These two catalytic functions are linked via the shuttling of alkene intermediates, thus requiring "intimacy" (but not atomic contact), so that the metal function can maintain equilibrium alkene concentrations within acid domains, but also serve to avoid the local equilibration of alkene interconversions, thus rendering the isoalkenes less prone to secondary isomerization or β scission by hydrogenating them [4-7]. When such intimacy criteria are met, the observed reaction rates reflect the intrinsic catalytic properties of Brønsted acid sites, but selectivities may still be influenced by local equilibration and diffusion-enhancements of secondary reactions of the primary alkene isomers formed [8-11].





JOURNAL OF CATALYSIS Such effects are most evident when acid sites reside within voids of molecular dimensions, because they restrict diffusional egress and also make acid sites more reactive via van der Waals stabilization of isomerization and β -scission transition states. Local equilibration and diffusion-enhanced secondary interconversions become most prevalent as methyl branches form, because branched molecules are more reactive than linear ones as a result of their more stable carbenium ion transition states; these branched molecules also diffuse more slowly than their less branched analogs. In such systems, the chemistry that occurs at the scale of a Brønsted acid site becomes inextricably linked with configurational effects that determine diffusivities and confinement effects, precisely the benefits sought by the use of microporous solids.

The physical characteristics of the diffusive medium, such as channel size, connectivity and crystal size, and the number of acid sites for which molecules must arrive via diffusion, become consequential for measured rates and selectivities for these systems. Therefore, mechanistic descriptions of the chemistry from measurements, as well as predictions of performance, require diffusion-reaction treatments and accurate assessments of the size and diffusive properties of acid domains, the number of acid sites within such domains, and the location of the metal function relative to the active intracrystalline protons.

The location of the metal function, typically as nanoparticles, is seldom evident in practice or accessible to direct inquiry [12,13]. This becomes most relevant for practical catalyst composites, which are "constructed" via impregnation of metal precursors onto composites typically consisting of mixtures of mesoporous binders and zeolite crystallites [14,15]. Nevertheless, nanoscale metal–acid intimacy is often invoked to account for observed differences in reactivity and selectivity [15-18], seldom through direct evidence or firm mechanistic underpinnings. Our previous studies circumvented such uncertainties by placing the metal function exclusively within a mesoporous non-acidic support and using intimate physical mixtures with well-defined acid domains, determined by the zeolite crystals [8,9].

This study provides evidence for the consequences of such inherent diffusion-reaction interplay within zeolite crystals for reactivity and selectivity by placing Pt nanoparticles within zeolite domains (MFI, BEA, and FAU) instead of exclusively at extracrystalline regions, thus significantly decreasing metal-acid distances from those in bifunctional physical mixtures. n-Heptane conversion turnover rates (per H⁺) increased (up to 10-fold) when Pt nanoparticles were dispersed within MFI crystals and used in concert with mixed Pt/SiO₂ catalysts. Such rate enhancements were strongest for medium-pore zeolites (MFI) and weaker (BEA) or negligible (FAU) for large-pore zeolites; their magnitude increased as the metal-acid inter-function distances in MFI was purposely decreased through changes in the intracrystalline density of either protons or Pt nanoparticles.

These observed n-heptane isomerization rate enhancements can reflect chemical differences caused by the presence of intracrystalline nanoparticles or by the synthetic protocols used to disperse them:

- (i) different number or reactivity of the sites that provide each of the two required functions;
- (ii) the presence of metal-proton adducts with unique reactivity;
- (iii) pathways mediated by molecular shuttles other than alkenes, made possible by nanometer-scale proximity between functions.

Such plausible chemical origins were assessed and ruled out through experiments or theory. Probe reactions of the metal (CO oxidation) and acid (CH_3OH dehydration) functions showed that

neither the number nor the chemical properties of the respective sites were influenced by confining Pt nanoparticles within zeolite crystals; these conclusions were confirmed by infrared spectra of chemisorbed CO and zeolitic O–H groups, which precluded the presence of metal-proton adducts and ruled out any changes in their respective properties. Density functional theory (DFT) showed that pathways involving dienes as inter-function shuttles do not enable more competent isomerization reaction channels; allylic transition states (TS) involved in diene-mediated isomerization routes were, in fact, significantly less stable than the carbenium-ion TS structures in alkene-mediated routes, a conclusion consistent with measured isomerization rates that were a single-valued function of n-heptane/H₂ reactant ratios on all catalysts.

The exclusion of such chemical underpinnings for rate enhancements (and selectivity changes) led to alternate hypotheses based on diffusion-reaction formalisms that assess intracrystalline concentration gradients and the local approach to equilibrium for sequential alkene skeletal isomerization events. Such descriptions account for the observed effects of metal-acid proximity; intermediate isomerization events approach equilibrium as the size of metal-free acid domains increases, because the isoalkenes formed can be scavenged (thus circumventing equilibration) only via hydrogenation at a metal function. Such local equilibrium-shifting events also inhibit β -scission reactions of dimethylpentenes on acid sites through the intervening hydrogenation steps. The intracrystalline Pt function also acts to replenish, through local dehydrogenation events, reactant alkenes within acid domains via dehydrogenation of n-heptanes. Higher intracrystalline concentrations of n-heptene regioisomers and the circumventing of isomerization equilibrium bottlenecks via hydrogenation (instead of β scission) account for the observed effects of intracrystalline Pt nanoparticles on rates and selectivities. Such diffusion-reaction coupling is unavoidable and useful in practice; it brings forth challenges in mechanistic analysis but provides, in exchange, design criteria useful to adapt multi-site-catalyzed reaction chemistries for specific purposes solely by controlling the distances separating two functions without altering their respective chemical properties. Such designs provide significant incentives to control, through synthetic protocols, and to detect, through analytic methods, the location of each function within the complex composites used as catalysts in hydroisomerization and hydrocracking practice.

2. Materials and methods

2.1. Catalyst synthesis and characterization protocols

The zeolite and Pt-zeolite materials used in this study are listed in Tables 1 and 2, respectively, along with the notation used and the physicochemical properties of these samples. Zeolites were synthesized either by established protocols (FAU [19]) or obtained from commercial sources (BEA, MFI: Zeolyst). These samples were treated in flowing dry air (2.5 cm³ g⁻¹ s⁻¹, extra dry, Praxair) by heating to 823 K at 0.0167 K $\ensuremath{s^{-1}}$ and held for 4 h before use; they were then converted to their NH₄⁺-forms by contacting with 0.1 M NH_4NO_3 (>98 % Sigma-Aldrich; 300 g solution [g zeolite]⁻¹) and subsequent filtration (three cycles). Solids were washed with deionized water (resistivity > 17.6 Ω cm⁻²) until the filtrate conductivity was < 50 S/m and then treated at 298 K under dynamic vacuum for 12 h. Proton densities for NH₄⁺-MFI were measured from the amount of NH₃ desorbed during rapid heating using protocols described previously [8]. The proton densities in FAU and BEA were measured by titration with 2,6-di-tert-butylpyridine during n-heptane reactions [8].

Table 1

Composition and source of zeolites.

Material	Source	Si/Al ^a	H⁺/AI
FAU	[19]	7.5	0.39 ^b
BEA	Zeolyst	11.8	0.27 ^b
MFI-1	Zeolyst	168.3	0.62 ^c
MFI-2	Zeolyst	43.8	0.89 ^c
MFI-3	Zeolyst	29.2	0.64 ^c

^aElemental analysis ICP-OES (Galbraith Laboratories).

^bFrom titration with 2,6-di-*tert*-butylpyridine during n-heptane isomerization reactions[8].

^cFrom the amount of NH₃ evolved during rapid heating of NH₄⁺-zeolites.

Zeolites containing Pt nanoparticles were prepared using ion exchange of aqueous Pt cations into NH₄⁺-zeolites and subsequent thermal treatments in flowing H₂. Aqueous tetraamineplatinum (II) nitrate (Sigma-Aldrich; 0.005 M solution) was added dropwise to a NH₄⁺-zeolite suspension (100 g deionized water [g zeolite] ⁻¹; water resistivity > 17.6 Ω cm⁻²) and stirred at ambient temperature for 24 h. Solids were collected by filtration and washed with deionized water (resistivity > 17.6 Ω cm⁻²; ~1500 g [g zeolite] ⁻¹). They were then treated in flowing dry air (2.5 cm³ g⁻¹ s⁻¹, extra dry, Praxair) at 383 K (0.033 K $\rm s^{-1})$ for 3 h and at 723 K (0.025 K s^{-1}) for 4 h; samples were cooled to ambient temperature and then treated in 10 % H_2/He flow (2.5 cm 3 g $^{-1}$ s $^{-1}$; 99.999 %Praxair H₂; 99.999 % Praxair He) by heating to 623 K (at 0.025 K s⁻¹) and holding for 3 h before cooling to ambient temperatures. Their chemical composition (Si, Al, and Pt content) was determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES, Galbraith Laboratories).

A Pt/SiO₂ (2.0 % wt.) co-catalyst was prepared by incipient wetness impregnation of SiO₂ (Sigma-Aldrich, Davisil grade 646; treated before use in 2.5 cm³ g⁻¹ s⁻¹ air (extra dry, Praxair) at 923 K for 5 h (0.083 K s⁻¹)) with aqueous H₂PtCl₆·6H₂O (Aldrich) solutions using previously reported protocols [8].

The (fractional) Pt dispersion of Pt/SiO₂ (0.88) and Pt-zeolite (Table 2) samples was determined from H₂ chemisorption uptakes (at 373 K) by assuming a 1:1 H:Pt_s stoichiometry. Dispersion values for PtFAU and PtBEA (0.78 and 0.89, respectively; Table 2) correspond to Pt nanoparticles with mean diameters of 1.3–1.4 nm, assuming spherical particles with the density of bulk Pt. These values are consistent with those for previously reported materials synthesized using similar protocols and precursors [20]. Pt particles are slightly larger than the size of the largest void in these frameworks (0.67 and 1.1 nm for BEA and FAU, respectively [21]), indicative of local distortions and fractures that inhibit their further growth [20,22].

Dispersion values for PtMFI samples are smaller (0.30–0.77; Table 2) than for PtFAU or PtBEA. These dispersion values for PtMFI

samples correspond to mean Pt nanoparticle sizes 1.5–3.8 nm in diameter (Table 2), with the larger particles (>2 nm) presumably at zeolite external surfaces. Transmission electron microscopy (FEI Tecnai 12, 120 kV accelerating voltage; bright field detector) was used to obtain particle size distributions for Pt nanoparticles (>300 particles counted per sample).

Intimate physical mixtures were prepared from Pt/SiO₂ and either zeolites or Pt-containing zeolites by mixing the two materials after grinding to < 125 μ m aggregates in a mortar and pestle, pressing into mixed pellets, crushing, sieving to retain aggregates with diameters between 180 and 250 μ m. These mixtures contained sufficient amounts of extracrystalline Pt/SiO₂ to ensure alkane dehydrogenation equilibrium within the extracrystalline fluid phase (Pt_s/H⁺ ratios > 7.8, as previously established [8]).

2.2. Infrared spectra measurements

Infrared spectra of zeolites and Pt-zeolites were used to probe any effects of an intracrystalline Pt function on the O–H stretch bands (3800–3400 cm⁻¹; Nicolet NEXUS 670 infrared spectrometer). Spectra were collected in transmission mode using a Hg-Cd-Te (MCT) detector. Self-supporting wafers (0.01–0.02 g cm⁻²) were placed within a quartz vacuum cell equipped with NaCl windows. Temperatures were controlled (Watlow) using a resistively-heated rod and measured with a K-type thermocouple aligned with the center of the wafer. Samples were treated in flowing H₂ (40 cm³ g⁻¹ s⁻¹; 99.999 %, Praxair) at 573 K (0.025 K s⁻¹) for 2 h before cooling to 548 K; they were then evacuated (<10⁻² Pa dynamic vacuum; Edwards E02 diffusion pump) and spectra were acquired (2 cm⁻¹ resolution, 400–4000 cm⁻¹, average of 64 scans) and normalized by the zeolite Si-O-Si bands (2100–1750 cm⁻¹).

Infrared spectra were also used to probe the intensity and vibrational frequency of chemisorbed CO species at Pt surfaces on Pt/ SiO₂ and Pt-zeolites (Nicolet 8700 infrared spectrometer) in transmission mode using an MCT detector. Self-supporting wafers (0.0 $1-0.02 \text{ g cm}^{-2}$) were placed between CaF₂ windows within a custom flow cell [23]; samples were treated in flowing H₂ (40 cm³ g⁻¹ s⁻¹; 99.999 %, Praxair) at 573 K (0.025 K s⁻¹) for 2 h before cooling to 300 K and then exposed to flowing 1 % CO/He (certified standard, Praxair) and flushed with He for 0.3 h before collecting spectra (2 cm⁻¹ resolution, average of 64 scans).

2.3. Catalytic rate and selectivity measurements

2.3.1. n-Heptane isomerization rates and isomerization and β -scission selectivities

n-Heptane (nH) conversion rates and product selectivities were measured at 548 K on Pt/SiO_2 monofunctional catalysts mixed with

Table 2		
Physicochemical	properties	of Pt-zeolites.

Material	Pt content ^a	Pt dispersion ^b	d _{chem} nm ^c	Fraction Pt nanoparticles confined within zeolite crystals ^d	$\langle l_{Pt} angle {f nm}^{{f e}}$	$\langle H^+/Pt \rangle^{ m f}$	$\langle l_{H^+} angle { m nm}^{ { m g}}$
PtFAU	0.96 %	78 %	1.4	-	17	1600	1.5
PtBEA	1.03 %	89 %	1.3	-	14	480	1.8
PtMFI-1	0.36 %	50 %	2.3	0.46	26	620	3.0
PtMFI-2	1.09 %	36 %	3.1	0.56	26	1700	1.7
PtMFI-3a	2.63 %	30 %	3.8	0.47	22	2600	1.6
PtMFI-3b	1.17 %	56 %	2.0	0.73	20	1700	1.6
PtMFI-3c	1.78 %	76 %	1.5	0.77	12	380	1.6

^aElemental analysis ICP-OES (Galbraith Laboratories).

^bFrom H₂ chemisorption uptakes (373 K).

^cMean diameter of Pt nanoparticles from Pt_s obtained from H₂ chemisorption uptakes (373 K), assuming clusters are spherical and have the same density as the bulk metal. ^dFrom TEM, assuming particles < 2 nm are within the zeolite crystallite (TEM images and distributions in SI-S1).

^eMean Pt-Pt nanoparticle distance, calculated assuming random distribution of Pt clusters throughout zeolite crystallites; only accounts for intracrystalline Pt. ^f average number of protons per encapsulated Pt cluster, assuming random distributions of both.

 $^{\rm g}$ mean $\rm H^{*}\text{-}H^{*}$ distance, assuming their random distribution.

H-zeolite or Pt-zeolite samples and held within a tubular reactor (316 SS, 12 mm i.d.) with plug-flow hydrodynamics. Temperatures were maintained using a three-zone resistively-heated furnace (Applied Test Systems Series 3210) and electronic controllers (Watlow EZ-ZONE PM Series) and measured by a K-type thermocouple placed within a thermowell aligned with the midpoint of the bed. Samples were treated in flowing 10 % H₂/He mixture (0.83 $cm^3\ s^{-1};$ 99.999 % Praxair H_2; 99.999 % Praxair He) at 573 K (0.083 K s⁻¹) for 2 h then brought to the target reaction temperatures. n-Heptane (>99.5 %, Acros Organics) was introduced as a liquid and vaporized into H₂ and He streams (99.999 % H₂, Praxair; 99.999 % He, Praxair) metered independently (Parker 601 Series electronic mass flow controllers) to set n-heptane and H₂ pressures $((nH/H_2) \text{ molar ratios} \sim 0.005-0.15; 60-250 \text{ kPa } H_2)$. The system pressure was maintained using a dome-loaded back-pressure regulator (Tempresco). Reactant and product concentrations in the reactor effluent were measured by on-line gas chromatography (Agilent 6890N) using a methyl silicone capillary column (Agilent HP-1, 50 m \times 0.32 mm \times 1.05 $\mu m) and flame ionization detection.$

Measured rates were corrected for approach to equilibrium $(\eta_{j,nH} = {p_j \choose P_{nH}} K_{j,nH}^{-1})$ with respect to reactants to calculate forward reaction rates:

$$r_{\text{forward}} = r_{\text{net}} \left(1 - \left(\frac{P_j}{P_{\text{nH}}} \right) K_{j,\text{nH}}^{-1} \right)^{-1} \tag{1}$$

$$r_{\rm forward} = r_{\rm net} \left(1 - \eta_{j,\rm nH} \right)^{-1} \tag{2}$$

Here, $K_{i,nH}$ is the equilibrium constant for forming each alkane product j from the alkane reactant (from gas phase thermodynamics [24]) and $\frac{P_i}{P_{riv}}$ is the measured ratio of pressures of each product j to that of the nH reactant. Product selectivities for nH reactants were also measured as the number of accessible protons increased monotonically with time by the desorption of pre-adsorbed NH₃ titrants, which bind reversibly at this reaction temperature (548 K). Detailed protocols were been previously reported for n-heptane, 2,4-dimethylpentane, and n-hexane reactants [8-10]. Rates and selectivities were measured on samples treated as described above and then exposed to a He stream (99.999 % Praxair) containing 0.5 kPa NH₃ (0.833 cm³ s⁻¹, 1 % NH₃ in He, Praxair) for 2 h (548 K). NH₃-titrated samples were then exposed to the reactant stream (100 kPa H_2 ; (H_2/nH) molar ratio ~ 200) and rates and selectivities (S_i , for each product *j*; Eq. (3)) were measured as NH₃ gradually desorbed and made protons accessible, thus increasing nH reaction rates (per g_{cat}; to > 80 % of rates before titrant adsorption after \sim 2 h). Selectivities are reported as:

$$S_j = \frac{r_{\text{nH}j}}{\sum_j r_{\text{nH}j}} \tag{3}$$

where $r_{nH,j}$ is the measured formation rate of each product *j* from n-heptane. The relative rate at each time *t* during titrant desorption ($\chi(t)$) is defined as:

$$\chi(t) = \frac{r_{\rm nH}(t)}{r_{\rm nH}} \tag{4}$$

where $r_{nH}(t)$ is the reaction rate at a given time during NH₃ desorption, and r_{nH} is nH reaction rate at steady-state before titrant adsorption.

2.3.2. *Methanol dehydration rates*

Methanol dehydration rates (423 K; reactant conversion < 5 %) were measured on MFI-3 and PtMFI-3c (the PtMFI sample with the largest nH isomerization rate enhancement) using the same reactor used to measure isomerization rates. Samples were pressed, crushed, and sieved to retain aggregates between 180 and 250 μ m. The sieved samples (0.03–0.10 g) were mixed with SiO₂

(Cab-O-Sil HS-5, washed with 1.0 M HNO₃, 180–250 μ m aggregates) and treated in flowing 10 % H₂/He mixture (0.83 cm³ s⁻¹; 99.999 % Praxair H₂; 99.999 % Praxair He) at 573 K (0.083 K s⁻¹) for 2 h before cooling to reaction temperatures. Liquid methanol (99.8 %, Sigma-Aldrich, used without further purification) was introduced into flowing He streams (99.999 % Praxair) at 423 K using a syringe pump (Cole-Parmer 780200C Series). The concentration of reactants and products in the reactor effluent were measured using the chromatographic protocols described above.

2.3.3. CO oxidation rates

CO oxidation rates (443 K; reactant conversion < 0.7 %) were measured on Pt/SiO₂ and PtMFI-3c. Samples were crushed and mixed together with SiO₂ (Cab-O-Sil HS-5, washed with 1.0 M HNO₃) to give 1:10 mass ratios (Pt:diluent) and the mixtures were pressed and sieved to retain 180–250 μ m aggregates. Samples were held on a quartz frit within a tubular reactor (quartz, 7.0 mm i.d.). The bed temperature was measured using a K-type thermocouple in contact with the external wall and aligned with the middle of the catalyst bed. Temperatures were maintained using a three-zone resistively heated furnace (Applied Test Systems Series 3210) with each zone equipped with an independent controller (Watlow Series 96).

All samples were treated in flowing 50 % H₂/He mixture (1.67 cm³ s⁻¹; 99.999 % % Praxair H₂; 99.999 % Praxair He) at 573 K (0.083 K s⁻¹) for 2 h before cooling to the reaction temperature. Reactant flows (1 % CO/He, certified standard, Praxair; 25 % O₂/He, 99.999 % Praxair; He, 99.999 % Praxair) were metered using electronic mass flow controllers. Reactant and product concentrations in the reactor effluent were measured by chromatography (Shimadzu GC-2014; Porapak Q (80/100 mesh, SS, 0.32 cm o.d., 0.02 cm i.d.) using thermal conductivity detection.

2.4. Density functional theory calculations

The energies and structures of bound intermediates and transition states were determined using periodic models and density functional theory (DFT) methods (Vienna ab initio simulation package, VASP [25-28]); a periodic plane-wave basis set (energy cutoff of 396 eV) was used to represent wave functions and projectoraugmented wave (PAW) pseudopotentials [29,30] were used to describe electron-core interactions. The revised Perdew-Wang (PW91) functional was used [31]. Model solid Brønsted acids, tungsten-containing Keggin-type polyoxometalate clusters (POM) with well-defined chemical composition and connectivity, were used as an illustrative acid function to assess plausible alternate isomerization routes involving dienic intermediates. Transition state carbocations for alkene- and diene-mediated pathways, alkyl-substituted cyclopropyl carbocations, are likely similar in size and in charge distribution, which together lead to similar stabilization by zeolitic voids and similar sensitivities to changes in acid strength (deprotonation energies) [10,11,32]. As a result, trends calculated for POM apply to zeolite solid acids, despite their lack of microporous voids and their smaller deprotonation energies (and greater acid strength) than zeolites. POM clusters (1.1 nm diameter) were placed within 3 \times 3 \times 3 nm^3 unit cells to preclude electronic interactions from neighboring cells. The structure of the POM cluster with a P central atom and the proton used as the Brønsted acid site are indicated in Figure S3 of the Supporting Information (SI); the two remaining accessible protons on the POM cluster remained unchanged.

Transition state structures were isolated using nudged elastic band methods [33], and Henkelman's Dimer method [34] was used to refine structures (convergence criteria: energies $< 1 \times 10^{-6}$ eV, forces < 0.05 eV Å⁻¹; also used for geometry optimizations). Frequency calculations were conducted to obtain values for zero-

point vibration energies (ZPVE) and vibrational free energies (G_{vib}); for gas-phase molecules, translational and rotational free energies were also obtained (G_{trans} , G_{rot} , respectively). Low frequency modes of weakly-bound adsorbates were excluded and replaced with a fraction (0.7) of translational and rotational entropies of gas-phase analogs, shown to accurately estimate entropies of adsorbates on oxide surfaces [35].

3. Results and discussion

3.1. n-Heptane isomerization and β -scission reactions: Reaction network and elementary steps

n-Heptane isomerization and β -scission rates and selectivities were measured on three-dimensional zeolites (FAU, BEA, and MFI; MFI samples with a range of Si/Al values) and on these same zeolites with intracrystalline Pt nanoparticles. Both Pt-zeolite and zeolite samples were evaluated as mixtures with Pt/SiO₂, present in amounts sufficient to ensure equilibrium alkene concentrations in the extracrystalline fluid phase (as determined from rates that were a single-valued function of nH/H₂ reactant ratios and unaffected by larger amounts of Pt/SiO₂ [8]).

Primary reactions of n-heptenes and secondary reactions of isoheptenes are depicted in Scheme 1 (using the saturated analogs of each skeletal alkene isomer for illustrative purposes). Linear heptenes (nH⁼) form as a mixture of equilibrated regioisomers from nheptane on Pt/SiO₂ and then undergo skeletal isomerization at acid sites to form 2-methylhexenes (2MH⁼) and 3-methylhexenes (3MH⁼) regiosomers; these methylhexene isomers interconvert via facile methyl shifts into equilibrated 2MH⁼-3MH⁼ mixtures that are treated here as a chemical lump (MH⁼) in accounting for their secondary reactions. MH⁼ isomers undergo skeletal isomerization to form dimethylpentenes (2,4; 2,3; 2,2; and 3,3), which also undergo facile methyl and hydride shifts and are also treated here as lumped pseudospecies (DMP⁼); these DMP⁼ isomers act as the sole precursors to β -scission products (propene and isobutene) [8]. All isomerization and β -scission products form through an initial isomerization step, which converts nH⁼ to MH⁼ isomers. Consequently, the combined rates of n-heptane conversion to all products represent the rate of the initial isomerization events that form 2MH⁼ and 3MH⁼ from nH⁼.

n-Heptane isomerization turnover rates on FAU, BEA, and MFI-3 (per H⁺) are shown in Fig. 1a at different inlet (nH/H₂) reactant ratios. Turnover rates on other MFI samples (MFI-1, MFI-2) show similar trends as on MFI-3 (Figure S5). Inlet (nH/H₂) ratios determine the concentration of nH⁼ regioisomers at zeolite crystallite surfaces when (as in this study) the amount of the extracrystalline Pt/SiO₂ component is sufficient to maintain equilibrium concentra-

tions of $nH^{=}$. Isomerization rates increased proportionally with the prevalent $nH^{=}$ pressures at low (nH/H_2) ratios and then sublinearly at higher ratios, in a manner described accurately by the kinetic rate equation:

$$\frac{r_{\rm isom}}{\rm H^+} = \frac{k_{\rm isom} K_{\rm ads} K_{\rm d,nH} \left(\frac{\rm nH}{\rm H_2}\right)}{1 + K_{\rm ads} K_{\rm d,nH} \left(\frac{\rm nH}{\rm H_2}\right)} \tag{5}$$

Here, $K_{d,nH}$ is the equilibrium constant for n-heptane dehydrogenation to $nH^{=}$ regioisomers ($K_{d,nH}$ = 19.8 Pa at 548 K [24,36]), K_{ads} is the equilibrium constant for the formation of the ensemble of bound heptoxide attachment isomers from the equilibrated nH⁼ regioisomers, and k_{isom} is the rate constant for the isomerization of such an ensemble of bound heptoxides. These kinetic and thermodynamic constants were regressed from the rate data in Fig. 1a and S5 to the functional form of Equation (5) and are shown in Table 3. Equation (5) is consistent with elementary steps that involve the protonation of a pool of equilibrated linear alkenes to the corresponding pool of equilibrated alkoxides having the backbone of their alkene precursors, but with all possible attachment points to framework O-atoms. In the sole kinetically-relevant step, this pool of equilibrated alkoxides converts to alkoxides with methylhexene backbones, which then deprotonate to form their gaseous analogs.

The premise that concentration gradients of reactant alkenes are inconsequential for rates is required for the chemical interpretation of Equation (5); in such instances, their intracrystalline concentrations are constant and equal to those present in the extracrystalline fluid phase and given by $K_{d,nH}\left(\frac{nH}{H_2}\right)$. Such a presumption, however, is not consistent with the effects of intracrystalline Pt nanoparticles on rates, as discussed later in this section; yet, it remains a functional form that faithfully describes measured rates even in the presence of diffusional corruptions.

Any effects of intracrystalline concentration gradients of $nH^{=}$ reactants within acid domains would depend on a Thiele modulus (ϕ); in the first-order regime (e.g., low (nH/H_2) ratios) ϕ is given by [37,38]:

$$\phi^2 = \frac{k\rho_{\rm H^+} L^2}{2} \tag{6}$$

where *k* is the first-order rate constant for nH⁼ isomerization to MH⁼ (corresponding to $k_{isom}K_{ads}$ in Eq. (5)), ρ_{H^+} is the volumetric proton density within zeolite crystallites, *L* reflects the size of zeolite crystallites, and *D* is the diffusivity for nH⁼ within acid domains. Such ϕ parameters reflect the ratio of characteristic reaction and diffusion rates and arise directly from differential mole balances within acid domains, expressed in dimensionless form [37,38]. Small ϕ values (\ll 1) lead to concentration gradients that are not



Scheme 1. Isomerization and β -scission reaction network for C₇ alkenes on bifunctional physical mixtures of Brønsted acid catalyst and Pt/SiO₂. Dashed boxes around isomers with the same degree of branching indicate facile interconversion and isomers treated as a kinetic lump. Reactions are mediated by alkenes but are shown by alkane analogs for visual clarity.



Fig. 1. n-Heptane isomerization turnover rates (per H⁺) as a function of (nH/H₂) molar ratio in reactant stream on physical mixtures of Pt/SiO₂ and (a) FAU (squares), BEA (circles), or MFI-3 (triangles); or (b) PtFAU (squares; left axis), PtBEA (circles; left axis), PtMFI-2 (diamonds; left axis), or PtMFI-3c (triangles; right axis) (548 K, 0.2–14 kPa nH, 60–100 kPa H₂). Dashed lines represent regression to the functional form of Equation (5).

Table 3

First- $(k_{isom}K_{ads})$ and zero-order (k_{isom}) rate constants for n-heptane isomerization (per H^{*}, 548 K), as defined in Equation (5), on mesoporous and microporous aluminosilicates.

Sample	k_{isom}K_{ads} (Pa H ⁺ ks) ⁻¹	k_{isom} (H ⁺ ks) ⁻¹
FAU	8.88 (±0.38) ^a	46.5 (±35)
BEA	88.7 (±4.7)	80.4 (±19.4)
MFI-1	103 (±1.3)	111 (±14)
MFI-2	93.5 (±3.5)	158 (±43)
MFI-3	117 (±8.5)	108 (±34)
PtFAU	11.0 (±0.2)	99.7 (±111)
PtBEA	197 (±19)	102 (±27)
PtMFI-1	130 (±5.8)	136 (±25)
PtMFI-2	199 (±20)	173 (±58)
PtMFI-3a	154 (±4.1)	239 (±48)
PtMFI-3b	519 (±39)	714 (±285)
PtMFI-3c	1210 (±110)	1260 (±813)

 $^{\rm a}$ Values in parentheses represent 95 % confidence intervals from regression of rate data to Equation (5).

consequential for rates, while large ϕ values (\gg 1) lead to rates that decrease with increasing proton density (ρ_{H+}) and crystallite size (*L*) because of reactant depletion within acid domains, as described in detail in Section 3.6, through diffusion–reaction formalisms and mathematical treatments that describe isomerization and β -scission events.

The regressed values of first-order isomerization rate constants $(k_{isom}K_{ads}, Table 3)$ are similar among MFI samples without an intracrystalline Pt function, in spite of their different Thiele moduli [8]. These measurements would indicate, at first glance, that intracrystalline nH⁼ gradients are kinetically-inconsequential. The $k_{isom}K_{ads}$ values (94–120 (Pa H⁺ ks) ⁻¹, Table 3) on MFI are slightly larger than on BEA (89 (Pa H⁺ ks) ⁻¹, Table 3) and much larger than on FAU (8.9 (Pa H^+ ks) $^{-1}$, Table 3). These different first-order rate constants reflect, at least in part, confinement effects on transition state stability mediated by van der Waals interactions between carbenium-ion transition states and the zeolite framework [8,39,40]. The larger voids in FAU (1.1 nm supercages with 0.74 nm windows [21]) lead to less effective van der Waals contacts than in BEA (0.59 nm channels with 0.69 nm intersections [21]) or MFI (0.47 nm \times 0.45 nm intersecting channels with 0.64 nm diameter intersections [21]). The larger voids in BEA and FAU, in turn, allow faster molecular diffusion than those in MFI.

The less reactive protons, taken together with the faster diffusion of reactants and products, in BEA and FAU lead to less severe concentration gradients than in MFI zeolites with similar proton densities and crystal dimensions.

The primary MH⁼ products formed in isomerization steps are more reactive and diffuse more slowly than their nH⁼ precursors, leading to a propensity for diffusion-enhanced secondary isomerization, the extent of which depends on the Thiele modulus for such secondary reactions ($\phi_{MH^{=}}$ for MH⁼, Eq. (6)) [8]. Their subsequent isomerization leads, in turn, to even more reactive and slower diffusing DMP⁼ isomers (thus even larger $\phi_{\text{DMP}^=}$, Eq. (6)), which represent the predominant reactants for β -scission events. The size of acid domains, defined as the continuous volume containing acid sites before molecules are able to contact a metal function and hydrogenate, can be made smaller by placing Pt nanoparticles within zeolite crystals. Previous interpretations (based on the data in Table 3) led to an expectation that nH isomerization turnover rates would be unaffected by such a decrease in the acid domain size (because of inconsequential intracrystalline nH⁼ gradients even without an intracrystalline hydrogenation function), while the selectivity to primary products may increase as a result of the smaller $\phi_{\rm MH^{=}}$ and $\phi_{\rm DMP^{=}}$ values characteristic of smaller acid domains.

The data in Fig. 1b contradict these expectations about the strict chemical origins of measured isomerization rates. nH isomerization rates were 1.3–10 times larger when Pt nanoparticles were dispersed within BEA and MFI crystallites than for the parent zeolites (in both cases as physical mixtures with Pt/SiO₂). Fig. 1b shows nH isomerization turnover rates on PtFAU, PtBEA, PtMFI-2, and PtMFI-3c catalysts (with extracrystalline Pt/SiO₂) at different reactant (nH/H₂) ratios (similar trends on PtMFI-1, PtMFI-3a and PtMFI-3b are reported in Fig. S5b). These isomerization rates remain well described by the functional form of Equation (5) on all samples and retain a single-valued dependence on the (nH/H₂) ratios in reactant streams.

The first-order rate constants obtained by regressing the data in Fig. 1b (and Fig. S5b) to the functional form of Equation (5) are shown in Table 3. The enhancement factors (ω) resulting from intracrystalline Pt nanoparticles, defined as:

$$\omega = \frac{(k_{\rm isom} K_{\rm ads})_{\rm Pt-zeo}}{(k_{\rm isom} K_{\rm ads})_{\rm zeo}} \tag{7}$$

are shown in Fig. 2a. Here, $k_{isom}K_{ads}$ is the first-order rate constant for nH isomerization and the subscript "Pt-zeo" and "zeo"

represent that for the Pt-containing zeolites and the parent (H-form) zeolites, respectively (both as mixtures with extracrystalline Pt/SiO₂). These ω values are larger for samples with higher intracrystalline Pt contents, plausibly as a result of smaller sizes of acid domains and greater metal-acid site intimacy.

The acid domain size is determined by the mean Pt interparticle distance ($\langle l_{Pt} \rangle$), which also affects Pt-H⁺ distances and the ratio of H^+ to the number of encapsulated Pt nanoparticles (H^+/Pt); these values were estimated (Table 2) by assuming that all nanoparticles smaller than 2 nm in diameter (from TEM) reside and are distributed uniformly within zeolite crystals. Some extracrystalline particles may be present and lead to underestimation of Pt-Pt distances, but with a bias that is similar for all samples (given their similar size distributions; Fig. S2). The micrographs (representative examples in Fig. S1) also do not provide any evidence for nonuniform spatial distributions. Measured ω values (Fig. 2a) increase with decreasing $\langle l_{Pt} \rangle$ (Table 2) on PtMFI samples, suggesting that metal-acid site proximity may indeed matter for n-heptane isomerization rates, as a result of chemical or diffusional effects that are considered in the next sections. Such proximity effects are also evident from measured selectivities to isomerization and β scission products (Fig. 2b and 2c); these selectivity trends are discussed and described in terms of diffusion-reaction formalisms in Section 3.6.

Direct atomic contact between a proton and a Pt nanoparticle may affect, however, the chemical and catalytic properties of either or both functions; it may even create hybrid metal-proton adducts with unique chemical or electronic properties. Circumstantial evidence from H-D isotopic exchange rates during cyclopentane reactions on Pt nanoparticles within MOR zeolites and infrared spectra of bound CO have implicated such metal-proton adducts as mediators of bifunctional routes [41,42]. Also, reactive intermediates present at equilibrium concentrations much lower than alkenes, such as dienes and trienes, may become competent molecular shuttles when they can be replenished by a more proximate metal function. These plausible chemical interpretations are examined through spectroscopic and functional assessments of the acid (Section 3.2) and metal (Section 3.3) sites and theoretical estimates of activation barriers required for the involvement of diene intermediates in acid-catalyzed isomerization events (Section 3.4).

3.2. Assessments of the number, structure, and reactivity of zeolitic O– H groups

The kinetic relevance of the acid function in n-heptane isomerization reactions may cause rate enhancements by modifying acid sites through interactions with vicinal Pt nanoparticles, whether in the number or acid strength. The grafting of Pt²⁺ cations from aqueous media during ion exchange synthesis protocols removes some of the intracrystalline protons, but they re-form upon reduction of Pt²⁺ and nucleation of Pt⁰ nanoparticles [43]. As a result, the proton densities (ρ_{H^+}) and properties are not expected to be affected by these exchange-reduction protocols, leading to rates on acid sites unaffected by the presence of intracrystalline Pt nanoparticles.

Exchange of H^+ by Pt^{2+} cations and reduction would cause higher rates on acid sites only when synthesis protocols (i) change the number of H^+ ; (ii) lead to a local decrease in void sizes because of occlusion of intracrystalline volume by nanoparticles (thus influencing confinement effects on transition state stability, as found for detrital AlO_x domains within FAU voids [39]); or (iii) perturb acid strength through atomic contact between Pt nanoparticles and H^+ . These plausible hypotheses are shown next to be inconsistent with the spectroscopic and kinetic evidence obtained on

PtMFI-3c, the materials that exhibited the largest nH isomerization rate enhancements ($\omega \sim 10$; Fig. 2a).

The vibrational frequency of acidic O–H groups (\sim 3600 cm⁻¹) at Si-O-Al moieties in zeolites is sensitive to the size of the confining voids [44,45] as in the case, for instance, of protons in side pockets (8-MR; 3590 cm⁻¹; 0.30 nm) and straight channels (12-MR; 3610 cm⁻¹; 0.67 nm) in MOR [45]. Fig. 3a shows the O–H infrared bands in MFI-3 and PtMFI-3c samples treated in H₂ at 573 K and then evacuated at 548 K. These bands are identical in intensity and frequency for the two samples, consistent with protons that are unaffected in the number or environment by intracrystalline Pt nanoparticles.

CH₃OH dehydration rates (r_{DME}) depend on the number, strength and environment of acid sites [39,44]. Fig. 3b shows these rates at 423 K and different CH₃OH pressures on MFI-3 and PtMFI-3c. These rates are described by the equation [44]:

$$\frac{r_{\text{DME}}}{H^+} = \frac{k_1(\text{CH}_3\text{OH})^2}{(\text{CH}_3\text{OH}) + \frac{k_1}{k_0}(\text{CH}_3\text{OH})^2} = \frac{k_1(\text{CH}_3\text{OH})}{1 + \frac{k_1}{k_0}(\text{CH}_3\text{OH})}$$
(8)

where k_1 and k_0 denote first- and zero-order rate constants. CH₃OH conversion to CH₃OCH₃ at these conditions involves direct/associative routes mediated by the sequential formation of Hbonded monomers and protonated dimers, as evident from infrared, kinetic and theoretical studies [44]. The form of Equation (8) reflects elementary steps that involve: (i) quasi-equilibrated formation of H-bonded CH₃OH monomers; (ii) their reaction with another CH₃OH molecule to form a protonated dimer also in quasi-equilibrated steps; and (iii) the rotation of such dimers to eliminate H₂O in the sole kinetically-relevant step. These rate constants depend on how acid strength and confinement stabilize the bimolecular transition states, in the case of k_1 relative to one Hbonded CH₃OH and one unperturbed CH₃OH(g) molecule and in the case of k_0 relative to confined protonated dimers [44].

MFI-3 and PtMFI-3c show similar rates and kinetic trends (Fig. 3b); their k_0 and k_1 parameters (inset in Fig. 3b) are essentially identical, consistent with spectroscopic evidence that the observed large differences in their isomerization rate constants do not reflect differences in the number, strength, or confining environment of Brønsted acid sites, the kinetically-relevant function in bifunctional alkene isomerization events.

3.3. Binding properties and reactivity of Pt nanoparticles

Infrared spectra of bound CO and the turnover rates for $CO-O_2$ reactions are shown in this section as probes of the properties of Pt nanoparticles (PtMFI-3c) within zeolite crystals and within mesoporous environments (Pt/SiO₂) to assess any effects of metal-acid distance or hybrid adducts [43,46-50] on the dispersion or surface properties of Pt nanoparticles.

The evidence for metal-proton adducts relied on the appearance of bound CO infrared bands at 2132 cm⁻¹ [48,51], distinct from those for linear CO species bound at atop positions on unperturbed Pt nanoparticles (2060 cm⁻¹) [52]. Fig. 4a shows infrared spectra for Pt/SiO₂ and PtMFI-3c after exposure to 1 kPa CO and its removal from the fluid phase by He flow at 300 K. Both spectra show a sharp band for linear CO bound at atop locations (2060 cm^{-1} [52]) and a broader feature for bridge-bonded CO (1820–1880 cm⁻¹). The atop to bridge CO intensity ratio is slightly larger for PtMFI-3c than Pt/ SiO₂, as expected from the smaller Pt nanoparticles in PtMFI-3c (1.1 nm vs. 1.3 nm mean diameters from TEM). These spectra do not show any spectral features previously attributed to Pt-H⁺ adducts [48,51]; they indicate, instead, that Pt nanoparticles dispersed within MFI-3 and onto mesoporous SiO₂ bind CO in similar configurations and in amounts commensurate with the respective Pt dispersion in each sample.



Fig. 2. (a) Enhancement factor ω (Eq. (7)) that reflects the ratio of first-order rate constants on Pt-zeolites and H-zeolites (548 K); (b) methylhexanes and (c) β -scission selectivities during steady-state nH isomerization reactions on physical mixtures of Pt/SiO₂ and H-zeolites (white) or Pt-zeolites (grey) (548 K, 0.01 (nH/H₂) molar ratio).



Fig. 3. (a) Infrared spectra of PtMFI-3c (top) and MFI-3 (bottom), under dynamic vacuum $(10^{-2} Pa; 548 K)$ after pretreatments (Section 2.2). (b) CH₃OH dehydration turnover rates (per H⁺) on MFI-3 and PtMFI-3c (423 K). Inset values represent rate constants regressed to the functional form of Equation (8); the dashed curve represents the fit using regressed parameters.

CO oxidation turnover rates (per exposed Pt atom, Pt_s , from H_2 chemisorption uptakes, Section 2.1) were compared on PtMFI-3c and Pt/SiO₂. CO oxidation [53-57] is an emblematic structure-insensitive monofunctional metal-catalyzed reaction; CO oxidation turnover rates are essentially independent of Pt dispersion and expected to be similar on PtMFI-3c and Pt/SiO₂, in the absence of different electron densities for Pt nanoparticles within zeolites or within mesoporous SiO₂. CO oxidation rates on Pt nanoparticles (r_{COox} , per Pt_s) are described by the rate equation [52,55,57]:

$$\frac{r_{\rm COox}}{Pt_{\rm s}} = k_{\rm eff} \frac{(O_2)}{(CO)} \tag{9}$$

where $k_{\rm eff}$ is an effective rate constant and (O₂) and (CO) are the respective reactant pressures. Kinetic data, isotopic experiments, in situ infrared spectra, and theoretical treatments show that rates are limited by dissociation of O₂ assisted by vicinal chemisorbed CO species on Pt surfaces nearly-saturated with chemisorbed CO. Fig. 4b shows measured CO oxidation turnover rates on Pt/SiO₂ and PtMFI-3c and predicted $k_{\rm eff}$ values regressed from all rate data to the functional form of Equation (9). These rate constants are $0.73 \pm 0.05 \text{ ks}^{-1}$ on Pt/SiO₂ and $0.68 \pm 0.03 \text{ ks}^{-1}$ on PtMFI-3c, consistent with Pt nanoparticle surfaces that are similar in electron density and in their interaction with CO adsorbates, whether they reside within zeolite crystals or mesoporous SiO₂.

These data and those in Section 3.2 indicate that the acid and metal functions in PtMFI-3c ($\omega \sim 10$) are similar to those in the monofunctional MFI-3 and Pt/SiO₂ samples, respectively; these observations preclude the presence (and catalytic role) of metal-acid hybrid sites that would require inter-function atomic contact or any detectable differences in the properties of either of the two functions in their respective roles as (de)hydrogenation and acid catalysts. The proximity effects that lead to the 10-fold enhancements in n-heptane isomerization rates in this sample cannot arise from detectable changes in the chemical properties of either function. Such enhancements must therefore reflect a consequence of nanoscale metal-acid site proximity that cannot be attributed to chemical origins.

3.4. Unsaturated molecular shuttles as mediators of bifunctional isomerization cascades

Alkenes act as the accepted molecular shuttles that enable metal and acid functions to detect their respective presence and intervening distances in isomerization and β -scission reactions.



Fig. 4. (a) Infrared spectra of strongly chemisorbed CO species on PtMFI-3c (top) and Pt/SiO₂ (bottom) (exposure: 300 K, 1 kPa CO, followed by He flow). (b) Parity plot for CO oxidation turnover rates (per Pt_s) on Pt/SiO_2 and PtMFI-3c (443 K, 0.008–0.15 kPa CO, 4–10 kPa O_2). Inset values represent rate constants regressed to the functional form of Equation (9). Calculated rates are those derived from Equation (9) using regressed parameters. The dashed line represents parity.



Fig. 5. (a) DFT-derived free energies for conversion of linear heptenes to $2MH^{=}$ on POM through diene-derived (dashed line) and alkene-derived (solid line) pathways. Transition state structures are included in Figure S4; (b) nH isomerization turnover rates (548 K) on PtMFI-3c as a function of reactant (nH/H₂) molar ratios for different H₂ pressures (60–250 kPa, colors indicated in the inset gradient). Dashed line represents regression to the functional form of Equation (5).

Nanoscale intimacy between metal and acid functions may allow less stable (and less abundant) dienes and trienes to act as alternate mediators, thus allowing isomerization channels that are not possible at larger metal-acid distances. Such bifunctional cascades could involve alkadienes that form on metal surfaces, but at equilibrium concentrations much smaller than for alkenes; this would then require much smaller metal-acid distances to maintain diffusive fluxes required for measurable contributions to isomerization rates. Alkadienes may be able to isomerize at higher rates than alkenes because of resonance stabilization of allylic carbocationic transition states [58]; such higher reactivity must compensate for their much smaller equilibrium concentrations than for their alkene precursors.

DFT calculations are used here to assess whether dienes can compensate for their lower equilibrium pressures through more stable TS structures. Estimates of activation free energies for isomerization turnovers mediated by alkene and alkadiene intermediates in equilibrium with nH-H₂ mixtures reflect the free energy of formation of such TS structures from an alkane with the evolution of one (for alkenes) or two (for alkadienes) H_2 molecules, respectively.

Alkadiene-derived allylic carbocations show a higher activation free energy than alkene-derived cyclopropyl carbocations (72 vs. 48 kJ mol⁻¹, respectively, Fig. 5a). Such higher activation free energies (by ~ 25 kJ mol⁻¹) indicate that diene-mediated pathways are unlikely to contribute detectably to measured isomerization rates, even if dienes were formed and present at their equilibrium concentrations and metal–acid site distances were sufficiently proximate to provide the requisite diffusive fluxes.

Measured isomerization rates are single-valued functions of (nH/H_2) reactant ratios, irrespective of the H₂ and alkane pressures used in setting such ratios (PtMFI-3c, 60–250 kPa H₂; Fig. 5b); these kinetic trends are indicative of equilibrated alkenes as kinetically-relevant shuttles. An alternate (or additional) involvement of alkadienes (or other unsaturated intermediates such as trienes) present at equilibrium concentrations would make rates determined by $(nH)/(H_2)^2$ ratios (or $(nH)/(H_2)^3$ for trienes), inconsistent with the trends in measured rates (Fig. 5b). Consequently,

pathways mediated by dienes (or other unsaturated species) cannot contribute detectably to measured isomerization rates, even for samples that show 10-fold increases in isomerization rates when Pt nanoparticles are placed within zeolite crystals.

These experimental and theoretical observations confirm that rate enhancements upon dispersing Pt nanoparticles within zeolite crystals do not arise from alternate mediators of bifunctional cascade reactions, made feasible at the much shorter diffusion distances in zeolites with an intracrystalline dehydrogenation function.

3.5. Interlude

Sections 3.2-3.4 show evidence against chemical origins for the observed rate enhancements (and selectivity trends) when Pt nanoparticles are placed within zeolite crystallites. These effects do not arise from differences in the number or reactivity of Brønsted acid sites (Section 3.2) or of Pt surface atoms (Section 3.3) or from the formation of less stable (but more reactive) dienes or trienes, replenished more effectively by more proximate Pt nanoparticles (Section 3.4). Such systematic falsifications of any chemical origins for these effects direct our search, in part through a process of elimination, towards explanations based on the inherent coupling between diffusion and reaction in bifunctional routes that occur within voids of molecular dimensions.

Alkane isomerization and β -scission involve bifunctional cascades that are "initiated" and "terminated" via dehydrogenation and hydrogenation events, respectively, at a metal function. Consequently, the intervening "clock" for the "propagation" events that react alkenes at acid sites (isomerization and β -scission) is set by a diffusional distance (L), defined by the mean size of the acid domains through which alkene intermediates diffuse and react before they encounter a metal function that hydrogenates them to their less reactive alkane analogs. This is defined in practice by the mean distance among the Pt nanoparticles when such particles are embedded within acid domains. Such distances are much smaller when Pt nanoparticles are dispersed within intracrystalline domains (10-25 nm, Table 2) than when they are exclusively placed as a separate function outside crystallites, which defines L as the zeolite crystallite diameter (e.g., ~400 nm for MFI-3). The smaller L values for samples with intracrystalline Pt nanoparticles lead, in turn, to smaller Thiele moduli (ϕ , Eq. (6)) and to smaller concentration gradients of alkene reactants and isoalkene products within acid domains. These smaller ϕ values do not strongly influence rates in all instances, as shown from rates and rate parameters that did not vary significantly over a small range of ϕ for physical mixtures of Pt/SiO₂ and acid zeolites with different L values (as described in reference [8] and Section 3.1). These expectations are informed by assumptions that nH⁼ isomerization to MH⁼ and DMP⁼ remains far from equilibrium within acid domains. Yet, measured rate enhancements (ω , Eq. (7)) reached values as large as 10 for given zeolite catalysts when Pt nanoparticles are dispersed within zeolite crystallites (Fig. 2a). Such rate enhancements are likely to reflect the shifting of equilibrium bottlenecks for alkene isomerization events as they approach thermodynamic equilibrium within zeolite crystallites. These local shifts occur via facile hydrogenative scavenging of isoalkene products because of the intimate presence of Pt functions, which preserves their skeleton intact, or via secondary isomerization and β -scission that scavenge the MH⁼ products to make thermodynamically favorable smaller molecules that can rapidly egress.

Smaller diffusion distances and ϕ values (or equivalently shorter diffusion timescales) allow reactive isoalkenes to hydrogenate, thus becoming less reactive, as they diffuse through acid domains; consequently, the likelihood of secondary isomerization and

 β -scission reactions decreases, thus preserving "earlier" isomer products along the isomerization sequence. Samples with smaller diffusion distances (PtMFI-3a and b), set by the mean Pt nanoparticle distance ($\langle l_{Pt} \rangle$, Table 2), showed a monotonic decrease in β scission selectivity (S_{β} , Fig. 2c) and higher selectivities to primary MH⁼ products (S_{MH} , Fig. 2b), the expected consequence of concomitantly smaller ϕ values.

These transport effects on rates and selectivities require mathematical diffusion-reaction formalisms that account for intracrystalline gradients in reactant and product concentrations and for the local equilibration of alkene interconversion steps. Such descriptions are then embedded within a plug-flow convection-reaction constructs that describe the distribution of products formed as concentration gradients developed within crystallites and along the packed-bed reactor.

3.6. Diffusion-reaction treatments at the crystallite and bed length scales

3.6.1. Mathematical descriptions of coupled diffusion-convectionreaction systems

The inextricable coupling of diffusive and reactive processes within voids of molecular dimensions requires descriptions of local gradients within acid domains, as well as the updating of the conditions at the boundaries of these domains along the reactor, as chemical reactions deplete reactants and form products. Within acid domains, isomerization and β -scission rates are described by coupled mole balances for n-heptenes (denoted as A), methylhexenes (B), and dimethylpentenes (C); the balance for β -scission products is not required because of their faster diffusion, less reactive nature, and irreversible formation steps. Section 3.1 and earlier work [8] have shown that n-heptane isomerization rates are described accurately by a Langmuirian equation (Eq. (5)) in terms of the nH/H₂ molar ratios that determine the prevalent equilibrium n-heptene pressures. Rate enhancements obtained from these mathematical treatments are defined as the ratio of regressed first-order rate parameters for systems with and without intracrystalline Pt nanoparticles (ω , experimental values in Fig. 2a) to the functional form of Equation (5).

Here, a mathematical treatment for diffusional corruptions of first-order reactions is used as an illustrative case, because concentration gradients become monotonically less consequential as rates become independent of prevalent n-heptene concentrations (set by nH/H_2 ratios). The complete rate expression (Eq. (5)) can be used without significant computational hurdles, but without the pedagogical and heuristic benefits of these simpler kinetic trends. Modest intraparticle gradients do not distort measured rates detectably from their Langmuirian functional form; the regression of diffusion-corrupted rates, however, leads to values of first-order rate constants that are influenced by the prevalent gradients, as discussed in detail in later work. Such matters do not affect the conclusions of this work, but they are likely to have led to underestimates of the severity of intracrystalline gradients in previous analyses of these reactions [8].

The dimensionless differential diffusion-reaction mole balances are:

$$\frac{d^2 Y_A}{d\xi^2} = -\phi_A^2 \cdot [Y_B - Y_A] \tag{10}$$

$$\frac{d^2 Y_B}{d\xi^2} = -\phi_B^2 \cdot [Y_A \cdot \Theta_1 - Y_B + Y_C \cdot \Theta_2 \cdot (1 - \Theta_1)]$$
(11)

$$\frac{d^2 Y_{\rm C}}{d\xi^2} = -\phi_{\rm C}^2 \cdot [Y_{\rm B} - Y_{\rm C}] \tag{12}$$

where ξ is the dimensionless position ($\xi = x/L$) within acid domains ($\xi = 0$ at the centerline; Scheme 2). Y_A , Y_B , and Y_C are dimensionless concentrations of nH⁼, MH⁼ and DMP⁼ lumps (defined in Table 4). Θ_1 and Θ_2 are ratios of rate constants (Table 4). The ϕ_A , ϕ_B , ϕ_C parameters are the Thiele moduli for the three alkene lumps in the context of their interconversion reactions:

$$\phi_{\rm A}^2 = \frac{k_{\rm A}L^2}{D_{\rm A}}\rho_{\rm H^+} \tag{13}$$

$$\phi_{\rm B}^2 = \frac{(k_{\rm A} + k_{\rm B})L^2}{D_{\rm B}} \rho_{\rm H^+} \tag{14}$$

$$\phi_{\rm C}^2 = \frac{(k_{-{\rm B}} + k_{\rm C})L^2}{D_{\rm C}} \rho_{\rm H^+} \tag{15}$$

L is the characteristic size of the acid domains (half the slab thickness or the radius of a quasi-spherical crystallite), k_i (i = A, B, and C, same after) is the forward first-order rate parameter for isomerization and β -scission events, k_{-i} denotes the reverse first-order rate parameter, D_i is the diffusivity of species i, and ρ_{H^+} is the volumetric proton density within zeolite crystallites. An infinite slab geometry is used here (thickness 2 *L*), but the results are readily extended to other geometries (e.g., spherical) by using a shape factor $\left(\left(\frac{V_p}{S_p}\right); V_p$ is the particle volume and S_p is its external surface area) to replace the characteristic distance *L* in Equations 13–15 [59].

These equations contain five dimensionless parameters: ϕ_A , Θ_1 , Θ_2 , D_A/D_B and D_B/D_C . The use and choice of these dimensionless parameters minimize the number of adjustable parameters in the model, while retaining the consistency with those typically used in the field. The Thiele modulus ϕ_A is the ratio of the characteristic time for diffusion of nH⁼ within acid domains to that for isomerization of nH⁼ to MH⁼, leading to ϕ_A values that directionally describe the severity of diffusional effects on the reactions that consume nH⁼ as it diffuses from Pt nanoparticles where it forms. The ϕ_B and ϕ_C parameters reflect similar ratios for the respective alkene lumps and their reactions; they are related to ϕ_A through properties that are unique for each given zeolite framework:

(i) Θ_1 and Θ_2 are rate constant ratios $(\frac{k_{-A}}{k_{-A}+k_B}$ and $\frac{k_{-B}}{k_{-B}+k_C}$, respectively; Table 4); they are smaller than unity and reflect the fractions of isomerization events that convert a given species to its precursor along the reaction sequence in Scheme 2;

(ii) D_A/D_B and D_B/D_C are diffusivity ratios; they are larger than unity because skeletal branches lead to smaller diffusivities [8,9].

Such diffusional effects become more consequential as molecules and voids become similar in size, because tighter confinement leads to greater differences in reactivity and in diffusivity among the skeletal isomers involved in the reactions described in Scheme 2 [60,61].

The boundary conditions for Equations 10–12 evolve axially along the reactor as reactions occur (Scheme 2). For first-order isomerization and β -scission reactions and plug-flow hydrodynamics at the bed scale, this evolution is described by coupled differential mole balances:

$$\frac{dX_{nH}}{d\gamma} = (1 - X_{nH})(\Theta_1)(I_A - I_B)$$
(16)

$$\frac{dX_{\rm MH}}{d\gamma} = (1 - X_{\rm nH})(\Theta_1 I_{\rm A} - I_{\rm B} + (1 - \Theta_1)\Theta_2 I_{\rm C}) \tag{17}$$

$$\frac{dX_{\text{DMP}}}{d\gamma} = (1 - X_{\text{nH}})(1 - \Theta_1)(I_{\text{B}} - I_{\text{C}})$$
(18)

where X_j (j = nH, MH, DMP) is the fractional conversion of alkane reactants (j = nH) or the ratio of the concentration of each product alkane at each axial position to that of the nH reactant at the bed inlet (j = MH, DMP), γ is the dimensionless bed length, and I_i

(*i* = A, B, C) is the dimensionless concentration of each alkene species *i* (integrated across the acid domain) at axial position γ . The definitions of γ and I_i are described in Table 4.

At the conditions of this study (with excess H₂ consumed only in β -scission events), equilibrium alkene concentrations in the fluid phase remain below detection limits; they can be inferred, however, from the H₂ and alkane pressures at each position together with gaseous thermodynamic data (after demonstrating, as done here, that additional amounts of extracrystalline Pt function do not affect rates or selectivities). Consequently, the coupling between the bed (Eqs. 16–18) and the acid domain (Eqs. 10–12) scales requires a description of the axial concentration gradients of alkanes along the bed. Such requirements are met by using Equations 16– 18 and the boundary conditions for Equations 10–12:

$$\left. \frac{dY_i}{d\xi} \right|_{\xi=0} = 0 \tag{19}$$

$$Y_A|_{\xi=1} = 1/\Theta_1 \tag{20}$$

$$Y_{\mathsf{B}}|_{\xi=1} = \frac{1}{K_{\mathsf{A}}\Theta_{1}} \frac{X_{\mathsf{M}\mathsf{H}}}{1-X_{\mathsf{n}\mathsf{H}}} \frac{K_{\mathsf{d},\mathsf{M}\mathsf{H}}}{K_{\mathsf{d},\mathsf{n}\mathsf{H}}}$$
(21)

$$Y_{C}|_{\xi=1} = \frac{1}{K_{A}K_{B}\Theta_{1}\Theta_{2}} \frac{X_{DMP}}{1-X_{nH}} \frac{K_{d,DMP}}{K_{d,nH}}$$
(22)

where $K_A = k_A/k_{-A}$, $K_B = k_B/k_{-B}$; $K_{d,nH}$, $K_{d,MH}$ and $K_{d,DMP}$ are the equilibrium constants for the dehydrogenation of nH, MH and DMP lumps to their respective lumped alkene regioisomers. Equation (19) establishes a symmetry condition at the centerline of the acid domain, while Equations 20-22 set the reactant and product alkene concentrations at the acid domain boundary. Such a boundary is defined by the location of the Pt nanoparticles, with their mean interparticle distance determining the relevant characteristic diffusion length. This boundary differs from the physical boundary of zeolite crystals but lies within them; it is where reactant and product alkenes convert to their respective local alkanes through hydrogenation-dehydrogenation equilibration at the Pt function. This is reflected in Equation (20) for reactant nH⁼ and in Equations (21) and (22) for MH⁼ and DMP⁼ products, respectively. Equations 10-12 and 16-18 were solved concurrently using MATLAB® (Boundary Value Problem (BVP) solver bvp4c; ODE solver ode45 or 15s, respectively).

This mathematical framework was also used to describe an intentional temporal increase in the number of accessible protons during transient desorption of pre-adsorbed NH₃ (Section 2.3.1). This merely requires the use of a time-dependent proton density ($\rho_{\rm H^+}(t)$, Eq. (23)) that leads, in turn, to time-dependent Thiele moduli (Eqs. 13–15) and to a change in the number of accessible protons within the bed ($W_{\rm H^+}$, grouped into γ , Table 4). For desorption rates proportional to the number of residual bound NH₃, the time-dependent proton density is:

$$\rho_{\rm H^+}(t) = [1 - \exp(-k_{\rm des}t)]\rho_{\rm H^+}^{\infty}$$
(23)

where *t* is time after start of desorption, k_{des} is the first-order NH₃ desorption rate constant and $\rho_{\text{H}^+}^{\infty}$ is the proton density before NH₃ titration (and also after its complete desorption). The magnitude of $\rho_{\text{H}^+}(t)$ increases with time and reaches an asymptotic value of $\rho_{\text{H}^+}^{\infty}$ after the time required for desorption to be complete.

3.6.2. Diffusional and thermodynamic constraints within acid domains

In this section, acid domains are first examined at conditions prevalent at the bed inlet in order to assess the effects of intracrystalline diffusions on rates and selectivities using the diffusion-reaction formalisms described above at low reactant conversion (Eqs. 10–12); the axial position along the bed does not distinctly influence measured rates and selectivities ([8,9] and Section S4



Scheme 2. Schematic depiction of the coupled diffusion-convection-reaction system for bifunctional isomerization and β -scission cascades. Acid domains are represented by the inset solid rectangles, the catalyst bed is denoted by the surrounding dashed rectangle. Metal functions and acid sites (H⁺) are also displayed. k_i and k_{-i} (i = A, B, C) are first-order rate constants; D_i (j = A, B, C, D) is diffusivity for nH⁺, MH⁺, DMP⁺ and β -scission products, respectively.

 Table 4

 Nomenclature and dimensionless parameters used in diffusion-convection-reaction mathematical treatments.

C _i C ₄	Local concentration of <i>i</i> (<i>i</i> = A, B, C) within acid domains Concentration of n-heptene at the outer boundary of acid domains
$C_{nH,0}$	Concentration of n-heptane at the inlet of the catalyst bed
C _{H2.0}	Concentration of H ₂ at the inlet of the catalyst bed
F _{nH,0}	Molar rate of n-heptane at the inlet of the catalyst bed
W_{H^+}	Moles of accessible protons in the catalyst bed
Y_A	$rac{k_{-A}+k_B}{C_{A_S}k_{-A}}C_A$
Y_B	$rac{k_{-A}+k_B}{C_{A_S}k_A}C_B$
Y _C	$rac{k_{-A}+k_B}{C_{A_S}k_A}rac{k_C+k_{-B}}{k_B}C_C$
Θ_1	$\frac{k_{-A}}{k_{-A}+k_B}$
Θ_2	$\frac{k_{-B}}{k_{-B}+k_{C}}$
γ	$k_A W_{H^+} \frac{C_{nH,0}}{F_{nH,0}} \frac{K_{d,nH}}{C_{H2,0}}$
I_i	$\int_0^1 Y_i d\xi \ (i = A, B, C)$

for PtMFI-3c). In these treatments (Eqs. 10–12), the ϕ_A term is treated as the sole independent parameter that denotes the severity of transport restrictions; the values of ϕ_B and ϕ_C are proportional to ϕ_A through factors that are unique characteristics of a zeolite framework (Section 3.6.1). The effects of Pt-H⁺ distances are included in ϕ_A through the size of acid domains (L). D_A/D_B and $D_{\rm B}/D_{\rm C}$ were inferred from literature diffusivity data [24,36,61]. The diffusivity of n-heptane within MFI zeolites is about sevenfold larger than for 2MH (318 K), which, in turn, is about ten-fold larger than for 24DMP (423 K) [61]. These data are used to set plausible ranges for these diffusivity ratios ($D_A/D_B=5$, $D_B/D_C=10$). The diffusivities for alkanes are used here (instead of alkenes), because reactions of alkenes at relevant conditions preclude direct measurements of alkene diffusivities. The effects of the magnitude of Θ_1 and Θ_2 on rates and selectivities were first examined by sampling a broad range of different values and then chosen (Θ_1 =0.4, Θ_2 =0.75) by benchmarking the model-derived selectivities against those measured on MFI-3 (detailed discussion in Section S5). The values chosen for Θ_1 , Θ_2 , D_A/D_B , and D_B/D_C lead to ϕ_B and ϕ_C values that are 1.2 and 3.8 times larger than for ϕ_A , respectively.

Fig. 6 shows concentration profiles for reactant and product alkenes within acid domains for different ϕ_A values (and Pt-H⁺ distances). Such intracrystalline profiles are inaccessible to experimental inquiry, but they determine measured rates and

selectivities. These concentration profiles are reported by normalizing the dimensionless concentration by that of nH⁼ at the external boundary of the slab ($Y_A|_{\xi=1}$). The two chosen ϕ_A values (0.3, 10) represent systems with weak and strong diffusional effects, respectively. The nH⁼ concentrations decrease weakly with distance away from the domain boundary ($\xi = 1$) for ϕ_A of 0.3, but much more sharply for the larger ϕ_A value (Fig. 6a). For small ϕ_A values, acid sites are exposed to nH⁼ concentrations that resemble those prevalent at the locations of Pt nanoparticles, but large ϕ_A values lead to the local depletion of reactant alkenes within acid domains. Consequently, isomerization turnover rates (and effectiveness factors α , Eq. (26)) decrease as ϕ_A values increase. These trends are similar for MH⁼ and DMP⁼ (Fig. 6b and c), but their respective involvement in subsequent reactions leads to maximum concentrations at intermediate distances between the centerline and the boundary of the acid domain (ξ = 0.85) for large ϕ_A values Eq. (10). These maxima represent the zero local net flux of MH⁼ and DMP⁼, which results from the combined fluxes outward within the near-boundary region ($\xi > 0.85$) by the lower concentrations at the acid domain boundary (Y_B|_{\xi=1}=0, Eq. (21); Y_C|_{\xi=1}=0, Eq. (22); conversion corresponding to the bed inlet) and inwards towards the centerline ($\xi < 0.85$) because of their ultimate conversion to β -scission products (C_3^{-} and C_4^{-}). C_3^{-} and C_4^{-} concentrations remain very low and resemble extracrystalline values (zero; not reported) because of their fast diffusion and the unreactive nature of the alkanes formed upon facile hydrogenation by the Pt function placed at acid domain boundaries.

These concentration profiles are used next to estimate approach to equilibrium values for nH⁼ reactions that form MH⁼ (η_1) and for MH⁼ conversion to DMP⁼ (η_2) at different locations within acid domains (values of ϕ_A : 0.3–50; bed inlet conditions; Fig. 7). The η values for β -scission of DMP⁼ are not considered because the favorable thermodynamics, low reactivity, and fast diffusion of C₃⁻ and C₄⁻ make the approach to equilibrium for this reaction negligible and thus inconsequential for rates or selectivities.

The boundary conditions for this example set the MH⁼ concentration at zero at the acid domain boundary $(Y_B|_{\xi=1} = 0, \text{ Eq. (21)})$, leading to small η_1 values at such surfaces (Fig. 7a). The η_1 values increase towards the center of the acid domain; they do so more strongly as ϕ_A values increase and ultimately reach an asymptotic value of 0.87 for ϕ_A values larger than about 5. Such asymptotic η_1 values (and the asymptotic η_2 , Fig. 7b) reflect the pseudo steady-



Fig. 6. Concentration profiles of (a) MH^{+} , (b) MH^{-} and (c) DMP^{-} (relative to the dimensionless concentration of nH^{-} at the boundary) along dimensionless distance of the slab, calculated by Eqs. 10–12 at conditions corresponding to the bed inlet with two different ϕ_A values (0.3 and 10).



Fig. 7. Approach to equilibrium for (a) MH^{*} with respect to nH^{*} (η_1) and (b) DMP^{*} with respect to MH^{*} (η_2) as a function of dimensionless position in the acid domain (ξ) for ϕ_A values varied from 0.3 to 50, calculated by Eqs. 10–12 at conditions corresponding to the bed inlet.

state concentrations of products and reactants within strongly diffusion-limited domains, and their values represent the approximate perturbation solutions to Equations 10–12 for large Thiele moduli (η_1^{asym} ; detailed derivations in Section S6):

$$\eta_1^{\text{asym}} = -\frac{\phi_B^2}{2\phi_A^2} \cdot (1 - \Theta_2 + \Theta_1 \Theta_2) \\ -\sqrt{\left(-1 + \Theta_2 - \Theta_1 \Theta_2 + \frac{\phi_A^2}{\phi_B^2}\right)^2 + \frac{4\Theta_1 \phi_A^2}{\phi_B^2} - \frac{\phi_A^2}{\phi_B^2}}$$
(24)

Such diffusional hurdles locally bottleneck the isomerization steps in the reaction sequence (Scheme 2) through thermodynamic constraints on nH⁼ conversion to MH⁼, resulting in much lower net rates than the forward rates of nH⁼ isomerization to MH⁼. These thermodynamic effects, combined with the local nH⁼ depletion as ϕ_A increases (Fig. 6a), lead to lower total nH conversion rates, because all isomer and β -scission products must traverse the initial step that converts nH⁼ to MH⁼ (Scheme 2).

The η_2 values also increase with distance towards the domain center. Its profile rises to higher levels with increasing ϕ_A values (Fig. 7b), indicative of thermodynamic constraints for the isomer-

ization of MH⁼ to DMP⁼. Given that ϕ_C values are even larger than ϕ_A (3.8 times) and ϕ_B (3.2 times), these severe diffusional hurdles for the DMP⁼ products and their higher reactivity (than nH⁼ and MH⁼) favor the cracking of DMP⁼ to C₃⁻ and C₄⁻, leading to very low DMP⁼ selectivities and to large β -scission selectivities because of such diffusional enhancements of secondary reactions [8], as described next.

3.6.3. Consequences of intracrystalline Pt nanoparticles for rates and selectivities

The reaction-transport models described in the previous section are used here to interpret the observed rate enhancements and selectivity changes when Pt nanoparticles are dispersed within MFI, BEA and FAU (Fig. 2). Fig. 8a shows model-derived effectiveness factors (α , Eq. (26)) and mean values of η_1 and η_2 within acid domains (η_1^* and η_2^* , respectively, Eq. (25)) for different values of ϕ_A (0.1–10; range corresponding to ϕ_B : 0.12–12, ϕ_C : 0.38–38):

$$\eta_i^* = \int \eta_i d\xi \tag{25}$$

where η_i is the local approach to equilibrium for a given species *i* at each location within an acid domain.



Fig. 8. (a) Effectiveness factor (α , Eq. (26)) and mean η_1^* and η_2^* values within the acid domain (Eq. (25)) as a function of Thiele modulus ϕ_A ; (b) selectivities to MH⁺, DMP⁺ and $C_3^*+C_4^*$ as a function of ϕ_A , calculated by Eqs. (10)–(12) at conditions corresponding to the bed inlet.

The effectiveness factor α is the ratio of the nH⁼ conversion rate for each ϕ_A value to that in the absence of diffusional hurdles $(\phi_A \ll 1)$:

$$\alpha = \frac{J_A}{J_0}\Big|_{\xi=1} = -\frac{\Theta_1}{\phi_A^2} \cdot \frac{dY_A}{d\xi}\Big|_{\xi=1}$$
(26)

Here, J_A is the diffusive flux of nH⁼ for each ϕ_A , J_0 is the nH⁼ flux for ϕ_A and η_1 values much smaller than unity throughout the acid domain (i.e., in the absence of diffusional or thermodynamic constraints). The α values are near unity for ϕ_A values smaller than 0.5, but decrease to about 0.1 for ϕ_A values >10 (Fig. 8a, left axis). These trends are also evident from the more severe concentration gradients (Fig. 6a) and the larger η_1^* and η_2^* values observed with increasing ϕ_A (Fig. 8a).

The selectivity to species *i* is given by the ratio of their respective net diffusive fluxes leaving an acid domain to that of nH^{-} reactants entering the domain:

$$S_i = \frac{J_i}{J_A}\Big|_{\xi=1} \tag{27}$$

The MH⁼ selectivity (S_B, Fig. 8b) is near unity for ϕ_A of 0.1, leading to S_C (DMP⁼ selectivity) and S_D (β -scission selectivity) values that approach zero, as expected from the exclusive formation of the primary MH⁼ products at the bed inlet under conditions of strict kinetic control. Larger values of ϕ_A (and concomitantly larger ϕ_B and ϕ_C) lead to diffusion-enhanced secondary reactions [8], the effects of which are made more evident by the higher reactivity and slower diffusivity of the more highly-branched products (MH⁼ and DMP⁼) compared with nH⁼ reactants; these reactive and diffusive properties favor secondary isomerization and ultimate β -scission events as the primary MH⁼ products egress from acid domains, leading to larger S_D and smaller S_B values as ϕ_A increases (Fig. 8b). These two selectivities reach asymptotic values (S_B = 0.67; S_D = 0.31) for ϕ_A values >5, the conditions that lead to severe diffusional restrictions. Such asymptotic selectivities, taken together with the nearly constant values of η_1^* and η_2^* at large ϕ_A values (Fig. 8a), indicate that severe diffusional hurdles cause thermodynamic constraints among isomerization of all isomers (nH⁼ to MH⁼ and MH⁼ to DMP⁼) and establish pseudo steady-state concentrations within the acid domain, as discussed in the context of the asymptotic η_1 and η_2 values (Fig. 7). S_C remains very low (<0.04) for all ϕ_A values, consistent with the slow diffusion of DMP⁼ and its high β -scission reactivity.

The acid domain boundary is defined by the location of Pt nanoparticles (Section 3.6.1), where nH⁼ concentrations are "reset" to their levels in equilibrium with nH and where MH⁼ and DMP⁼ products are scavenged to form their less reactive alkane analogs (MH, DMP), thus removing the thermodynamic constraints in sequential alkene isomerization steps (Scheme 2). Intracrystalline Pt nanoparticles lead to much smaller *L* values (i.e., the size of acid domains) in ϕ_A , ϕ_B , and ϕ_C (Eqs. 13–15) than with only an extracrystalline Pt function. The value of *L* decreases as the density of intradomain Pt nanoparticles increases and as the distance among such nanoparticles decreases (Section 3.5). Such decreases in *L* lead to proportional decreases in the value of ϕ_A (Eq. (13)) and consequently to larger α values and MH⁼ selectivities (Fig. 8).

These expectations are met by the observed rate and selectivity trends on MFI-3, PtMFI-3a, PtMFI-3b, and PtMFI-3c, which show an increase in rates (ω : 1.3 for PtMFI-3a to 10 for PtMFI-3c, Fig. 2a) and MH selectivities (0.68 for MFI-3 to 0.80 for PtMFI-3b, Fig. 2b) as the size of acid domains decreases ($\langle l_{Pt} \rangle$: ~400 nm for MFI-3 to 20 nm for PtMFI-3b and 12 nm for PtMFI-3c, Table 2), as expected from the concomitant decrease in ϕ_A (Fig. 8). As ϕ_A becomes smaller than unity, further decreases in ϕ_A do not detectably influence rates (ϕ_A : 0.3 to 0.1; α values: 0.96 to 0.99; Fig. 8a).

The larger voids in BEA and FAU zeolites lead to less effective van der Waals contacts with transition states [8] and consequently to lower intrinsic isomerization and β -scission rates, but also to faster molecular diffusion (Section 3.1) than within MFI. As a result, ϕ_A values become progressively smaller for BEA and FAU. Indeed, the presence of Pt nanoparticles within BEA and FAU crystals ($\langle l_{Pt} \rangle$: 14 nm for PtBEA, 17 nm for PtFAU; Table 2) leads to much smaller rate enhancements on PtBEA ($\omega = 2.2$) than on PtMFI and to ω values of unity on PtFAU (Fig. 2a).

The PtMFI-3c sample shows the largest rate enhancement ($\omega = 10$, Fig. 2a); it has the smallest *L* value ($\langle l_{\rm pt} \rangle = 12$ nm, Table 2) and thus the smallest ϕ_A value (Eq. (13)) among all MFI-3-based samples. The expectations from the reaction-transport model that it would exhibit the largest α value and rate enhancement (Fig. 8a) are indeed met ($\omega = 10$, Fig. 2a). The MH selectivity, however, is smaller than expected from its small ϕ_A value (experiments: 0.49, Fig. 2b; model: >0.9 for $\phi_A < 1$, Fig. 8b). Such an apparent inconsistency reflects the frequent presence of intervening "obstacles" along diffusive paths within zeolite crystals of this sample. These obstructions interfere with diffusion, specifically by decreasing the apertures along MFI channels, in a manner reminiscent of

how small changes in the "fit" of guest molecules within voids lead to very large differences in diffusivities. For instance, a small difference in the ratio of the sizes of guest molecules and apertures (0.74 to 0.86; MFI at 300 K: 10^{-11} for n-butane (size ratio: 0.74), 10^{-14} for 2-methypentane (size ratio: 0.86), unit: $m^2 s^{-1}$ [60,61] leads to very large (>10³-fold) differences in molecular diffusivities. As a result, any obstacles would influence the local ability to traverse intracrystalline distances for branched MH⁼ and DMP⁼ products much more strongly than for nH⁼ reactants; this leads, in turn, to greater consequences for $D_{\rm B}$ and $D_{\rm C}$ than for $D_{\rm A}$ and to larger $D_{\rm A}/D_{\rm B}$ and $D_{\rm B}/D_{\rm C}$ ratios. These preferential effects on $D_{\rm B}$ and $D_{\rm C}$ offset any effects of L values that are smaller for PtMFI-3c than for MFI-3, PtMFI-3a and PtMFI-3b (Table 2) as channel intersections are restricted by their increasing occupation by Pt nanoparticles, leading to larger tortuosity and concomitant lower diffusivities and ultimately the more selective sieving of molecules based on size and shape. The much less perturbed $D_{\mathbb{A}}$ does not distort the effect of the smallest *L* value within PtMFI-3c, which leads to its ϕ_A value that remains low and consequently to high observed rates (Fig. 8a).

Such obstructions and their consequences for selectivities were assessed by using much larger values of D_A/D_B (up to 10³-fold; 5 to 5×10^3) and $D_{\rm B}/D_{\rm C}$ (up to 10⁴-fold; 10 to 10⁵) within the reactiontransport models. Fig. 9 shows S_B values as a function of ϕ_A for different D_A/D_B and D_B/D_C ratios (S_C remains nearly zero so S_D \approx (1– S_B) and is therefore not reported). S_B decreases (e.g., 0.96 to 0.41 at ϕ_A = 0.5) when D_A/D_B and D_B/D_C increase 200-fold (from 5 to 10³) and 10³-fold (from 10 to 10⁴), respectively. The preferential impediments to the diffusional egress of branched MH⁼ and DMP⁼ products lead to their diffusion-enhanced secondary isomerization and β -scission reactions (Scheme 2), which favor the formation and the ultimate egress of the smaller C_3^{-} and C_4^{-} fragments. These results indicate that, even as the intradomain concentration gradients of reactant alkenes remain inconsequential (small ϕ_A values and high measured rates, Fig. 8a), diffusional hurdles for branched product alkenes (larger ϕ_B and ϕ_c) imposed by intracrystalline Pt nanoparticles lead to S_B values much smaller than unity, as found experimentally from the concurrent observance of large rate enhancement (ω = 10, Fig. 2a), but low MH selectivities (0.49, Fig. 2b) on PtMFI-3c.

3.6.4. Monotonic changes in Thiele moduli and consequences for rates and selectivities

The consequences of intracrystalline concentration gradients for rates and selectivities depend on the density of protons within acid domains ($\rho_{\rm H^+}$) through its effects on the magnitudes of the Thiele moduli (ϕ_A , ϕ_B , and ϕ_C ; Eqs. 13–15). These $\rho_{\rm H^+}$ values can be increased monotonically with time by the desorption of preadsorbed NH₃ titrants (Section 2.3.1) during reaction ($\rho_{\rm H^+}(t)$, Eq. (23)). The concomitant increase in Thiele moduli would consequently cause increases in diffusion-enhanced secondary reactions and lower MH selectivities as NH₃ desorbs. These processes are considered next in the context of experimental observations and the diffusion-convection-reaction formalisms developed earlier (Eqs. 10–12 and 16–18).

Fig. 10 shows relative rates ($\chi(t)$, Eq. (4), relative to those before NH₃ titration; black circles, Fig. 10a) and selectivities (black symbols, Fig. 10b) on PtMFI-3c measured during transient NH₃ desorption depicted as a function of ϕ_A , the value of which is used as a surrogate for the (time-dependent) proton density ($\phi_A \propto \sqrt{\rho_{\text{H}^+}(t)}$, Eq. (13)). This temporal ϕ_A evolution corresponds to a ϕ_A value of 0.5 before NH₃ titration (or after complete NH₃ desorption); this value is chosen as an illustrative example for the small ϕ_A values that are required to account for the smallest size of acid domains



Fig. 9. Selectivities to $MH^{=}(S_B)$ as a function of ϕ_A for different D_A/D_B and D_B/D_C ratios (values denoted in parentheses), calculated by Eqs. 10–12 at conditions corresponding to the bed inlet.

within PtMFI-3c (Table 2; Eq. (13)) and for its largest rate enhancement ($\omega = 10$, Fig. 2a).

During the initial stages of NH₃ desorption, the density of accessible protons ($\rho_{H^+}(t)$) is very small, leading to small nH isomerization rates and low nH conversions ($\chi(t) = 0.11$ for $\phi_A = 0.02$; black circles, Fig. 10a) and to ϕ_A values much smaller than unity. These small ϕ_A values lead to high MH selectivities (S_B = 0.99 for $\phi_A = 0.01$; curves, Fig. 10b), indeed consistent with the high measured MH selectivity during such initial times (0.95 for $\phi_A = 0.02$; black squares, Fig. 10b).

The $\rho_{\rm H^+}$ values increase as NH₃ desorbs (Eq. (23)), leading to a concomitant increase in Thiele moduli (Eqs. 13-15) and in nH isomerization rates (black circles, Fig. 10a). These larger Thiele moduli reflect the gradual emergence of more severe diffusional effects and intracrystalline concentration gradients (Fig. 6), leading to lower values of the effectiveness factor (α , Eq.26; Section 3.6.3) and to less steep local slopes of the $\chi(t)$ profile (black circles, Fig. 10a). The observed decrease in MH selectivities and increase in cracking selectivities (black symbols, Fig. 10b) manifest the consequences of diffusion-enhanced secondary isomerization and β scission events, the extent to which becomes greater as NH₃ desorbs and the values of Thiele moduli concomitantly increase. The MH selectivities decrease to values (0.35 for $\phi_A = 0.37$; black squares, Fig. 10b) that are even smaller than that before NH₃ titration (0.49, Fig. S6), indicative of additional enhancements of secondary reactions brought forth by NH₃. Such NH₃-derived effects presumably reflect the consequences of replacing H⁺ by the larger NH₄⁺ moieties, which, in addition to the intracrystalline Pt nanoparticles, introduce more "obstacles" to the MFI channels and cause additional preferential diffusional hurdles for the branched product alkenes (MH⁼ and DMP⁼; Section 3.6.3).

These trends are well captured (grey curves, Fig. 10) by the diffusion–convection–reaction formalisms (Eqs. 10–12 and 16–18) upon regressing the rate and selectivity data to the model, with D_A/D_B and D_B/D_C as the adjustable parameters (regressed values: 2400 and 10⁴, respectively), while with a given ϕ_A value of 0.5 (before NH₃ titration) and Θ_1 (0.4) and Θ_2 (0.75) the same as those used in Section 3.6.2 and 3.6.3. The model is less sensitive to D_B/D_C , because the large value of D_A/D_B (2400) and consequently the large ϕ_B/ϕ_A ratio (26.4, Eqs.10–11) lead to asymptotic solutions for Equations 11–12 and to the differential mole balances



Fig. 10. Measured (\bullet) and calculated (grey curves) (a) relative rates $\chi(t)$ and (b) selectivities for MH⁻ (\blacksquare), DMP⁻ (\blacklozenge) and β -scission products (\blacktriangle) as a function of ϕ_A during NH₃ desorption. Experimental condition: 548 K; 0.005 nH/H₂ molar ratio, 100 kPa H₂.

(Eqs. 10–12) that degenerate to only two equations that are independent of ϕ_c (Section S5). In light of such complexities in the mathematical framework, these parameter values are used here for illustrative purposes; they are, nevertheless, within reasonable ranges expected from the present experimental observations and literature results (e.g., a small ϕ_A value for the smallest $\langle l_{\rm Pt} \rangle$ in PtMFI-3c; large diffusivity ratios rendered by the obstacles associated with intradomain Pt nanoparticles and NH⁴₄), and provide faithful descriptions for the observed trends in rates and selectivities.

Therefore, these reaction-transport formalisms accurately describe the rates and selectivities observed on zeolites with different topologies (MFI, BEA, FAU) and different proximities between the metal and acid functions, highlighting the indispensable—but seldom rigorously treated—reaction–diffusion interplays within voids of molecular dimensions. Such analysis and mathematical treatments, illustrated in this work using isomerization and β -scission mediated by bifunctional catalytic cascades as an example, are heuristic and can be generalized to other reactions that implicate molecular shuttling of reactive intermediates.

4. Conclusions

The rate enhancements and selectivity changes in n-heptane isomerization on zeolites with nanoscale metal-acid proximity conferred by intracrystalline Pt nanoparticles were systematically assessed in this work. Such rate enhancements do not reflect changes in the number or properties of the metal and acid functions, nor the involvement of diene-mediated routes rendered possible by smaller Pt-H⁺ distances. Instead, these rate enhancements reflect the consequences of intracrystalline reaction-transport interplays. Confining Pt nanoparticles within zeolite crystallites decreases the size of acid domains and consequently the values of Thiele moduli, allowing to replenish local alkene reactants via dehydrogenation of n-heptanes and to scavenge isoalkenes via hydrogenation (to their less reactive saturated analogs) on these intradomain Pt functions to circumvent local thermodynamic constraints. Such effects are more consequential for medium-pore MFI zeolites, within which the more effective van der Waals contacts and slower molecular diffusion lead to prevalent diffusional hurdles, and become less so for large-pore BEA (weaker) and FAU (nondetectable) zeolites.

Measured selectivities also reflect such reaction-transport interplays. Moderate intracrystalline Pt nanoparticle densities decrease the contributions from secondary isomerization and β scission events via facile local hydrogenation of primary alkenes to their less reactive alkane analogs, leading to higher selectivities to primary singly-branched MH products. High intracrystalline Pt nanoparticle densities, however, lead to frequent presence of intervening "obstacles" along diffusive paths that interfere with molecular diffusion, causing preferential impediments to the diffusional egress of branched MH⁼ and DMP⁼ products and consequently their diffusion-enhanced secondary reactions and lower MH selectivities.

These reaction-transport effects on rates and selectivities are rigorously described by diffusion-convection-reaction formalisms. Such reaction-transport coupling is often unavoidable and useful in practice, as illustrated here in the context of n-heptane isomerization on bifunctional metal-acid catalysts; the formalisms and mathematical treatments developed in this work provide a way to accurately examine the consequences of such coupling, which can be generalized to other reactions that implicate molecular shuttling of reactive intermediates.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Enrique Iglesia reports financial support was provided by Chevron Energy Technology Company.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2023.06.001.

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