The nature of “hydrogen spillover”: Site proximity effects and gaseous intermediates in hydrogenation reactions mediated by inhibitor-scavenging mechanisms

Ari F. Fischer 1, Enrique Iglesia

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA

Article info
Article history:
Received 8 August 2022
Revised 4 October 2022
Accepted 7 November 2022
Available online 13 November 2022

Keywords:
Hydrogen spillover
Bifunctional cascades
Hydrogenation
Metal-support interactions
Aromatic hydrocarbons
Alkenes
Metal oxides

Abstract
Support effects in alkene and arene hydrogenations on metal catalysts attributed to “hydrogen spillover” are shown to reflect the desorption and hydrogenation of Pt-bound intermediates at acid-base pairs on certain oxides (e.g. Al2O3, TiO2, MgO). Toluene-H2 reactions on Pt nanoparticles dispersed on SiO2 (Pt/SiO2) occur on surfaces nearly saturated with a diverse pool of bound species differing in the locations of H-atoms and surface attachments. Their diverse coverages and reactivity cause Pt surfaces to become preferentially occupied by less reactive isomers at the expense of the more competent isomers that account for most hydrogenation turnovers. These less reactive species can desorb from Pt nanoparticles as gaseous methylcyclohexadiene molecules, which diffuse to and react at nearby oxide surfaces; such scavenging increases the relative abundance of the more reactive intermediates at Pt surfaces leading to the rate enhancements inaccurately denoted as “hydrogen spillover.” These rate enhancements become less pronounced as mean inter-function distances between Pt nanoparticles and acid-base pairs on oxide surfaces increase, and as methylcyclohexadiene molecules become less effectively scavenged as their rates of mass transfer become consequential. The Al2O3 surfaces considered here catalyze dihydrogen addition to cyclohexadiene and cyclohexene molecules (but not toluene); titration of acid-base pairs by propanoic acid suppresses such reactions, as well as the significant enhancements of toluene-H2 reaction rates observed when Al2O3 is mixed physically with Pt/SiO2. The rate enhancements conferred by these bifunctional routes represent a natural consequence of the diverse coverage and reactivity of many different species bound on crowded metal surfaces during arene and alkene hydrogenation reactions. Their desorption as partially-hydrogenated molecules enable their scavenging at a second function present within diffusion distances, without requiring inter-function contact or the surface diffusion of H atoms.

© 2022 Elsevier Inc. All rights reserved.

1. Introduction

Non-reducible oxides (e.g. Al2O3, SiO2, MgO) are ubiquitous supports for dispersed metal nanoparticles used as catalysts for hydrogenation reactions of unsaturated organic molecules [1,2], H2-mediated heteroatom removal processes (S,N,O) [2,3], as well as the Fischer-Tropsch synthesis and related COx-H2 reactions [2,4]; they are also used as inorganic scaffolds and binders in composite catalysts, such as those used in the abatement of emissions from combustion effluent streams [5]. These oxide supports are effective at stabilizing small nanoparticles and maintain their chemical and mechanical integrity at the demanding conditions of catalytic practice. Their role as nominally inert scaffolds is accompanied in the case of many arene and alkene hydrogenations by promotional effects that often lead to higher turnover rates (normalized per exposed metal atom) when nanoparticles dispersed on SiO2 [6], Al2O3 [7], and LTA [8] are present as physical mixtures with Al2O3 (or MgO and TiO2 as shown here), even for reactions that do not occur at detectable rates on the oxide alone.

These processes have been denoted as “hydrogen spillover,” a moniker that conjures additive hydrogenation routes mediated by H atoms formed on Pt from H2 and delivered via surface diffusion (in some activated form) to specific locations at oxide surfaces, thus rendering them competent for hydrogenating organic substrates [6,9–12]. Such proposals transfer concepts first derived from the known ability of H atoms to migrate (as neutral H⁺-e⁻...
pairs via sequential proton-coupled electron transfer) in conductive and reducible oxides (e.g. WO₃) when H₂ dissociation events occur on Pt nanoparticles in atomic contact with such oxides [13,14]; these processes lead to the incipient reduction of the oxides at much lower temperatures than in the absence of metal nanoparticles or metal-oxide atomic contact [13–15]. As elegantly articulated in a recent review article [12], such stable and mobile H⁻e⁻ pairs are implausible in the case of non-conducting oxides, such as Al₂O₃, because they would require charge separation processes that are energetically insusceptible. Insulators lack the accessible electronic conduction band and the reducible metal cations required to accept electrons, to mediate electron migration, and to stabilize the requisite H⁻e⁻ pairs along their diffusive journey. Al₂O₃ surfaces are therefore incapable of binding H atoms in configurations that can compensate for the endothermic cleavage of the metal-H bonds that form upon H₂ dissociation [12,15] or of allowing such species to migrate to a hydrogenation function on Al₂O₃ that lies beyond direct atomic contact with the metal nanoparticles.

The conceptual and practical objections against (and the lack of compelling direct evidence for) H-atom migration from metals and reactions at specific sites on Al₂O₃ surfaces [12,15] remain unchallenged, even after a myriad of publications (summarized in several review articles [12,16–18]) and five international conferences dedicated solely to ‘hydrogen spillover.’ These objections have led to alternate mechanistic proposals for the well-demonstrated effects of Al₂O₃ and other oxides on hydrogenation turnover rates on metal nanoparticles. The higher ethene hydrogenation rates observed on Pt/SiO₂ samples diluted with γ-Al₂O₃ (instead of SiO₂) were attributed in an early study to carbonaceous impurities that formed on Pt surfaces during thermal treatments in H₂ via the desorption of species bound at SiO₂ surfaces but scavenged by adsorption on Al₂O₃ [19]. These authors observed that a brief treatment in O₂ at 573 K eliminated rate enhancements and concluded that such treatments acted to remove such deposits [19]. Turnover rates for benzene hydrogenation [7] on Pt/γ-Al₂O₃ and for toluene hydrogenation on Pt/SiO₂ (this work) mixed with Al₂O₃ (or MgO and TiO₂ in this work) were higher, however, than on Pt/SiO₂ even after such treatments, indicating that the scavenging of adventitious impurities cannot account for the observed rate enhancements historically described as “hydrogen spillover.”

The mechanistic details of such rate enhancements became evident, as we describe in this study, only after significant details of monofunctional Pt-mediated hydrogenation routes were uncovered through theory and experiment. Unsaturated hydrocarbons, such as arenes and alkenes, form strong covalent bonds with metal surfaces, resulting in high surface coverages at conditions typical of their hydrogenation reactions [20,21]. These bound species undergo H-addition and H-abstraction reactions that form diverse bound structures with varying numbers of C-Pt contacts, binding orientations, and stereochemistry. Toluene-H₂ reactions on Pt surfaces, for example, form ensembles of intermediates with n different numbers of additional H atoms (denoted as THₙ⁺), each one of which consists of several structural isomers that differ in the location of the added H atoms and in the attachment of the C atoms to surfaces. These species are expected to vary in their reactivity and in the extent to which they contribute to (i) surface coverages and (ii) methyl-cyclohexane (MCH) formation rates. Such species include various bound methylcyclohexylene (MCHE) isomers, which can desorb as 1-methylcyclohexene (1MCHE), 3-methylcyclohexene (3MCHE), and 4-methylcyclohexene (4MCHE) to give pseudo-steady-state gas-phase concentrations during toluene-H₂ reactions on supported Pt nanoparticles [22]. These toluene-derived species also include bound forms of methycyclohexadiene (MCHD) isomers that also can desorb as their gaseous counterparts, albeit at levels below limits of detection even when they are in equilibrium with toluene-H₂ reactants.

Al₂O₃ surfaces are known to activate H-H [23,24] and C-H bonds [23] at coordinatively-unsatuated Al³⁺ centers and to catalyze propane dehydrogenation reactions [25–27]. Such sites may allow MCHD-H₂ and/or MCHE-H₂ reactions to occur at distances within access by diffusion from sites that can form (and desorb) them. Al₂O₃ is shown here to catalyze H₂ reactions with 1,3-cyclohexadiene (13CHD) (or 4MCHE) to form benzene, 1,4-cyclohexadiene, cyclohexene, and cyclohexane (or MCH and 1MCH), but not with toluene, thus demonstrating that bifunctional routes mediated by toluene-derived intermediates are indeed plausible. The Al₂O₃ sites responsible for such reactions are shown in the present study to be titrated by propanoic acid (PA), a molecule that irreversibly binds at Lewis acid-base pairs at oxide surfaces [28], but which does not affect monofunctional hydrogenation rates on Pt nanoparticles. Such titrations eliminate the effects of Al₂O₃ dilution on toluene hydrogenation turnover rates on Pt/SiO₂, consistent with the involvement of Al₂O₃-derived acid-base pairs in the kinetically-relevant steps that mediate the bifunctional routes responsible for the observed rate enhancements.

MCH formation rates on loose mixtures with different Pt/SiO₂ and Al₂O₃ aggregate sizes but similar diluent ratios (Al₂O₃ surface area to the number of exposed Pt sites) show that rate enhancements are smaller when larger aggregates of the two components are used. Such trends are consistent with the expected effects of diffusion distances among functions on the rate of bifunctional routes mediated by gaseous molecules, such as MCH or MCHD, which can diffuse between non-proximate functions to complete MCH formation turnovers [29]; these distance effects reflect concentration gradients of such molecular shuttles. The effects of dilution extent and inter-function distance on rates are consistent with two plausible bifunctional routes, denoted here as (i) additive/stoichiometric hydrogenation and (ii) inhibitor-scavenging routes.

The first route involves THₙ⁺ moieties that form from toluene-H₂ mixtures on Pt, desorb, diffuse, and react with H₂ at non-vicinal Al₂O₃ sites, thus circumventing the kinetic bottlenecks prevalent at strictly monofunctional Pt surfaces and leading to higher MCH formation rates. Such THₙ⁺ species must form before the kinetically-relevant steps at Pt surfaces for their desorption and hydrogenation on Al₂O₃ surfaces to influence toluene conversion rates. The second route posits the formation of unproductive THₙ⁺ species on Pt surfaces; such THₙ⁺ moieties form MCH much more slowly than other more reactive THₙ⁺ intermediates but occupy Pt surfaces thus competing with more reactive intermediates on the crowded surfaces that are ubiquitous during hydrogenation catalysis. These less competent THₙ⁺ species can, however, desorb and be scavenged via hydrogenation at Al₂O₃ surfaces, thus decreasing their surface coverages and leading to an increased prevalence of more competent intermediates. In the first route, additional MCH products are formed in amounts that are commensurate with the rates at which proposed molecular shuttles are hydrogenated by the oxoide function. The sites made available by scavenging such species in the second mechanism, on the other hand, convert multiple toluene molecules before being covered by new inhibitors, thus forming numbers of MCH products in large excess of the stoichiometric amounts of inhibitors converted. In both routes, gaseous species must migrate between the two functions at diffusion rates that are sensitive to the distances that separate them; neither route requires adventitious atomic contact between the two functions because they are mediated by gaseous molecular shuttles rather than surface-bound species that are transported across metal-oxide interfaces.

The trends in MCH formation rates and prevalent pseudo-steady-state gaseous MCHE concentrations with extent of dilution
with Al₂O₃ and aggregate domain size are assessed in the present study by comparisons with mechanism-based kinetic models derived for each bifunctional route. Both the MCH formation rates and the prevalent pseudo-steady-state MCHE pressures increased as the amount of Al₂O₃ in mixtures with Pt/SiO₂ increased in a manner that can only be accounted for by an increase in the number of Pt-sites that are made available by the scavenging of unreactive species for the kinetically-relevant H-addition reactions. These trends reflect a preeminent role of inhibitor-scavenging routes mediated by MCHD isomers that act as less reactive occupants of Pt surface atoms, and which inhibit rates by decreasing the surface coverages of more competent isomers. Reaction-transport models based on such MCHD-scavenging routes are consistent with the observed decrease in MCH formation rates on Pt/SiO₂-Al₂O₃ mixtures with increasing aggregate domain size of each function as the scavenging routes become limited by transport of MCHD isomers across increasingly far distances. Such rate increases are not limited to physical mixtures of Pt/SiO₂ with Al₂O₃ but are also observed for physical mixtures with MgO and TiO₂, showing that these bifunctional reaction processes are prevalent on other oxides with exposed Lewis-acid-base pairs at their surfaces. These \textit{“hydrogen spillover”} phenomena are most evident for small Pt nanoparticles because their surfaces expose a relatively higher fraction of vicinal Pt-site pairs compared with threefold hollow and fourfold bridge sites that are more prevalent on larger nanoparticles. (Methyl)cyclohexadiene isomers bind favorably to these bifunctional reaction processes are prevalent on other oxides with exposed Lewis-acid-base pairs at their surfaces, and thus a greater benefit for their scavenging. The observations described as \textit{“hydrogen spillover”} involve gaseous molecular shuttles instead of the surface migration of H atoms. Such phenomena become evident for hydrogenation reactions of alkenes and aromatics because they (i) occur on nearly saturated surfaces; (ii) involve the formation of diverse bound species with diverse reactivity; and (iii) some of the less competent intermediates are able to desorb and react on Lewis acid-base pairs on the surface of oxides used as nominally inert supports. Such scavenging of abundant and less reactive species at metal surfaces by reactions at nominally inert oxides (that are present within distances accessible by gaseous diffusion) constitute a plausible, and often-overlooked, alternate mechanism for the ubiquitous promotional effects of supports and diluents, often attributed to electronic metal-support interactions or to unique reactivity at metal-support interfaces.

2. Materials and methods

2.1. Catalyst synthesis and characterization.

\(\text{SiO}_2\) (Cabot (Cab-o-sil HS-5) and Sigma-Aldrich (Davisd Grade 62)), \(\gamma\)-\text{Al}_2\text{O}_3 (Sasol SBA200; denoted \text{Al}_2\text{O}_3-Sasol), and TiO₂ rutile (Sigma-Aldrich 99.5 %) were obtained from commercial sources. Another \text{Al}_2\text{O}_3 sample (denoted \text{Al}_2\text{O}_3-solgel) was prepared from aluminum isopropoxide (AIP; Sigma-Aldrich, 98 %) using sol–gel methods [35,36]. AIP was dissolved in deionized (DI) \text{H}_2\text{O} (resistivity \(\geq 17.6\) megaohm-cm at ambient temperature; \(10\) cm\(^3\) g\(^{-1}\) AIP) while stirring magnetically at \(358\) K for \(1\) h. \text{HNO}_3 (Sigma-Aldrich, 70 %) was then added dropwise (0.4 g\(^{-1}\) AIP) while stirring and subsequently stirred in ambient air for \(1\) h (358 K). The resulting sample was treated in ambient air for \(12\) h (at \(393\) K) to evaporate the solvent. The sample was then treated in flowing dry air (Praxair, ultra-zero purity) by heating to \(773\) K (at \(0.017\) K s\(^{-1}\)) and holding for 4 h, then heating to \(923\) K (at \(0.017\) K s\(^{-1}\)) and holding for 2 h to form porous \text{Al}_2\text{O}_3 aggregates. A MgO sample was prepared by treating magnesium carbonate (Fluka; basic; 40–45 % Mg (as \text{MgO} basis)) in flowing dry air by heating from ambient to \(723\) K (at \(0.017\) K s\(^{-1}\)) and holding for 2 h [37].

Pt nanoparticles were dispersed on \text{SiO}_2 (Pt/SiO₂) using electrostatic adsorption methods [38,39]. \text{SiO}_2 (Cab-o-sil or Davislil; washed with DI \text{H}_2\text{O}, treated in ambient air at \(373\) K for \(12\) h, and treated in ambient air at \(873\) K (0.017 K s\(^{-1}\); 4 h)) was added to a solution of Pt(NH}_2)_2(\text{NO}_3)_2 (Sigma-Aldrich, 99.995 %) in DI \text{H}_2\text{O} (4 cm\(^3\) g\(^{-1}\) \text{SiO}_2) and stirred magnetically for \(4\) h at ambient temperature. One of two different solid collection procedures were used: (i) the mixture was heated to \(353\) K while stirring and held for 2 h to evaporate the solvent and (ii) the mixture was collected by filtration and washed with DI water (100 cm\(^3\) g\(^{-1}\) \text{SiO}_2). In both cases, the resulting solids were collected and dried at \(383\) K in ambient air for 10 h. The dried solids were then treated (i) in flowing dry air at \(1.7\) cm\(^3\) g\(^{-1}\) s\(^{-1}\) by increasing the temperature from ambient to the target treatment temperature (0.017 K s\(^{-1}\)) and holding for \(3\) h, then decreasing the temperature at \(0.083\) K s\(^{-1}\) to \(373\) K; (ii) in flowing \text{He} (Praxair, 99.999 %) at \(373\) K for 0.5 h; (iii) in flowing \text{H}_2 (Praxair, 99.999 %) at \(1.7\) cm\(^3\) g\(^{-1}\) s\(^{-1}\) by increasing the temperature from \(373\) K to the target treatment temperature (0.017 K s\(^{-1}\)) and holding for 2 h, then decreasing the temperature at \(0.083\) K s\(^{-1}\) to below \(373\) K; and (iv) in flowing \(2\) % \text{O}_2/He (Praxair) at \(1.7\) cm\(^3\) g\(^{-1}\) s\(^{-1}\) for at least 1 h.

The Pt content of Pt/SiO₂ catalysts was measured using inductively-coupled plasma–atomic emission spectroscopy (ICP-AES; Galbraith Laboratories). \text{H}_2 chemisorption uptakes (Section S.1) were used to calculate saturation H coverages (denoted \(\theta_{H_{\text{sat}}}\)) and particle diameters for Pt nanoparticles (\(d_{Pt}\)) with surfaces that are capable of binding more than one H atom at saturation using a previously reported formalism [40] that related uptakes to mean diameter (\(d_{Pt}\)).

\begin{align}
\text{d}_{Pt} &= \frac{6N_{He} v_{He} \theta_{H_{\text{sat}}}}{2N_{Pt} \text{d}_{Pt} \theta_{H_{\text{sat}}}} \quad (1) \\
\theta_{H_{\text{sat}}} &= 1 + 0.0364 \left( d_{Pt}^{-1} \right) + 0.735 \left( d_{Pt}^{-2} \right) \quad (2)
\end{align}

where \(N_{He}\) represent a shape factor for hemispheres, \(N_{Pt}\) is the number of Pt atoms, \(N_{H_{\text{sat}}}\) is the number of H molecules dissociatively adsorbed at the surface, \(v_{He}\) is the atomic volume of a Pt atom in metal (15.10 \times 10^{-3} \text{ nm}^3), and \(a_{H}\) is the occupied area of a Pt atom on a bulk Pt(1 1 1) surface for an fcc lattice (6.7 \times 10^{-2} \text{ nm}^2) [41], the lowest energy crystal facet, and the 0.0364 and 0.735 coefficients are empirical parameters [40]. Dispersions were derived from \(\theta_{H_{\text{sat}}}\) values using [40]

\begin{align}
D &= \frac{2N_{H_{\text{sat}}}}{N_{Pt} \theta_{H_{\text{sat}}}} \quad (3)
\end{align}

Treatment temperatures, Pt nanoparticle dispersions, and mean Pt nanoparticle diameters are reported in Table 1.

Surface areas (m\(^2\) g\(^{-1}\)) and pore volumes (cm\(^3\) g\(^{-1}\)) of Al₂O₃ and SiO₂ powders were determined from N₂ adsorption uptakes at its normal boiling point (Micromeritics 3Flex Surface Analyzer) and summarized in Table S1 with adsorption and desorption isotherms shown in Figure S2. The Fe and Si content of \text{Al}_2\text{O}_3-Sasol (5.2 ppm Fe and 57 ppm Si) and \text{Al}_2\text{O}_3-solgel (139 ppm Fe and 220 ppm Si) were determined from ICP-AES. The packed densities of the \text{SiO}_2 (1.2 g cm\(^{-3}\)) and \(\gamma\)-\text{Al}_2\text{O}_3-Sasol (2.3 g cm\(^{-3}\)), which were necessary to estimate transport properties of diffusing molecules through the pores of catalyst pellets, were measured by pressing each respective powder into a wafer and measuring its volume and mass.
2.2. Catalytic rate and selectivity measurements on SiO₂-supported Pt nanoparticles and oxide surfaces.

The rates of product formation from toluene-H₂ and CO₂ reactants were measured on Pt/SiO₂ samples (0.001–0.05 g) using a fritted U-shaped quartz tube reactor (1.3 cm internal diameter). Catalyst powders were pressed into wafers then crushed and sieved to retain the target aggregate sizes. These Pt/SiO₂ aggregates were mixed with quartz powder (Sigma-Aldrich, 180–250 μm; treated in ambient air at 973 K) so as to maintain a bed height of 3 cm. In some experiments, an Al₂O₃-Sasol bed (treated in ambient air at 873 K for 4 h) was placed before a quartz-diluted Pt/SiO₂ bed (denoted Al₂O₃ pre-bed) separated by a 5 mm layer of quartz granules (0.5 g) in order to evaluate whether Al₂O₃ may influence rates by scavenging impurities from the inlet stream. The rates of product formation from toluene, 1,3-cyclohexadiene (13CHD), and 4-methylcyclohexene (4MCHE) reactions with H₂ were also measured on undiluted, Pt-free Al₂O₃-Sasol and Al₂O₃-solgel samples (0.03–0.1 g) present as powders using similar protocols to those used for the measurements on Pt/SiO₂.

Inter-pellet mixtures (denoted as loose mixtures) consisting of Pt/SiO₂ and Al₂O₃-Sasol (treated in ambient air at 873 K for 4 h), MgO, or TiO₂ (treated in ambient air at 673 K for 4 h) were prepared by pressing each of the two components into separate wafers, then crushing and sieving to retain aggregates with pellet radii in the ranges: 90–130 μm, 53–63 μm, 27–40 μm, and 6–27 μm. The Pt/SiO₂ and oxide aggregates were then interspersed loosely within the reactor.

Pt/SiO₂ powders were also formed into intra-pellet mixtures (denoted as intimate mixtures) with Al₂O₃-Sasol, Al₂O₃-solgel, or SiO₂ (Cab-o-sil; washed with DI H₂O, treated in ambient air at 737 K for 12 h, and treated in ambient air at 873 K, 0.017 K s⁻¹; 4 h) by (i) mechanical grinding the Pt/SiO₂ and oxide powders using a mortar and pestle for about 0.2 h, (ii) pressing into a wafer, then (iii) crushed and sieving to retain aggregates with 90–130 μm radii. Reactions of toluene-H₂ and CO₂ mixtures were measured using similar protocols to those used for testing single-component Pt/SiO₂ pellets. Nominal mass ratios of the two components ranged from 2 to 40 g oxide g⁻¹Pt/SiO₂. The resulting mass ratios from a subset of mixtures were determined by Pt contents measured using ICP-AES. The fractional Pt yields (defined as the ratio between the achieved and the nominal mass of the Pt in the mixture) were near unity for all SiO₂-diluted samples and were below unity (0.9–0.7) for Al₂O₃-diluted samples at all dilution extents (Section S.3). A linear trend relating the achieved and nominal Pt contents for these Al₂O₃-diluted mixtures was used to correct for the lower-than-expected Pt yields in Pt/SiO₂ + Al₂O₃ mixtures. Such lower-than-expected Pt yields suggest a preferential loss of the Pt/SiO₂ component in the fines of the crushed powders or by adherence to the walls of the mortar and pestle.

The catalyst samples were held within quartz cells as packed beds, and heated resistively (National Electric furnace); temperatures were kept constant using a Watlow controller and measured with a thermocouple placed within a dimple in the reactor wall at the axial midpoint in the bed. Catalysts were treated before rate measurements (i) in flowing 10 % O₂/He (Praxair) at 100–200 cm³ g⁻¹ catalyst s⁻¹ by increasing the temperature from ambient to 573 K at 0.033 K s⁻¹ and holding for 1 h; (ii) in flowing He (Praxair, 99.999 %) at 100–200 cm³ g⁻¹ Pt/SiO₂ s⁻¹ by holding at 573 K for 0.25 h; and (iii) in flowing H₂ (Praxair, 99.999 %) at 100–200 cm³ g⁻¹Pt/SiO₂ s⁻¹ by holding at 573 K for 1 h; samples were then brought to the target reaction temperature in flowing H₂ for hydrogenation reactions or 10 % O₂/He (for CO oxidation reactions). O₂/He, H₂, and H₂ inlet streams were purified by passage through moisture traps (Agilent BMT).

Inlet molar rates of all gases were set using electronic Parker mass flow controllers. Toluene (Sigma-Aldrich, 99.9 %), 1,3-cyclohexadiene (Sigma-Aldrich, 97 %), and 4-methylcyclohexene (Sigma-Aldrich, 99 %) were introduced as liquids into flowing H₂/He mixtures (100–200 cm³ g⁻¹Pt/SiO₂ s⁻¹) using a Parker Hamilton syringe pump. Propanoic acid (Sigma-Aldrich, 99.5 %) was mixed into the liquid toluene reactant for titration experiments. The effluent streams were analyzed using on-line gas chromatography (GC; Agilent 6890A) with flame ionization detection (FID) after molecular separation using a capillary column (Agilent; HP-1). Toluene, 1-methylcyclohexene, 4-methylcyclohexene, methylcyclohexane, benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, and cyclohexane were identified in the chromatograms by comparing their elution times to those of chemical standards. The elution time of 3-methylcyclohexene was inferred as the isomerization product in the effluent mixture produced by the reaction of 4-methylcyclohexene on Al₂O₃ under flowing He. The molar fractions of the components in product mixtures were determined from a carbon balance using their relative response factors [42]. All process lines between the liquid injection point and the analytical system were held at 373–473 K to prevent reactant and product condensation; these heated lines did not lead to detectable conversions of any reactants or products and contributed negligibly to measured rates and selectivities. The effluent stream from CO (Praxair; 1 % CO, 2 % Ar, He bal.) and O₂ reactions was analyzed using on-line GC with thermal conductivity detection (TCD) after molecular separation using a packed column (Agilent; Porapak Q).

2.3. Reaction-transport models that describe concentration gradients of reactive intermediates in bifunctional routes on Pt/SiO₂ + Al₂O₃ mixtures.

Reaction-transport models based on formalisms discussed by Weisz [29] were used to determine radial distributions in the concentrations of reactive intermediates (denoted as Iₜ) in bifunctional routes within the pores of Pt/SiO₂ and Al₂O₃ aggregates. The concentration of Iₜ within pores in quasi-spherical Pt/SiO₂ aggregates is described by the following dimensionless equation derived from the conservation of mass (Section S.4):

\[
\frac{1}{\xi^2} \frac{\partial}{\partial \xi^2} \xi^2 \frac{\partial \varphi_{\text{I}_{\text{t}}}}{\partial \xi} - \rho_{\text{I}_{\text{t}}} n_{\text{I}_{\text{t}}} R^2 \frac{\partial}{\partial \xi} \left[ \frac{\varphi_{\text{I}_{\text{t}}}}{I_{\text{t}}^*} \right] = 0
\]
where $\zeta$ is the radial coordinate within Pt/SiO$_2$ aggregates (normalized by their mean aggregate radius; $R_{\text{Pt}}$), $\varphi_{\text{iH}}$ is the dimensionless I$_H$ concentration (normalized by a reference concentration; $|I_{\text{iH}}|_0$), $\rho_{\text{Pt}}$ is the Pt/SiO$_2$ density, $n_{\text{Pt}}$ is the number of moles of surface Pt sites per mass Pt/SiO$_2$, $D_{\text{Pt}}$ is the effective diffusivity within the pores of the Pt/SiO$_2$ aggregates, and $r_{\text{iH}}^n$ is the net I$_H$ formation turnover rate at Pt nanoparticle surfaces. The concentration of I$_H$ within the pores of quasi-spherical Al$_2$O$_3$ aggregates is described by a similar dimensionless equation (Section S.4):

$$\frac{1}{\zeta^2} \frac{\partial}{\partial \zeta^2} \varphi_{\text{iH}} - \frac{\sigma_{\text{Al}} R_{\text{Al}}}{D_{\text{Al}}} \frac{r_{\text{iH}}^n}{|I_{\text{iH}}|_0} = 0$$

where $\zeta$ is the radial coordinate within Al$_2$O$_3$ aggregates (normalized by their mean aggregate radii; $R_{\text{Al}}$), $\sigma_{\text{Al}}$ is the Al$_2$O$_3$ surface area per volume, $D_{\text{Al}}$ is the effective diffusivity within Al$_2$O$_3$ pores, and $r_{\text{iH}}^n$ is the areal rate of I$_H$ formation at Al$_2$O$_3$ surfaces. The $D_{\text{Pt}}$ and $D_{\text{Al}}$ values were estimated from their molecular ($D_{\text{K}}$) and Knudsen ($D_{\text{e}}$) diffusivities combined as resistances in series in the Bosanquet equation [43] (Section S.4).

The radial profiles of the I$_H$ concentration within Pt/SiO$_2$ and Al$_2$O$_3$ aggregates were determined by solving the coupled differential equations (Eqs (4) and (5)) with four boundary conditions: (i) $\varphi_{\text{iH}} = 0$ at the center of each aggregate ($\zeta = 0$ and $\zeta = 0$) due to spherical symmetry; (ii) the net rate of I$_H$ egress from Pt/SiO$_2$ aggregates into the bulk fluid is equal to the total rate of I$_H$ ingress to Al$_2$O$_3$ aggregates from the bulk fluid:

$$W_{\text{iH}} = -\chi \frac{\partial W_{\text{iH}}}{\partial n_{\text{Pt}}}$$

where $W_{\text{iH}}$ and $W_{\text{iH}}^n$ are the rates of I$_H$ egress (per mass catalyst) from Pt/SiO$_2$ and Al$_2$O$_3$ aggregates, respectively. $\chi$ is the Al$_2$O$_3$ to Pt/SiO$_2$ mass ratio, and $\rho_{\text{Pt}}$ is the Al$_2$O$_3$ density; and (iv) the external surfaces of Pt/SiO$_2$ and Al$_2$O$_3$ aggregates are exposed to the same I$_H$ concentration.

These equations were used to determine the concentration profiles of prevalent intermediates in inhibitor-scavenging mechanisms across radial dimensions of the Pt/SiO$_2$ components of loose Pt/SiO$_2$ + Al$_2$O$_3$ mixtures. These concentrations were then used to evaluate MCH formation rate enhancement factors for such mixtures based on mechanism-based kinetic and transport models and compared to measured values.

3. Results and discussion

3.1. Effects of Pt/SiO$_2$ dilution with oxides on methylcyclohexane formation rates from toluene-H$_2$ reactants.

Fig. 1 shows turnover rates for methylcyclohexane (MCH) formation (mole MCH g-atom$^{-1}$ Pt s$^{-1}$) on Pt/SiO$_2$, (1.39 nm mean nanoparticle diameter) as the only other detectable products. 3-Methylcyclohexene (3MCH) could not be separated from the predominant products in the chromatograms. MCH formation rates increased monotonically with the amount of Al$_2$O$_3$-Sasol mixed with Pt/SiO$_2$ as intimate mixtures (denoted here as the ratio of the diluent surface area to the number of surface Pt atoms; $\beta$). Higher rates were also observed for mixtures with Al$_2$O$_3$-solgel; such similar rate enhancements for mixtures prepared using Al$_2$O$_3$ samples of different provenance and amounts of Si (57 (Al$_2$O$_3$-Sasol) and 220 (Al$_2$O$_3$-solgel) ppm; Section 2.1) and Fe (5.2 (Al$_2$O$_3$-Sasol) and 139 (Al$_2$O$_3$-solgel) ppm; Section 2.1) impurities suggests that rate enhancements arise from intrinsic chemical properties of Al$_2$O$_3$ surfaces and not as a consequence of adventitious impurities or of defect sites inherent in specific synthetic protocols. No products were detected from toluene-H$_2$ reactions on Pt-free Al$_2$O$_3$ at these conditions. MCH formation rates on Pt/SiO$_2$ were not affected by intimate mixing with SiO$_2$, indicative of the absence of any artifacts arising from heat or mass transfer; the severity and consequences of such artifacts would have been alleviated by the dilution with inert SiO$_2$ powders [44].

CO oxidation turnover rates (mole CO$_2$ g-atom$^{-1}$ Pt s$^{-1}$) on Pt/SiO$_2$, Al$_2$O$_3$, and Pt/SiO$_2$ + Al$_2$O$_3$-Sasol mixtures were not affected by dilution (473 K, 0.5 kPa CO, 5 kPa O$_2$; Fig. 2). Such rates are insensitive to the Pt nanoparticle diameter [45]; consequently, these data confirm that the number of exposed Pt-surface atoms were unaffected by the mechanical mixing and thermal treatment protocols used to form these mixtures or by the desorption of adventitious poisons of Pt nanoparticles. These similar turnover rates also show that the migration of Pt species from SiO$_2$ supports to the Al$_2$O$_3$ diluent, the formation of Pt nanoparticles with unique reactive properties (e.g. single-atoms or modified nanoparticles with modulated reactivity [46]), or the protection of Pt surfaces through scavenging of impurities by Al$_2$O$_3$ cannot account for the significant rate enhancements conferred by the presence of Al$_2$O$_3$ in these physical mixtures.

The rates reported in Figs. 1 and 2 were measured on Pt/SiO$_2$, Pt/SiO$_2$ + SiO$_2$, and Pt/SiO$_2$ + Al$_2$O$_3$ catalysts that were treated sequentially in 10 % O$_2$/He and 100 % H$_2$ flow at 573 K (Section 2.2). Such O$_2$ treatments would have removed any organic residues at Pt/SiO$_2$ or Al$_2$O$_3$ surfaces derived from exposure to ambient air [19], thus precluding the need for (and benefit of) scavenging such impurities by Al$_2$O$_3$ diluents. The rate enhancements, evident even after such
treatment protocols, indicate that any effects of Al₂O₃ in trapping such residues and in mitigating their titration of Pt nanoparticle surfaces (previously proposed to account for such rate enhancements [19]) are inconsequential in causing such “hydrogen spillover” effects.

Fig. 1 also shows MCH formation turnover rates measured on Pt/SiO₂ samples placed after an Al₂O₃-Sasol pre-bed. Any impurities present in the reactant stream that bind strongly to Al₂O₃ surfaces would be scavenged by this pre-bed before contacting Pt nanoparticles, thus preventing their poisoning of Pt nanoparticle surfaces [7,12]. MCH formation rates on Pt/SiO₂ were not affected by the presence of this pre-bed, indicating that Al₂O₃ present as mixtures with Pt/SiO₂ does not cause rate enhancements by removing toxic impurities present in the inlet stream [7,12].

Fig. 3 shows turnover rates for MCH formation from toluene-H₂ reactants on loose Pt/SiO₂ + Al₂O₃-Sasol mixtures (Section 2.2) at different extents of dilution for Pt/SiO₂ and Al₂O₃ aggregates with mean radii ranging from 13 to 110 nm (1.4 kPa toluene; 90 kPa H₂; 393 K) and with Pt/SiO₂ components with three different mean Pt-nanoparticle diameters (Pt/SiO₂-1.39, Pt/SiO₂-1.51, and Pt/SiO₂-1.67; Table 1). MCH formation rates on Pt/SiO₂-1.39 + Al₂O₃ mixtures with the smallest mean aggregate radius (13 nm) increased linearly with the amount of diluent, indicative of rate enhancements that persist even without the closer proximity inherent in intimate intra-aggregate mixtures. MCH formation rates on loose Pt/SiO₂-1.51 + Al₂O₃ mixtures also increased with dilution extent (37 µm aggregate radii), but with a smaller slope than for mixtures using the Pt/SiO₂-1.39 catalyst (with similar mean aggregate radii). The mixtures prepared using Pt/SiO₂-1.67, on the other hand, showed no rate enhancements. These results indicate a greater prevalence of MCH formation rate enhancements conferred by Al₂O₃ for Pt/SiO₂ catalysts with smaller mean nanoparticle diameter; the origins of this observation are explored in Section 3.6.

Fig. 3 also shows the MCH formation rates for loose Pt/SiO₂-1.51 mixtures with TiO₂ and MgO aggregates. As in the case of Al₂O₃, both oxides led to higher rates than for undiluted samples, with TiO₂ showing larger and MgO showing smaller rate enhancements than Al₂O₃ (for similar dilution extents). These data show that bifunctional synergies are not unique to the chemical properties of Al₂O₃ surfaces but reflect reactions and processes that are related to Lewis-acid-base pairs at oxide surfaces.

The rate enhancements observed on loose Pt/SiO₂-1.39 + Al₂O₃ mixtures decreased with increasing diameter of the Pt/SiO₂ and Al₂O₃ domains (at β = 4800 nm² Al₂O₃ g⁻¹ Pt⁻¹); thus, their magnitude depends on the mean distance between Pt nanoparticles and Al₂O₃ surfaces. Such domain size effects on rate enhancements are akin to those prevalent in bifunctional cascades of the type considered by Weisz [29]; such schemes involve (i) the formation of a reactive intermediate at a primary site, (ii) its gaseous diffusion to another site, and (iii) its reaction at such sites to complete a catalytic turnover. In what follows, plausible bifunctional reaction pathways are considered and the role of specific sites at Al₂O₃ surfaces are assessed using selective titrants for Lewis-acid-base pairs at such surfaces. The catalytic competence of such sites in the hydrogenation of intermediates that can form on and desorb from monofunctional Pt surfaces is explored by measuring rates of cyclohexene (4McHE) and cyclohexadiene (1,3-cyclohexadiene (13CHD)) reactions with H₂ on Al₂O₃. These inquiries are also informed by experimental and theoretical studies of the mechanism of toluene-H₂ reactions on monofunctional Pt nanoparticle surfaces [22].

3.2. Propanoic acid titrants and consequences for methylcyclohexane formation rates on Pt/SiO₂ and intimate Pt/SiO₂-Al₂O₃ mixtures.

Toluene-H₂ reactions on Pt surfaces form ensembles of bound intermediates with different numbers of H atoms (THⁿ⁺, denoting lumped toluene-derived intermediates with n added H atoms). Each lumped THⁿ⁺ moiety consists of several structural isomers that differ in the position of the n H atoms in and the specific C atoms that are bonded to surface Pt atoms; here, j-THⁿ⁺ denotes each distinguishable species (in structure, stability, and reactivity) within the THⁿ⁺ ensemble. These j-THⁿ⁺ moieties are expected to vary in their reactivity and in the extent to which they contribute...
to (i) surface coverages at Pt nanoparticles and (ii) MCH formation rates. The \(j\)-TH\(_n^*\) ensemble includes bound forms of MCHE isomers; their ability to desorb is evident from the detection of gaseous 1MCHE and 4MCHE. The \(j\)-TH\(_n^*\) ensemble includes the bound forms of MCHD isomers; these species can also desorb, but their equilibrium levels during toluene-H\(_2\) reactions are below chromatographic detection limits.

\(\text{Al}_2\text{O}_3\) surfaces are known to activate H–H [23,24] and C–H bonds [23] on Lewis–acidic sites consisting of coordinatively-unoccupied Al\(^{3+}\) centers and adjacent O\(^2–\); such sites may be able to catalyze hydrogenation reactions of Pt-derived MCHD and/or MCHE isomers in a manner that can supplement the rates of their monofunctional routes for MCH formation on Pt surfaces. Two such bifunctional routes are envisioned below; they are denoted as (i) additive/stoichiometric hydrogenation and (ii) inhibitor-scaping routes.

The first route considers hydrogenation reactions of Pt-derived MCHD or MCHE isomers at \(\text{Al}_2\text{O}_3\) sites, thus circumventing any kinetic bottlenecks for their ultimate conversion to MCH via strictly monofunctional Pt-mediated routes and leading to higher MCH formation rates. The second route involves the formation of unproductive \(j\)-TH\(_n^*\) species at Pt surfaces; these species form MCH more slowly than other (more reactive) intermediates, but they may bind to sites on crowded Pt surfaces at coverages that render them unavailable for the more reactive species. Some of these less competent \(j\)-TH\(_n^*\) species can desorb and be scavenged via hydrogenation at \(\text{Al}_2\text{O}_3\) surfaces, thus decreasing their prevalent coverages on Pt surfaces. The surface coverages of other \(j\)-TH\(_n^*\) species that convert more readily to MCH increase correspondingly, thus leading to higher MCH formation rates. Both routes require that \(\text{Al}_2\text{O}_3\) surfaces catalyze hydrogenation reactions of MCHD and/or MCHE isomers, either at rates commensurate with the increased rate of MCH formation in the case of route (i) or at rates similar to those of formation and desorption of these less reactive bound species in the case of route (ii).

Carboxylic acids bind to \(\text{Al}_2\text{O}_3\) surfaces on Lewis acid and Lewis (or Brønsted) base pairs [47–50]. One such carboxylic acid (propanoic acid (PA)) is a selective titrant of such acid-base pairs on ZrO\(_2\) and TiO\(_2\) surfaces that catalyze aldol condensation and ketonization reactions [51,52]; it is used here as a selective titrant of acid-base pairs at the \(\text{Al}_2\text{O}_3\) surface, which may provide active sites for hydrogenation reactions in either one of the proposed bifunctional routes.

Fig. 4 shows MCH formation rates on Pt/SiO\(_2\) during toluene-H\(_2\) reactions as a function of the time on stream before and during introduction of PA into the reactant flow (1.4 kPa toluene; 80 kPa H\(_2\); 3.2 Pa PA; 393 K). Rates were not affected by exposure to PA indicating that monofunctional MCH formation routes on Pt nanoparticles are insensitive to PA titrants. The inlet and effluent PA concentrations were the same, consistent with negligible PA binding or reactions at Pt nanoparticle surfaces. Fig. 4 also shows MCH formation rates on an intimate Pt/SiO\(_2\) + \(\text{Al}_2\text{O}_3\)-Sasol mixture (\(b = 470 \text{ nm}^2 \text{ Al}_2\text{O}_3\) Pt\(^{\text{atom}}\)) before and during exposure to PA, and the effluent PA pressure (1.4 kPa toluene; 80 kPa H\(_2\); 3.2 Pa PA; 393 K). In this case, rates decreased monotonically and almost linearly with time immediately after PA introduction and then more gradually after ~4 ks; rates asymptotically approached those measured on \(\text{Al}_2\text{O}_3\)-free monofunctional Pt/SiO\(_2\) (0.20 mol MCH g\(^{-1}\) Pt, s\(^{-1}\); Fig. 1). PA was nearly undetectable in the effluent stream up to ~4 ks and then gradually reached its inlet pressure (3.2 Pa) as binding sites on the \(\text{Al}_2\text{O}_3\) reached saturation coverages. The total amount of PA retained by the \(\text{Al}_2\text{O}_3\) surface that was needed to suppress increased MCH formation rates was 2.9 PA molecules per nm\(^2\).

The concurrent depletion of PA from the stream and the suppression of the rate enhancements as PA titrates sites at
examined instead of 1-methyl-1,3-cyclohexadiene (or other MCHD isomers) because it forms fewer alkadiene and alkene isomers, thus allowing for more accurate speciation and rate data.

Reactions of 13CHD-H$_2$ reactant mixtures on Al$_2$O$_3$-Sasol led to the formation of 1,4-cyclohexadiene (14CHD), benzene, cyclohexene (CHE), and cyclohexane (CHA) as detectable products (0–100 kPa H$_2$; 5–70 Pa 13CHD; 393 K). Fig. 5a shows benzene, CHE, and CHA areal formation rates on Al$_2$O$_3$-Sasol at different H$_2$ pressures (in each case, extrapolated to the time of initial contact with reactants to account for any intervening deactivation; Section S.5). 14CHD formation rates, in contrast, decreased rapidly with time thus precluding accurate assessments of the effects of H$_2$ on rates. Such fast deactivation may reflect acid-catalyzed C-C bond formation reactions to form oligomers that bind strongly at active sites. Such reactions are much less prevalent at the alkadiene concentrations present during toluene-H$_2$ reactions which cannot exceed their equilibrium levels ($\sim 10^{-4}$ Pa; 90 kPa H$_2$; 1.4 kPa toluene; 393 K; Table S3). CHA and CHE formation areal rates increased linearly with H$_2$ pressure, while benzene formed at rates influenced only slightly by H$_2$ pressure (and detectable even without H$_2$).

These data reflect parallel 13CHD hydrogenation routes involving (i) sequential H$_2$ addition to 13CHD to form CHE (step 1a; Scheme 1) and CHA (step 2a; Scheme 1), and (ii) bimolecular 13CHD hydrogen-transfer (H-transfer) reactions that form benzene and CHE (step 1b; Scheme 1) and similar bimolecular reactions between CHE and 13CHD to form CHA and benzene (step 2b; Scheme 1). Each H-transfer event forms one benzene molecule; thus, the rate of benzene formation is equal to the rate of H-transfer. The molar rates of CHE and CHA formation when H$_2$ was present (10–100 kPa) were much higher than benzene formation, indicative of the prevalent formation of hydrogenated products via reactions of 13CHD with H$_2$ (steps 1a-2a; Scheme 1) instead of only bimolecular hydrogen-transfer events. A hydrogen balance then gives the rate of H$_2$ consumption ($r_{\text{H}_2}$) from the rates of CHA ($r_{\text{CH}_A}$) and CHE ($r_{\text{CHE}}$) formation and H-transfer ($r_{\text{H}_2}^{\text{HT}}$) through:

$$r_{\text{H}_2}^{\text{HT}} = 2r_{\text{CH}_A}^{\text{H}_2} + r_{\text{CHE}}^{\text{H}_2} - r_{\text{H}_2}$$

(7)

Fig. 5b shows areal rates of H-transfer and H$_2$ consumption ($r_{\text{H}_2}^{\text{H}_2}$, where i denotes a given reaction) at different 13CHD pressures on Al$_2$O$_3$-Sasol powders (0–100 kPa H$_2$; 5–70 Pa 13CHD; 393 K; extrapolated to initial contact with reactants). These areal rates are accurately described for both reactions by a Langmuirian kinetic equation:

$$r_{\text{H}_2}^{i} = \frac{\delta_{\text{H}_2}^{i}[\text{HC}]}{1 + K_{\text{H}_2}^{i}[\text{HC}]}$$

(8)

where $s_{\text{Al}}$ is the Al$_2$O$_3$ surface area, [HC] is the hydrocarbon (13CHD) concentration and $K_{\text{H}_2}^{i}$ is the equilibrium constant for 13CHD adsorption at Al$_2$O$_3$ sites. Here, $\delta_{\text{H}_2}^{i}$ is a pseudo-first-order rate constant containing the kinetic and thermodynamic constants and H$_2$
pressures that describe the formation and reaction of the reactive intermediates derived from 13CHD and H₂ that are involved in 13CHD hydrogenation at Al₂O₃ surfaces. The precise determination of the kinetic and thermodynamic parameters and H₂ pressure dependences that comprise χᵣ would require a detailed mechanistic inquiry into the nature and kinetic relevance of the elementary steps involved, but it is not necessary to derive the conclusions drawn in the present study. These χᵣ and Kᵣ parameters were determined by regressing all rate data (Fig. 5b) to the functional form of Equation (8) and are shown in Table 2. The linear trends in H₂ consumption and H-transfer rates with 13CHD pressure below 10 Pa (Fig. 5b; Kᵣ[H₂] < 1) indicate that these 13CHD pressures lead to low coverages of 13CHD-derived intermediates at Al₂O₃ surface sites; these data demonstrate that both reactions occur on sites essentially uncovered by 13CHD-derived species. The weaker effects of 13CHD pressure above 60 Pa reflect a concomitant increase in the Kᵣ[H₂] denominator term and the gradual saturation of such active sites.

Reactions of 4MCHE-H₂ mixtures on Al₂O₃ were also observed demonstrating that these gaseous intermediates, present during toluene-H₂ reactions on Pt nanoparticles, can also react on Al₂O₃ surfaces. Rates were measured on Al₂O₃-Sasol and Al₂O₃-solgel samples, both of which conferred MCH formation rate enhancements when mixed with Pt/SiO₂ (Fig. 1). These 4MCHE-H₂ reactions formed isomers (1MCH and 3MCH) and saturated products (MCH), without the detectable formation of MCHD isomers or toluene (toluene-3MCH chromatographic separation became feasible at the low prevalent concentrations in these experiments). The absence of dehydrogenation products demonstrates that MCH formation rates exclusively reflect hydrogenation by H₂, without any contributions from bimolecular H-transfer reactions.

Fig. 6 shows areal rates of 4MCHE hydrogenation (to form MCH) and 4MCHE isomerization (to form 1MCH and 3MCH) for 4MCHE-H₂ mixtures at different H₂ (Al₂O₃-solgel) and 4MCHE (Al₂O₃-Sasol and Al₂O₃-solgel) pressures (0–100 kPa H₂; 10–150 Pa 4MCHE; 393 K). These rates were extrapolated to the initial time of contact with reactants to account for deactivation trends (Section S.5). The values of the χᵣ and Kᵣ coefficients in Equation (8) were obtained by regressing all rate data (Fig. 6) to the form of this equation and are reported in Table 2. MCH formation rates showed a linear increase with 4MCHE pressure at low values (Fig. 5b; <30 Pa; Kᵣ[H₂] < 1) indicating that active sites are essentially uncovered by 4MCHE-derived species. The weaker pressure effects at higher 4MCHE pressures (>50 Pa) reflect the gradual saturation of active sites with 4MCHE-derived surface species as the Kᵣ[H₂] denominator term becomes larger. Isomerization rates, in contrast, increased linearly with 4MCHE pressure at all pressures, but showed non-zero rates when extrapolated to zero 4MCHE pressures. MCH formation and 4MCHE isomerization rates on Al₂O₃-solgel increased linearly with H₂ pressure and the former, but not the latter, approached zero as H₂ pressures decreased. The finite 4MCHE isomerization rates as H₂ pressures decreased show that this reaction can occur on Al₂O₃ without the involvement of H₂, but the effects of H₂ pressure on these rates suggest that H₂-mediated regio-isomerization can also occur, plausibly through bound H₂-derived species, on Al₂O₃ surfaces [23].

These reported rates for 4MCHE-H₂ and 13CHD-H₂ reactions, evident for broad ranges of H₂ and hydrocarbon pressures, thus demonstrate that the Al₂O₃ component in mixtures with Pt/SiO₂ is able to hydrogenate MCHD and MCH isomers that form and desorb during toluene-H₂ reactions on Pt nanoparticles, even though it is not able to catalyze toluene-H₂ reactions at detectable rates. The active sites for these reactions are likely to involve coordinately unsaturated Al₃⁺ centers that have been shown to cleave H-H and C-H bonds [23,53] and that are effectively stabilized by high coverages of hydroxyl groups (which persist following low pretreatment temperatures [2]). The sections that follow

---

**Table 2**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction</th>
<th>χᵣ (x10⁻⁶ molecules nm² s⁻¹ Pa⁻¹)</th>
<th>Kᵣ (x10⁻⁴ s⁻¹ Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13CHD-H₂</td>
<td>H₂</td>
<td>12±2</td>
<td>17 ± 2</td>
</tr>
<tr>
<td></td>
<td>consumption</td>
<td>2.0±0.1</td>
<td>0.21±0.03</td>
</tr>
<tr>
<td></td>
<td>H transfer</td>
<td>9.1±0.6</td>
<td>18 ± 2</td>
</tr>
</tbody>
</table>

*aFrom Equation (8).* Rateme data are reported in Figs. 5 and 6. The errors indicate 95% confidence intervals. **d**20° and 90° kPa H₂. ***Per H₂** catalyzed. The H₂ consumption rate constant corresponds to a 13CHD consumption rate constant of 1.1±0.1)x10⁻⁶ 13CHD molecules nm² s⁻¹ Pa⁻¹.
assess the role (and magnitude) of Al$_2$O$_3$-catalyzed MCHE and MCHD hydrogenation reactions on MCH formation turnover rates for mixtures of Pt/SiO$_2$ and Al$_2$O$_3$ in order to assess their contributions to the rate enhancements historically denoted as “hydrogen spillover.”

### 3.4. Mechanistic details of additive/stoichiometric hydrogenation routes and their contributions to methylcyclohexane formation turnover rates on Pt/SiO$_2$ + Al$_2$O$_3$ mixtures.

The previous sections provide evidence for the ability of Al$_2$O$_3$ to catalyze H$_2$ addition to cyclic alkadienes and alkenes (Section 3.3), but not to toluene; similar reactions of gaseous MCHE and MCHD intermediates formed from toluene-H$_2$ reactants on Pt nanoparticles and present in Pt/SiO$_2$ + Al$_2$O$_3$ mixtures must also occur. MCHE and MCHD hydrogenation reactions can, in principle, circumvent the elementary steps that limit MCH formation on Pt surfaces via the desorption of these species and their subsequent reaction on Al$_2$O$_3$, thus leading to higher MCH formation rates. Scheme 2 shows such a sequence of reaction steps, which is denoted here as the additive/stoichiometric hydrogenation route.

Steps 1–4 (Scheme 2) depict elementary reactions that form MCH from toluene-H$_2$ reactants on Pt surfaces via a sequence of H-addition events. The sites that bind toluene and the various j-TH$_n^*$ species derived from toluene are denoted as *-sites and the residual interstitial “spaces” within saturated adlayers, which bind H atoms, are denoted as S-sites. Such a distinction between active sites is based on precedents well-established for reactions on hydrocarbon-covered metal surfaces [54–58] and proved essential in describing MCH formation rate and MCHE pressure dependences on toluene pressure from toluene-H$_2$ reactants on monofunctional Pt/SiO$_2$ catalysts, on which the Pt nanoparticles act as the sole mediator of toluene hydrogenation catalysis [22].

Scheme 2. Proposed sequence of steps describing toluene hydrogenation to form methylcyclohexane via a monofunctional Pt-catalyzed route (steps 1–4) and a bifunctional route coupling reactions at Pt and oxide surfaces mediated by Pt-derived gaseous molecules (steps 5–10). The (* *) term denotes an ensemble of adjacent *-sites that binds the respective hydrocarbon intermediate; the number of adjacent sites ($\gamma_{\text{env}}$) that bind each toluene-derived intermediate and that are formed or consumed by reactions at the Pt surface (steps 1–4) are omitted for readability.

Step 1 (Scheme 2) shows quasi-equilibrated molecular adsorption of toluene at an unoccupied ensemble with $\gamma_{\text{env}}$ adjacent *-sites. Steps 2–4 (Scheme 2) depict a sequence of six H-addition events that ultimately form gaseous MCH from each bound toluene. These steps include the adsorption of H$_2$ and subsequent reaction with (i) bound toluene to form TH$_2^*$ (step 2; Scheme 2), (ii) TH$_2^*$ to form TH$_4^*$ and an ensemble of ($\gamma_{\text{env}} / C_0$) adjacent vacant *-sites (step 3; Scheme 2), and (iii) TH$_4^*$ to form TH$_6$ and an ensemble of $\gamma_{\text{env}}$ adjacent vacant *-sites (step 4; Scheme 2).

Scheme 2 shows the location of the added H atoms for species in the ensembles with TH$_2^*$ and TH$_4^*$ stoichiometries. The subset of species within these ensembles with gaseous counterparts (those with closed-shell structures including MCHD and MCHE isomers) are highlighted. Steps 5–10 (Scheme 2) account for MCH formation via additive/stoichiometric hydrogenation routes of Pt-derived MCHD and MCHE intermediates at Al$_2$O$_3$ sites located within distances accessible by gas-phase diffusion from Pt nanoparticles. Steps 5 and 6 (Scheme 2) show the desorption of bound MCHD and MCHE isomers, respectively, from Pt surfaces and their diffusion to Al$_2$O$_3$ surfaces. Steps 7 and 9 (Scheme 2) show interconversions among MCHD and MCHE isomers via Al$_2$O$_3$-catalyzed isomerization reactions. Step 8 (Scheme 2)
describes the formation of MCHE isomers from Al₂O₃-catalyzed H₂ reactions with MCHD isomers, while step 10 (Scheme 2) shows the formation of MCH from Al₂O₃-catalyzed H₂ reactions with MCHD isomers.

Reactions of such MCHD and MCHE intermediates can only increase MCH formation rates if they (i) form in reversible steps at the Pt surface such that their hydrogenation at Al₂O₃ surfaces circumvents kinetic bottlenecks in monofunctional Pt-catalyzed MCH formation routes and (ii) are present in the fluid phase at concentrations sufficient to allow their diffusion from Pt/SiO₂ to Al₂O₃ domains at rates commensurate with excess rates reflected in the observed rate enhancements. The following sections discuss whether additive/stoichiometric hydrogenation meet these requirements for the desorb-able MCHD and MCHE isomers formed during steady-state catalysis on Pt/SiO₂ (+Al₂O₃).

3.4.1. Assessing contributions from additive/stoichiometric methylcyclohexene hydrogenation routes to methylcyclohexene formation rates.

1MCHE and 4MCHE molecules are evident in the contacting fluid phase during toluene-H₂ reactions (0.7 kPa toluene, 80 kPa H₂, 393 K; Table 3) on Al₂O₃-free Pt/SiO₂ (at 0.029 and 0.14 Pa, respectively); their respective pressures remain nearly constant as toluene conversion varies with changes in bed residence time on Pt/SiO₂ catalysts [22]. Such pressures thus reflect a balance between the rates at which they form and further on Pt surfaces at pseudo-steady state; they are much lower (-10⁻²-fold) than predicted from their equilibrium with toluene-H₂ reactants at these conditions (Table 3) indicative of their formation in essentially irreversible steps. These toluene-H₂ reactions form 1MCHE and 4MCHE isomers at a ratio (4.6; 393 K) near their equilibrated conversion to MCH on Al₂O₃ surfaces. As with the pseudo-steady-state gaseous concentrations of these MCHE isomers ([HC]⁺/PS) reflect the balance between their formation via desorption of their Pt-bound counterparts and their consumption via hydrogenation at Al₂O₃ surfaces. Their pseudo-steady-state surface coverages (θ⁺/PS) reflect the balance between their formation from bound toluene and H⁻5 at, consumption via reactions with H⁻5 at, and desorption from Pt surfaces. Their functional forms (derived in Section S.6) are given by:

\[
\frac{r_{\text{MCHI}}}{L_{\text{Pt}}} = \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} = \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} + \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}},
\]

(11)

and

\[
\frac{r_{\text{MCHI}}}{L_{\text{Pt}}} = \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} = \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} + \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}},
\]

(12)

Here, \( \delta_{\text{MCHI}}^\text{PS} \) and \( \theta_{\text{MCHI}} \) are the rate constants for the adsorption and desorption of a given MCHE species at ensembles of vicinal *-sites, respectively; \( \theta_{\text{MCHI}} \) is the number of adjacent *-sites that bind and react the MCHE isomer, \( \kappa \) is the equilibrium constant for toluene adsorption. The \( \delta_{\text{MCHI}}^\text{PS} \) term, as in the case of \( \delta_{\text{MCHI}}^\text{PS} \), is the pseudo-first-order rate constant for the formation and reactions of intermediates that limit the conversion of bound toluene to each given MCH moiety on Pt surfaces.

The enhancement factors for MCH formation rates via the hydrogenation of a given MCHE isomer (\( \eta_i \)) are given by the ratio of the MCH formation rate on Pt/SiO₂ + Al₂O₃ mixtures (\( r_{\text{MCHI}} \)) and on Al₂O₃-free Pt/SiO₂ catalysts (denoted as \( r_{\text{MCHI}}^\text{PS} \)):

\[
\eta_i = \frac{r_{\text{MCHI}}}{r_{\text{MCHI}}^\text{PS}}
\]

(13)

Equation (13) can be restated by substituting \( r_{\text{MCHI}}^\text{PS} \) and \( r_{\text{MCHI}}^\text{PS} \) with their functional forms (Eq. (10); with \( \beta = 0 \) for \( r_{\text{MCHI}}^\text{PS} \)). The resulting \([HC]_i^\text{PS} \) and \( \theta_{\text{MCHI}} \) terms are then replaced by their pseudo-steady-state values from Equations (11) and (12), respectively, to give the following simplified expression:

\[
\eta_i = \frac{\left( \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} \right)}{\left( \frac{\delta_{\text{MCHI}}^\text{PS}}{\theta_{\text{MCHI}}} \right)}
\]

(14)

This equation does not depend on any parameters specific to a given MCHE intermediate indicating that the rate enhancement factor for a given MCHE isomer (\( \eta_i \)) is equivalent to that of the overall MCH formation rate (\( \eta \)). These \( \eta \) values do not depend on the extent of dilution (\( \beta \)) or on the rate constant for MCHE hydrogenation at Al₂O₃ surfaces (\( \delta_{\text{MCHI}}^\text{PS} \); therefore, combined rates of MCH formation on Pt/SiO₂ + Al₂O₃ mixtures do not benefit from increased rates of MCHE hydrogenation catalyzed by Al₂O₃ surfaces. This reflects the irreversible nature of MCHE hydrogenation which makes MCH
formation and toluene conversion rates the same at pseudo-steady state.

At higher temperatures (>500 K), on the other hand, MCHE iso-
mers form as equilibrated mixtures with toluene-H₂ reactants
[22]; under such conditions, MCH formation becomes limited by
MCHE hydrogenation reactions rather than the reaction steps that
govern their formation from toluene-H₂ reactants. Hydrogenation
reactions of such MCHE molecules on Al₂O₃ surfaces could indeed
circumvent kinetic bottlenecks in strictly monofunctional Pt-
catalyzed routes, thereby causing stoichiometric increases in the
amounts of MCH formed. Such additive/stoichiometric routes are
likely to underlie the prevalent increases in MCH formation rates
observed for loose mixtures of Pt/SiO₂-1.51 with Al₂O₃-Sasol and
MgO at these higher temperatures, which are shown in the sup-
porting information (493 K; Section S.9).

3.4.2. Assessing the contributions from additive/stoichiometric
methylcyclohexadiene hydrogenation routes to methylcyclohexane
formation rates.

Gaseous MCHD isomers, unlike 1MCHE and 4MCHE, are not
detectable in the fluid phase during toluene-H₂ reactions on Pt/
SiO₂, even if present in thermodynamic equilibrium with toluene-
H₂ reactants (of order 10⁻⁶-10⁻⁴ Pa, depending on the iso-
er, at 393 K, 1.4 kPa toluene, 90 kPa H₂; Table S3). The quasi-
equilibrated nature of toluene adsorption and methylcyclohexene
desorption during toluene-H₂ reactions on Pt surfaces [22] never-
thless suggests fast desorption of bound precursors to MCHD iso-
ers from the crowded Pt surfaces present under typical toluene
hydrogenation conditions. Once desorbed, their additive hy-
drogenation at Al₂O₃ surfaces would increase MCH formation rates
stoichiometrically. Such additive routes could account for the
higher MCH formation rates observed when Al₂O₃ is mixed with
Pt/SiO₂ only if the prevalent concentrations of such MCHD isomers
are sufficient to establish diffusive fluxes commensurate with the
magnitude of the observed rate enhancements.

The characteristic MCHD diffusion rates in loose Pt/SiO₂ + Al₂O₃
mixtures are compared next with observed MCH formation rate
enhancements (Fig. 3) in order to assess whether MCHD hydro-
genation rates on Al₂O₃ represent a plausible mechanism for these
hydrogenation conditions. Once desorbed, their additive hy-
drogenation at Al₂O₃ surfaces would increase MCH formation rates
stoichiometrically. Such additive/stoichiometric routes could account for the
observed rate enhancements only when the excess MCH formation rates (rMCH
for a given mixture) are smaller than the maximum rates at which MCHD isomers can egress from Pt/SiO₂ aggregates through boundary-layer transport. The corresponding
ratio of the maximum diffusion rate to the excess MCH hydrogena-
ration rate (λ) is given (with derivation in Section S.8) as:

\[ \lambda = \frac{4nR_p k_g [MCHD]^{eq}}{r_{MCH}^\frac{1}{2} C_{138}^{eq} N_{Pt}} \]

Here, R_p is the Pt/SiO₂ aggregate radius, k_g is the mass transfer coeffi-
cient at external surfaces of Pt/SiO₂ aggregates, [MCHD]^{eq} is the total equilibrium concentration of all MCHD iso-
ers, and N_{Pt} is the number of exposed Pt sites in each Pt/SiO₂ aggregate.

Table 4 shows these λ values, the excess MCH formation rates, and the largest possible rates of MCHD transfer from aggregates to the bulk fluid for loose Pt/SiO₂ + Al₂O₃ mixtures with 13 to 110 μm mean aggregate size. The values of [MCHD]^{eq} (which could not be found in the literature) were estimated using coupled cluster single-double (CCSD) and statistical mechanics methods
(Table S3). These λ values (Eq (15)) are much smaller than unity
for all mixtures (5.3–6.9 x10⁻⁴), indicating that measured excess rates could not be sustained by the prevalent MCHD mass transfer rates among domains. Consequently, the insufficient rates of mass transport between Pt/SiO₂ and Al₂O₃ aggregates indicate that additive/
stoichiometric MCHD hydrogenation routes cannot account for the rate enhancements conferred by the presence of Al₂O₃ in these loose mixtures.

These results, combined with the conclusion that additive/stoi-
chiometric MCHD hydrogenation routes cannot increase MCH for-
mation rates (because toluene consumption, and therefore MCH
formation, on Pt surfaces is limited by MCHD formation from
toluene-H₂ reactants (Section 3.4)), indicate that neither MCHE nor MCHD iso-
ers can act as molecular shuttles in additive/stoichiometric hydrogenation that are able to account for the observed bifunc-
tional synergies. The alternate bifunctional route, involving the
scavenging of less reactive species on Pt by their desorption and hydrogenation at Al₂O₃ surfaces (Section 3.2), is considered in the
next section.

3.5. Mechanistic details of inhibitor-scavenging routes and their
contributions to methylcyclohexane formation turnover rates.

Arenes and their partially-hydrogenated products form strong
covalent bonds with metal surface atoms [21,68–71] leading to
to hydrogenation reactions that invariably occur on surfaces densely
covered with such species. Benzene-H₂ reactions, for instance, occur on surfaces covered with mixtures of benzene molecules
[70] and a myriad of isomers of partially (de)hydrogenated ben-
zene derivatives with different H content and surface attachment
mode [57,72,73] as the proposed most abundant surface interme-
diates (MASI). These species are present at coverages that depend
on their different stability as bound species, and they react at dif-
ferent rates as they add H atoms on their path to “desorb-able”
products. Density functional theory (DFT)-derived energies for spe-
cific rates as they add H atoms on their path to “desorb-able”
products. Density functional theory (DFT)-derived energies for spe-
cific species and elementary steps involved in benzene-H₂ reactions on Pt
[111] periodic models indicate that benzene-derived species, sim-
ilar in H-content but with H atoms at different locations, differ in
reactivity for subsequent H-addition steps [69,73–75]; the most
reactive species place the added H atom at the C atom vicinal to
that which formed in a previous H-addition step (denoted as ortho-
hydrogenation routes) [73,74].
Table 4
Excess MCH formation turnover rates (excess rate), maximum rates of egress of MCHD isomers from Pt/SiO₂ aggregates (egress rate), and maximum MCHD egress to excess MCH formation rate ratios (b) for loose Pt/SiO₂ + Al₂O₃ mixtures.

<table>
<thead>
<tr>
<th>Mean aggregate radius (µm)</th>
<th>Excess rate (mole MCH g⁻¹ Pt⁻¹ s⁻¹)</th>
<th>Egress rate (10⁻⁶ mole MCHD g⁻¹ Pt⁻¹ s⁻¹)</th>
<th>λ (x10⁻⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>0.34</td>
<td>23</td>
<td>6.6</td>
</tr>
<tr>
<td>37</td>
<td>0.24</td>
<td>13</td>
<td>6.9</td>
</tr>
<tr>
<td>57</td>
<td>0.16</td>
<td>8.7</td>
<td>5.3</td>
</tr>
<tr>
<td>110</td>
<td>0.068</td>
<td>4.7</td>
<td>5.6</td>
</tr>
</tbody>
</table>

*Defined as the difference between the turnover rate on a given Pt/SiO₂ + Al₂O₃ mixture and Al₂O₃-free Pt/SiO₂. Maximum rates of egress were determined from Equation S11 (Section S.4) with equilibrium MCHD values calculated using coupled cluster single-double (CCSD) theory and statistical mechanics approaches and reported in Section S.8. Rates measured at 393 K, 1.4 kPa toluene, and 90 kPa H₂ with extents of Pt/SiO₂ dilution with Al₂O₃ of 4800–5400 nm²/Al₂O₃ surface Pt atom (Pt₁)⁻¹.

Other routes and species that contribute less significantly to the formation of saturated products may still be present at high surface coverages, thus decreasing the coverages of the more reactive species at the nearly saturated metal surfaces present during arene and cycloalkene hydrogenations on metal nanoparticles. The ability to desorb these less reactive bound species and to hydrogenate them on Al₂O₃ (and other oxide) surfaces, located within distances accessible by diffusion from Pt nanoparticles, would provide a competitive route for their consumption thus decreasing the prevalent surface coverages of these less reactive species. Such processes would increase the relative abundance of the more competent leading to higher MCH formation rates on monofunctional Pt surfaces, with oxide surfaces merely scavenging gaseous forms of less competent species at rates much smaller than stoichiometric MCH formation rates.

The functional form of Equation (14) shows that MCH formation rate enhancements (γ) would benefit from fractional coverages of empty *-sites (θ_0) that are larger on Pt/SiO₂ + Al₂O₃ than on Pt/SiO₂. These θ_0 values are determined by a site balance for the pool of m different prevalent bound species (present at coverages θ_i,) and which ultimately form MCH with different reactivities:

\[
1 = \theta_0 + \sum_{i=1}^{m} \theta_i
\]

(16)

where θ_0 denotes the *-site fractional coverage of each bound moiety. The dense hydrocarbon adlayers prevalent in arene hydrogenation lead to θ_0 values much smaller than unity.

Bound forms of MCHD and MCHE isomers account for some of these bound species (Scheme 2); they can desorb as gaseous molecules (denoted here as "desorb-able"). The other bound species form via H-addition sequences that place new C–H bonds at C-positions that isolate Pt-C bonds with vicinal C atoms present as saturated CH₃ groups and can desorb only as unstable radicals; they are denoted here as stranded species. The site balance in Equation (16) can be restated by separating the summation term into groupings of the n desorb-able species and the p stranded ones:

\[
1 = \sum_{i=1}^{n} \theta_i + \sum_{j=1}^{p} \theta_j
\]

(17)

where θ_i and θ_j denote the *-site fractional coverages of each desorb-able and stranded moiety, respectively. These desorb-able intermediates are formed at pseudo-steady state, reflecting the balance between their formation from Pt-catalyzed toluene-H₂ reactions, their consumption via subsequent Pt-catalyzed reactions with H–S, and their desorption from Pt surfaces. Their surface coverages during steady-state catalysis are determined by equating these formation and consumption rates in a manner similar to that done for bound forms of MCHE isomers in Section 3.4.1 (Eq (12)) and derived in detail for all isomers in Section S.10:

\[
\theta_i = \frac{\theta_i^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} [\text{tol}]^{\theta_i^{\text{Pt} \cdot \text{tol}}}}{2 \theta_i^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} + \theta_i^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} [\text{tol}]^{\theta_i^{\text{Pt} \cdot \text{tol}}}}
\]

Here, γ_i and μ_i are the numbers of adjacent *-sites that bind and react the hydrocarbon moiety, respectively, and the θ_i^{\text{Pt} \cdot \text{tol}} term is a lumped coefficient containing kinetic and thermodynamic parameters and H₂ pressure dependences that describe the formation and reaction of reactive intermediates involved in the conversion of bound toluene to a given moiety at Pt surfaces. The θ_i^{\text{Pt} \cdot \text{tol}} and θ_i^{\text{Pt} \cdot \text{tol}} terms consist of similar groupings of parameters involved in the conversion of a given moiety to bound toluene and MCH, respectively. As with the lumped coefficients introduced in earlier sections, the precise determination of the parameters that determine these coefficients is not essential to derive the conclusions reached here.

The stranded species, in contrast, are present at coverages strictly determined by their relative rates of formation and consumption at Pt surfaces because they cannot desorb; their surface coverages are consequently unaffected by the presence or the amount of Al₂O₃. Their values during steady-state catalysis (θ_j) are thus described by a simplified form of Equation (18) with the third term in the denominator, pertaining to desorption and adsorption processes, equal to zero:

\[
\theta_j = \frac{\theta_j^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} [\text{tol}]^{\theta_j^{\text{Pt} \cdot \text{tol}}}}{2 \theta_j^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} + \theta_j^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} [\text{tol}]^{\theta_j^{\text{Pt} \cdot \text{tol}}}}
\]

Here, all of the terms from Equation (18) containing the i index are replaced with j but otherwise have the same meaning.

Changes to the *-site vacancy coverage (θ_0) underpin any enhancements in MCH formation rates (γ) brought forth by these routes on Pt/SiO₂ + Al₂O₃ mixtures, as indicated by Equation (14). These vacancy coverages are related to the extent of Pt/SiO₂ dilution with Al₂O₃ (β) through Equation (17) (with θ_0, replaced with their respective values from Eqs (16) and (17)), thus accounting for the effects of β on MCH formation rates (via Eq (12)). The complexity of this equation precludes a closed-form solution for θ_0, thus obscuring the trends of γ with β. These trends can be garnered from closed-form solutions for θ_0 for asymptotic cases, such as when there is a single desorb-able species (denoted as θ_0^*) as MASi that requires a *-site ensemble for its adsorption and reactions of the same size as that for toluene (γ_0 = γ_1 = γ_2 = 0) and is formed irreversibly from toluene. The resulting expression for γ (derived in Section S.10) is:

\[
\eta = \frac{[\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}}{2 \theta_0^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} - \frac{\delta_{\text{MCHH}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}}{K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}} [\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}} + \left[ \frac{\delta_{\text{MCHH}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}}{K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}} - \frac{2 \theta_0^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}}{[\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}} + 4 \delta_{\text{MCHH}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}} [\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}} \right]^{1/2}
\]

(20)

The rate enhancements at small extents of dilution (η_0) follow a linear dependence on β given by the first-order Taylor series expansion of Equation (20) at a β value of zero:

\[
\eta_0 = 1 + \beta \left( \frac{[\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}}{2 \theta_0^{\text{Pt} \cdot \text{tol}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}} - \frac{\delta_{\text{MCHH}} K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}}{K_{\text{tol} \cdot \text{tol} \cdot \text{MCH}}} [\text{tol}]^{\theta_0^{\text{Pt} \cdot \text{tol}}}} \right)
\]

(21)
This asymptotic limit can be restated with the slope expressed in terms of two rate ratios including: (i) the ratio of the turnover rate (per Pt\(_i\)) that \(I_H^-\) is formed (from gaseous toluene; \(r_{P+}^{\text{tol}}\)) and the turnover rate (per Pt\(_i\)) that \(I_H^-\) is consumed by subsequent reactions with H→S (to form MCH; \(r_{P+}^{\text{MCH}}\)) at the Pt surface, and (ii) the ratio of the areal rate (per nm\(^{-2}\) Al\(_2\)O\(_3\)) that \(I_H^-\) hydrogenates (to form MCH) at Al\(_2\)O\(_3\) surfaces (\(r_{P}^{\text{MCH}}\)) to the turnover rate (per Pt\(_i\)) that \(I_H^-\) adsorbs and reacts at the Pt surface (\(r_{P}^{\text{MCH},i}\)) to form MCH:

\[
\eta_0 = 1 + \frac{\beta}{2} \left( \frac{r_{P}^{\text{MCH},i}}{r_{P}^{\text{MCH}}} \right) \quad (22)
\]

The presence of the \(\left( r_{P}^{\text{MCH},i}/r_{P}^{\text{MCH}} \right)\) ratio in the slope of Equation (22) indicates that MCH formation rate enhancements become more significant when \(I_H^-\) hydrogenation areal rates at Al\(_2\)O\(_3\) surfaces (\(r_{P}^{\text{MCH},i}\)) are large compared to \(I_H^-\) hydrogenation turnover rates at Pt surfaces (\(r_{P}^{\text{MCH}}\)). This tendency reflects the requirement that Al\(_2\)O\(_3\) surfaces scavange desorbed \(I_H^-\) intermediates at rates that are competitive with their rates of hydrogenation at Pt surfaces in order to decrease pseudo-steady-state \(I_H^-\) pressures and thus \(I_H^-\) coverages. The presence of the \(\left( r_{P}^{\text{MCH},i}/r_{P}^{\text{MCH}} \right)\) ratio in the slope of Equation (22) indicates, moreover, that MCH formation rate enhancements become more pronounced when turnover rates for \(I_H^-\) formation (\(r_{P}^{\text{MCH},i}\)) are large compared to its consumption (\(r_{P}^{\text{MCH}}\)). This ratio indicates that the presence of admixed Al\(_2\)O\(_3\) increases MCH formation rates by \(I_H^-\) scavenging most effectively when \(I_H^-\) species are formed rapidly from toluene but are slow to react further at the Pt surfaces, thereby accumulating at large pseudo-steady-state coverages.

The slope in Equation (22) consists of the product of these two rate ratios, indicating that MCH formation rate enhancements depend not only on the supplemental rates of \(I_H^-\) consumption via Al\(_2\)O\(_3\)-catalyzed routes, but also on a multiplicative factor reflecting the relative rates of \(I_H^-\) formation and consumption at the Pt surface. Such a multiplicative increase in MCH formation rate enhancements due to \(I_H^-\) scavenging demonstrates that the amounts of \(I_H^-\) converted need not be commensurate with the stoichiometric amounts of MCH formed by Al\(_2\)O\(_3\)-catalyzed \(I_H^-\) hydrogenation routes, as was the case for the additive/stoichiometric routes (Section 3.4.1). Disproportionate increases in MCH formation rates due to the scavenging of intermediates such as MCHD isomers, which diffuse and react at rates too slow to be of catalytic significance for additive/stoichiometric routes, could thus plausibly mediate these inhibitor/scavenging routes.

The maximum rate enhancement factor (\(\eta_{\text{max}}\)) obtained at large extents of Pt\(_S\)/SiO\(_2\) dilution with Al\(_2\)O\(_3\) is given by Equation (20) with \(\beta \gg 1\):

\[
\eta_{\text{max}} = 1 + \frac{k_{-i}}{\gamma_{\text{MCH},i}} \left( \frac{r_{P}^{\text{MCH},i}}{r_{P}^{\text{MCH}}} \right) \quad (23)
\]

These maximum rate enhancements are independent of \(\beta\), indicative of amounts of Al\(_2\)O\(_3\) sufficient to scavenge all \(I_H^-\) that desorbs from the Pt surface. The form of Equation (23) indicates that MCH formation rates reach a maximum value when \(I_H^-\) desorption (\(k_{-i}\)) from Pt surfaces is much faster than its hydrogenation (\(\gamma_{\text{MCH},i}\)) and when Al\(_2\)O\(_3\) surfaces are present in amounts sufficient to scavenge all desorbed \(I_H^-\) molecules.

MCH formation rate enhancements (\(\eta\)) are given by Equation (20) only for a single desorb-able intermediate with a site requirement of \(\gamma_{\text{tot}}\) adjacent sites, but the trends inferred from these asymptotic examples hold true in general; these implicit equations can be obtained by substituting the value of \(\theta_{\text{tot}}\) in Equation (14) with that from Equation (17). These general trends indicate that the scavenging of Pt-derived desorb-able MCHE or MCHD isomers can account for the rate enhancements for MCH formation (and for other hydrogenation reactions) commonly attributed to "hydrogen-spillover" phenomena. The specific roles of MCHD and MCHE isomers as the desorb-able species and the consequences of their scavenging, via Al\(_2\)O\(_3\)-catalyzed reactions, on observed MCH formation rates are examined next for two cases: (i) MCHE isomers from the effects of cofeeding them during toluene-H\(_2\) reactions (Section 3.5) and (ii) MCHD isomers by assessing the consequences of their reactions for MCH formation rates and prevalent MCHD pseudo-steady-state pressures using kinetic and reaction-transport models (Sections 3.5.2 and 3.5.3).

### 3.5.1. Assessing the role of desorb-able methylcyclohexene intermediates as persistent "inhibitors" on Pt surfaces

This section examines how 1MCHE or 4MCHE molecules added to toluene-H\(_2\) reactants influence MCH formation rates via their expected increase in surface coverage. These bound moieties may consist of minority bound species, in which case such higher coverages would not influence MCH formation rates, or of species present at kinetically detectable coverages thus displacing more competent intermediates and decreasing rates of toluene conversion.

Table 5 shows MCH formation turnover rates, the (fractional) conversion of added 1MCHE or 4MCHE, the turnover rates for 1MCHE and 4MCHE consumption, and the inlet and outlet 1MCHE and 4MCHE pressures (80 kPa H\(_2\); 0.7 kPa toluene; 4.5 Pa 1MCHE or 5.3 Pa 4MCHE; 393 K). 1MCHE pressures (for toluene-1MCHE-H\(_2\) mixtures) decreased from 4.5 Pa at the inlet to 2.9 Pa at the outlet; these pressures were larger than the pseudo-steady-state value detected during toluene-H\(_2\) reactions on Pt/SiO\(_2\) (0.14 Pa). 4MCHE pressures (for toluene-4MCHE-H\(_2\) mixtures) decreased from 3.3 Pa at the inlet to 0.96 Pa at the outlet and were also much larger than the pseudo-steady-state value (0.03 Pa). The higher pressures present throughout the length of the catalyst bed are expected to lead to higher coverages of their bound counterparts on Pt surfaces than in the absence of added MCHE isomers.

Measured MCH formation rates from toluene-H\(_2\)-1MCHE (or toluene-H\(_2\)-4MCHE) mixtures reflect the combined rates of MCH formation from toluene consumption and from 1MCHE (or 4MCHE). 1MCHE (and 4MCHE) form irreversibly from toluene-H\(_2\) reactions on Pt/SiO\(_2\) (Table 3), indicating that its dehydrogenation is slow relative to its hydrogenation to MCH. Such fast 1MCHE (and 4MCHE) hydrogenation reactions (compared with dehydrogenation) indicates that 1MCHE (and 4MCHE) converts predominantly to MCH when added to toluene-H\(_2\) mixtures; as a result, the excess rates of MCH formation when MCHE isomers are added equal the rates of conversion of coked MCHE. These measured 1MCHE and 4MCHE consumption rates (0.11 and 0.17 mol MCH g-atom\(^{-1}\) Pt\(_S\), respectively) are smaller than measured MCH formation rates (0.35 and 0.42 mol MCH g-atom\(^{-1}\) Pt\(_S\), respectively). Their differences reflect the contributions from toluene-H\(_2\) reactions to MCH formation (0.24 and 0.25 mol MCH g-atom\(^{-1}\) Pt\(_S\), respectively); these rates are similar to measured MCH formation rates from toluene-H\(_2\) mixtures (0.24 mol MCH g-atom\(^{-1}\) Pt\(_S\), respectively). These data show that rates of toluene conversion to MCH are not affected by the higher prevalence of bound intermediates derived from added 1MCHE or 4MCHE, indicating that such bound species are not present at kinetically detectable coverages. These data thus rule out bound MCHE-derived species as the prevalent intermediates that could enhance MCH formation rates through their scavenging on Al\(_2\)O\(_3\) surfaces, because the gas-phase concentrations of MCHE isomers do not influence toluene-H\(_2\) reaction rates on Pt surfaces. Any contributions to rate enhancements from inhibitor-scavenging routes must therefore involve MCHD isomers, the only other desorb-able toluene-derived intermediates that could plausibly form during toluene-H\(_2\) reactions.
3.5.2. Site requirements for 4MCHE formation and consumption steps on Pt surfaces and their response to changes to Pt-adlayer composition.

The \( \text{Al}_2\text{O}_3 \)-mediated scavenging of any desorb-able MCHD intermediates present at significant coverages but contributing minimally to MCH formation rates would shift the composition of the pool of bound species towards others more competent in toluene conversion to MCH (Section 3.5.1). Toluene conversion to MCH can be considered as two separate half reactions: (i) the formation of bound MCHE moieties from toluene-H\(_2\) reactions (steps 2–6; Scheme 2) and (ii) the conversion of bound MCHE moieties to MCH (steps 7–8; Scheme 2). The elementary steps that govern the formation of bound MCH from toluene-H\(_2\) reactants at Pt surfaces (steps 2–6; Scheme 2) involve bound intermediates at ensembles containing \( \gamma_{\text{MCHE}} \) adjacent \(*\)-sites (Section 3.4). The elementary steps that govern the conversion of bound MCH to MCH at Pt surfaces (steps 7–8; Scheme 2), in contrast, are mediated by bound intermediates requiring \( \gamma_{\text{MCHE}} \) adjacent \(*\)-sites (Section 3.4). The coverages of these intermediates are proportional to the number of such \(*\)-site ensembles, which increase as vacant sites become more available through \( \text{Al}_2\text{O}_3 \)-mediated scavenging of MCHD inhibitors. The larger ensembles required to form MCH from toluene than for further MCH reactions would lead to rates that are more sensitive to an increase in the number of vacant \(*\)-site ensembles; as a result, such scavenging processes would cause an increase in the steady-state concentrations of gaseous MCH during toluene-H\(_2\) reactions when \( \text{Al}_2\text{O}_3 \) is present (and leads to MCH formation rate enhancements).

The gaseous concentrations of MCHE isomers formed during toluene-H\(_2\) reactions on \( \text{Pt}/\text{SiO}_2 + \text{Al}_2\text{O}_3 \) mixtures (\( \text{MCHE}^{\text{PSS}} \); Eq (9)) reflect the balance between their formation rates (via desorption of their bound precursors from Pt) and their consumption rates (by adsorption and reaction with \( H^−\cdot\)5 on Pt surfaces and by hydrogenation on \( \text{Al}_2\text{O}_3 \) surfaces) at pseudo-steady state (Section 3.4.1). A comparison between the rates of MCHE hydrogenation at Pt and \( \text{Al}_2\text{O}_3 \) surfaces is drawn next to assess the extent to which Pt dilution with \( \text{Al}_2\text{O}_3 \) effects pseudo-steady-state MCHE pressures.

Measured rates of 4MCHE hydrogenation on Pt-free \( \text{Al}_2\text{O}_3 \) catalyst surfaces (Section 3.3) present a general-first-order rate constant (\( \delta_{\text{Pt}}^a \)) of 9.1 \( \pm 0.6 \times 10^{-7} \) 4MCHE molecules nm\(^2\) \( \text{Al}_2\text{O}_3 \) s\(^{-1}\) Pa\(^{-1}\) (Table 2; 90 kPa H\(_2\); 393 K); this measured \( \delta_{\text{Pt}}^a \) value corresponds to a 4MCHE hydrogenation areal rate of 4.1 \( \pm 0.3 \times 10^{-4} \) 4MCHE molecules nm\(^2\) \( \text{Al}_2\text{O}_3 \) s\(^{-1}\) for 4MCHE present at its pseudo-steady-state pressure (on \( \text{Al}_2\text{O}_3 \)-free \( \text{Pt}/\text{SiO}_2 \); \( \text{MCHE}^{\text{PSS}} \); 0.045 Pa; Table 6). Multiplying the \( \text{Al}_2\text{O}_3 \)-catalyzed areal rate by the maximum dilution extent considered for \( \text{Pt}/\text{SiO}_2 + \text{Al}_2\text{O}_3 \) mixtures (5400 nm\(^2\) \( \text{Al}_2\text{O}_3 \) Pt\(^{\text{Pt}} \)) gives an \( \text{Al}_2\text{O}_3 \)-catalyzed 4MCHE hydrogenation rate (per Pt\(^{\text{Pt}} \)) of 2.2 \( \pm 0.2 \times 10^{-4} \) mole MCH g-atom\(^{-1}\) Pt\(^{\text{Pt}} \) s\(^{-1}\). 4MCHE is hydrogenated to MCH on Pt surfaces, on the other hand, with a turnover rate of 6.7 \( \pm 1.2 \times 10^{-2} \) mole MCH g-atom\(^{-1}\) Pt\(^{\text{Pt}} \) s\(^{-1}\) (90 kPa H\(_2\); 1.4 kPa toluene; 393 K), assuming that reactions of each MCHE isomer contribute equally to the rate that MCH is formed on \( \text{Pt}/\text{SiO}_2 \) (0.20 \( \pm 0.03 \) mole MCH g-atom\(^{-1}\) Pt\(^{\text{Pt}} \) s\(^{-1}\)).

### Table 5

<table>
<thead>
<tr>
<th>Hydrocarbon reactants</th>
<th>1MCHE (Pa)</th>
<th>4MCHE (Pa)</th>
<th>MCHE conv.</th>
<th>TOR (mole MCH g-atom(^{-1}) Pt(^{\text{Pt}} ) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>inlet [outlet]</td>
<td>inlet [outlet]</td>
<td></td>
<td>MCH</td>
</tr>
<tr>
<td>Toluene</td>
<td>0 [0.14]</td>
<td>0 [0.029]</td>
<td>- -</td>
<td>0.24</td>
</tr>
<tr>
<td>Toluene + 1MCHE</td>
<td>4.5 [2.9]</td>
<td>0 [0.17]</td>
<td>0.36</td>
<td>0.35</td>
</tr>
<tr>
<td>Toluene + 4MCHE</td>
<td>- -</td>
<td>3.3 [0.96]</td>
<td>0.71</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*0.7 kPa toluene and 80 kPa H\(_2\) at 393 K on Pt/SiO\(_2\) with a 1.39 nm mean Pt-nanoparticle diameter (Pt/SiO\(_2\)-1.39).*

### Table 6

<table>
<thead>
<tr>
<th>( \beta ) (nm(^2) ( \text{Al}_2\text{O}_3 ) surface Pt(^{\text{Pt}} ))</th>
<th>4-Methylcyclohexene pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.045</td>
</tr>
<tr>
<td>470</td>
<td>0.056</td>
</tr>
<tr>
<td>960</td>
<td>0.064</td>
</tr>
</tbody>
</table>

*1.4 kPa toluene and 90 kPa H\(_2\) at 393 K on Pt/SiO\(_2\) with a 1.39 nm mean Pt-nanoparticle diameter (Pt/SiO\(_2\)-1.39).*

Fig. 1. This rate is a factor of 300 larger than the \( \text{Al}_2\text{O}_3 \)-catalyzed 4MCHE hydrogenation rate on Pt/SiO\(_2\) + \( \text{Al}_2\text{O}_3 \) mixtures (per Pt\(^{\text{Pt}} \)), indicating that MCH reactions on \( \text{Al}_2\text{O}_3 \) surfaces do not contribute detectably to the rates of MCHE consumption. The expression for pseudo-steady-state MCHE pressures [Eq (11)] neglecting contributions from reactions on \( \text{Al}_2\text{O}_3 \) surfaces thus simplifies to:

\[
[H\text{C}_{\text{MCHE}}^{\text{PSS}}] = \frac{x_{\text{Pt}^{\text{Pt}}}^{\text{MCHE}}}{x_{\text{Al}_2\text{O}_3}^{\text{MCHE}}K_{\text{MCHE}}} \left( \frac{[\text{H}_2]}{[\text{tol}]} \right)^{\delta_{\text{MCHE}}-\gamma_{\text{MCHE}}} \tag{24}
\]

Here, \( K_{\text{MCHE}} \) is the equilibrium constant for the adsorption of a given MCHE isomer on Pt.

**Table 6** shows 4MCHE pressures [\( \text{MCHE}^{\text{PSS}} \)] during toluene-H\(_2\) reactions on Pt/SiO\(_2\) toluene-H\(_2\) reactions on Pt/SiO\(_2\) mixed with different amounts of Al\(_2\)O\(_3\)-Sasol (1.4 kPa toluene; 90 kPa H\(_2\); 393 K; 0–960 nm\(^2\) Al\(_2\)O\(_3\) Pt\(^{\text{Pt}} \)). These pressures increased monotonically with extent of dilution, a trend that indicates that rates of 4MCHE formation increase more (or decrease less) sensitively with extent of dilution than of 4MCHE conversion to MCH. The functional form of \( \text{MCHE}^{\text{PSS}} \) (Eq (24)) can be separated into two groupings of terms: (i) the coverage of vacant \(*\)-sites raised to an exponent that reflects the difference between the site ensembles required to bind and react toluene and MCH (\( \theta^{\delta_{\text{MCHE}}-\gamma_{\text{MCHE}}} \)) and (ii) a coefficient (\( x_{\text{Pt}^{\text{Pt}}}^{\text{MCHE}} / x_{\text{Al}_2\text{O}_3}^{\text{MCHE}} K_{\text{MCHE}} \)) a toluene pressure dependence, and the 4MCHE adsorption equilibrium constant (\( K_{\text{MCHE}} \)). This coefficient depends only on the nature of the Pt nanoparticle surface without any effects of \( \text{Al}_2\text{O}_3 \) surfaces present within diffusion distances. The monotonic increase in 4MCHE pressures with extent of dilution must consequently reflect an increase in the number of vacant \(*\)-site ensembles, providing direct evidence for the scavenging of \(*\)-site inhibitors by \( \text{Al}_2\text{O}_3 \) surfaces. These same increased coverages of vacant \(*\)-site ensembles are next shown to underpin MCH formation rate enhancements (\( \eta \)).

\[
[\text{MCHE}^{\text{PSS}}] = \frac{x_{\text{Pt}^{\text{Pt}}}^{\text{MCHE}}}{x_{\text{Al}_2\text{O}_3}^{\text{MCHE}}K_{\text{MCHE}}} \left( \frac{[\text{H}_2]}{[\text{tol}]} \right)^{\delta_{\text{MCHE}}-\gamma_{\text{MCHE}}} \eta^{1-\phi_{\text{MCHE}}} \tag{25}
\]
In this equation, \( \omega_{\text{one}} \) is defined as the ratio of the numbers of adjacent "*-sites required to bind MCHE isomers (\( \gamma_{\text{one}} \)) and toluene (\( \gamma_{\text{tol}} \)):

\[
\omega_{\text{one}} = \frac{\gamma_{\text{one}}}{\gamma_{\text{tol}}}
\]  

(26)

The \( \nu_{\text{one}} \), \( \theta_{\text{MCHE}} \), \( \theta_{\text{tol}} \), and \( \omega_{\text{one}} \) terms in Equation (25) depend solely on properties of Pt surfaces (as in the coefficient of Eq (22)). The ratio of the pressure of a given MCHE isomer on a Pt/SiO\(_2\) + Al\(_2\)O\(_3\) mixture (\( \gamma_{\text{MCHE}}/\gamma_{\text{tol}} \)) to that on Pt/SiO\(_2\) (\( \gamma_{\text{MCHE}}/\gamma_{\text{tol}} \); Eq (23)) with \( \eta = 1 \), denoted as \( \zeta \), therefore becomes a single-valued function of the rate enhancement factor for MCH formation:

\[
\zeta = \eta^{1-\omega_{\text{one}}}
\]  

(27)

Fig. 7 depicts values of the 4MCH pressure enhancement factor (\( \zeta_{4\text{M}} \)) and \( \eta \) for loose and intimate mixtures (Pt/SiO\(_2\)-1.39; 1.4 kPa toluene; 90 kPa H\(_2\); 393 K) with different dilution extents and mean aggregate radii. These \( \zeta_{4\text{M}} \) values increased monotonically with increasing \( \eta \); the observed trends correspond to a \( \omega_{\text{one}} \) value of 0.62 \pm 0.02, which agrees well with that measured on catalyst Pt/SiO\(_2\)-1.39 (\( \omega_{\text{one}} = 0.7 \pm 0.02 \)) from the effects of toluene pressure on pseudo-steady-state 4MCH pressures in the absence of Al\(_2\)O\(_3\) [22].

\( \zeta_{4\text{M}} \) and \( \eta \) vary in a manner consistent with the mechanism-based inhibitor-scavenging model (Eq (27)), indicating that increased MCH formation rates and MCH pressures can both be attributed to a greater abundance of vacant "*-sites ensembles caused by Al\(_2\)O\(_3\)-mediated scavenging of desorbable inhibitors. This mechanistic origin of Al\(_2\)O\(_3\)-induced rate enhancements indicates that so-called "hydrogen spillover'' phenomena become evident for reactions occurring on metal surfaces densely covered with a diverse range of bound species that differ in coverage, in reactivity, and in their contribution to the formation of products. For such reactions, the Al\(_2\)O\(_3\) (and other metal oxide) co-catalyst provides an additional route for the consumption of desorbable species with high metal surface coverages and low reactivities, thereby uncovering the active sites that catalyze reactions of other intermediates with higher reactivities towards the ultimate products.

3.5.3. Effects of Pt/SiO\(_2\) and Al\(_2\)O\(_3\) aggregate domain size on methylcyclohexane formation rates and comparisons with predictions from inhibitor-scavenging routes.

Inhibitor-scavenging routes (Section 3.5) involving Pt-derived MCHD isomers on Pt/SiO\(_2\) + Al\(_2\)O\(_3\) mixtures would require the diffusion of MCHD isomers between Pt and Al\(_2\)O\(_3\) sites over length scales of micrometers (for loose mixtures) to complete a scavenging event. These MCHD intermediates can form on Pt surfaces, but at gas-phase concentrations no larger than those in equilibrium with toluene-H\(_2\) reactants (2–30 x10\(^{-15}\) mole cm\(^{-3}\), depending on the particular isomer; 1.4 kPa toluene; 90 kPa H\(_2\); 393 K (Table S3)). MCHD diffusion within porous aggregates of Pt/SiO\(_2\) and Al\(_2\)O\(_3\) and across boundary layers surrounding each aggregate occurs at rates driven by gradients in local MCHD concentration, leading to scavenging processes that become limited by transport as aggregate diameters increase. The resulting concentration gradients lead to the observed weakening of the rate enhancements with increasing diameter of Pt/SiO\(_2\) and Al\(_2\)O\(_3\) aggregates (at similar extents of dilution; Fig. 3).

The spatial segregation enforced by separate Pt/SiO\(_2\) and Al\(_2\)O\(_3\) aggregates in loose mixtures (and by the less well-defined boundaries among constitutive Pt/SiO\(_2\) and Al\(_2\)O\(_3\) regions in intimate mixtures) causes MCHD concentrations to be highest within Pt/SiO\(_2\) aggregates and lowest within Al\(_2\)O\(_3\) aggregates. Such concentration profiles of MCHD inhibitors across the radial dimensions of Pt/SiO\(_2\) and Al\(_2\)O\(_3\) aggregates are depicted in Scheme 3 for loose mixtures with mean aggregate radii between 13 and 106 \( \mu \)m. These MCHD concentration gradients become most evident for fast MCHD formation and consumption processes (relative to characteristic MCHD diffusion rates through intra-aggregate voids and external boundary layers in Pt/SiO\(_2\) and Al\(_2\)O\(_3\) domains). The coverages of the surface-bound counterparts of these MCHD isomers are related to their gaseous concentrations (\( \gamma_{\text{HC}} \)) from the balance at pseudo-steady state between their rates of formation from reactions of toluene (with H–S) and consumption by subsequent reactions (with H–S) at the Pt surface and their net rates of reversible desorption. These MCHD coverages (and thus gaseous MCHD concentrations) are components of the balance on "*-sites (Eq (17)); thus, they influence the coverage of vacant "*-sites and the MCH formation rate enhancement factors (\( \eta \); Eq (14)). MCHD formation rate enhancements at a given position within the Pt/SiO\(_2\) aggregates therefore depend on the local concentrations of these gaseous MCHD inhibitors, as they diffuse out of the aggregates where they form and react at Al\(_2\)O\(_3\) aggregates. These local rate enhancements thus exhibit gradients across the dimensions of the Pt/SiO\(_2\) aggregate voids.

The effects of gradients in local MCH formation rate enhancements across the dimensions of Pt/SiO\(_2\) aggregates on overall rate enhancements are determined by averaging their values across the aggregates’ volumes. These volume-averaged rate enhancement factors (denoted as (\( \eta \))) are determined by integrating the local rate enhancement factor (\( \eta \); Eq (14)) across the radial coordinate of the quasi-spherical Pt/SiO\(_2\) aggregates (assuming that MCHD concentrations are uniform in the angular dimensions):

\[
\langle \eta \rangle = \frac{3}{R^3_{\text{Pt}}} \int_0^{R_{\text{Pt}}} \frac{\eta_{\text{MCHE}}}{\gamma_{\text{MCHE}}} \pi R^2 \, dR
\]  

(28)

Here, R is the radial coordinate of the Pt/SiO\(_2\) aggregates and dR is the differential radial element.

The values of \( \langle \eta \rangle \) can be obtained using Equation (28) when the local values of \( \eta_{\text{MCHE}} \) are known at each radial position within Pt/SiO\(_2\) aggregates. There are five distinct gaseous MCHD isomers, all of
which may be present at significant coverages and each one of which may bind in different conformations and attachment positions at Pt surfaces; for any of these, desorption and subsequent scavenging would lead to an increase in $h_{tol}$. These gaseous MCHD isomers differ in their Gibbs free energy of formation from toluene and $H_2$ by about 10 kJ/mol (393 K; Table S3); such differences in thermodynamic properties suggest that their concentrations at pseudo-steady state, and therefore their rates of mass transfer between Pt/SiO$_2$ and Al$_2$O$_3$ aggregates in physical mixtures, would differ. Their bound counterparts, moreover, differ in the relative locations of C-Pt contacts, the strength of these C-Pt bonds, and their stereochemistry, leading to a broad range of formation energies (from toluene-$H_2$ reactants), reactivities (for their hydrogenation to MCH), and thus in their surface coverages and contributions to measured MCH formation rates. Such diversity of plausible inhibitors, differing in coverage and reactivity, precludes any accurate assessments of the extent to which their scavenging contributes to MCH formation rate enhancements. Instead, the minimum number of intermediates required to account for the weaker rate enhancements for larger aggregates in loose Pt/SiO$_2$ + Al$_2$O$_3$ mixtures (Fig. 3) is considered here to demonstrate that diffusional effects in inhibitor-scavenging routes are consistent with the effects of mean inter-function distances in these mixtures.

Reaction-transport models based on formalisms for bifunctional cascade reactions by Weisz [29] are able to describe the observed trends in MCH formation rates for the loose mixtures (Fig. 3; Pt/SiO$_2$-1.39 catalyst) even when considering only one desorb-able MCHD intermediate (denoted as $I_H$) as the sole MASI. In this case, the site balance (Eq (17)) simplifies to the following form:

\[ 1 = \theta_{I_H} \]  \hspace{1cm} (29)

where $\theta_{I_H}$ is the surface coverage of the prevalent desorb-able intermediate. This coverage is related to the gaseous concentration of its molecular counterpart from the balance of its formation and consumption at pseudo-steady state; an expression for its value is derived in Section S.11 and replaces the $h_{IH}$ term in Equation (29) to give:

\[ 1 = \frac{x_{tol} \cdot K_{I_H} \cdot |tol|}{k_{I_H} \cdot |I_H|_0} \cdot \left( \hat{\theta}_i - \frac{1}{x_{I_H}} \cdot \left( \alpha_{I_H} - 1 \right) \right) + \phi_{I_H} \hat{\theta}_i \]  \hspace{1cm} (30)

where the dimensionless vacant *-site coverage ($\hat{\theta}_i$) is defined as:

\[ \hat{\theta}_i = \left( \frac{k_{I_H} \cdot |I_H|_0}{K_{I_H}} \right) \theta_i^{ps} \]  \hspace{1cm} (31)

Here, $\phi_{I_H}$ is the dimensionless $I_H$ concentration ($\phi_{I_H} = [I_H]/[I_H]_0$) and $\alpha_{I_H}$ is the ratio of the number of adjacent *-sites occupied by the transition state that mediates $I_H$ conversion to MCH ($\gamma_{I_H}$) and that binds toluene at the Pt surface ($\alpha_{I_H} = \gamma_{I_H}/\gamma_{tol}$).

The $\phi_{I_H}$ and $\hat{\theta}_i$ values at each radial position within quasi-spherical Pt/SiO$_2$ and Al$_2$O$_3$ aggregates in loose mixtures are determined by the solution to the coupled ordinary differential equations (ODE) that account for MCHD diffusion and reaction in the Pt/SiO$_2$ (Eq (4)) and Al$_2$O$_3$ (Eq (5)) domains (Section 2.3). These equations contain terms for the net rate of MCHD formation from Pt surfaces ($r_{I_H}^{ps}$) and reaction at Al$_2$O$_3$ surfaces ($r_{I_H}^{al}$) (derivation details in Section S.10):
Table 7

Values of coefficients from reaction-transport models determined by regressing the observed methylcyclohexane formation rate enhancement factors to their model-predicted values with two different $\omega_{x,y,z}$ values for loose Pt/SiO$_2$ + Al$_2$O$_3$ mixtures.$^a,b$

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>$\omega_{x,y}^{0.5}$</th>
<th>$\omega_{x,y}^{1}$</th>
<th>$\omega_{x,y}^{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{x,y}/[h_{x,y}](\text{MCHD Pt$_x$ + Al$_2$O$_3$ s}^{-1})$</td>
<td>2 ($\pm 100$)$^c$</td>
<td>1 ($\pm 6000$) $\times 10^3$</td>
<td>1 ($\pm 6000$) $\times 10^3$</td>
</tr>
<tr>
<td>$\theta_{x,y,z}^{MCHD}[\text{MCHD nm}^2 \ \text{Pa}^{-1} \ \text{MCHD s}^{-1}]$</td>
<td>5 ($\pm 7$) $\times 10^3$</td>
<td>5 ($\pm 4$) $\times 10^3$</td>
<td>5 ($\pm 4$) $\times 10^3$</td>
</tr>
<tr>
<td>$x_{x,y,z}^{MCHD}[\text{tol}]/k_{v,y,z}^{MCHD} [\text{a.u.}]$</td>
<td>1 ($\pm 50$) $\times 10^{-2}$</td>
<td>3 ($\pm 10000$) $\times 10^{-5}$</td>
<td>3 ($\pm 10000$) $\times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ From Equation (28) with $\varphi$ from Equation (30) and $\varphi$ from the solution to coupled differential Equations (4) and (5). $^b$ Ratio of the number of adjacent $\gamma$-sites that mediate $\mathrm{H}_2$ hydrogenation and binds tolueene ($\omega_{x,y}^{0.5}$ / $\omega_{x,y}^{m}$), taken to be $\omega_{x,y}^{m}$ (0.62; Fig. 7) or 1. $^c$Values with two different $\varphi$. $^d$Values with two different $\varphi$. $^e$Values with two different $\varphi$.

The catalytic-radiative transport models for loose mixtures with dilution extents ranging from 1000 to 5000 nm$^2$ Al$_2$O$_3$ Pt$_x$ and mean aggregate radii ranging from 13 to 110 μm (90 kPa H$_2$; 1.4 kPa toluene; 393 K). Two sets of coefficients were determined using different $\omega_{x,y}$ values that reflect (i) equivalent ensembles of adjacent $\gamma$-sites that are required to hydrogenate $\mathrm{H}_2$ and (ii) a smaller ensemble of adjacent $\gamma$-sites (which resembles that which binds MCH) that is required to hydrogenate $\mathrm{I}_H$. Their values and uncertainty ranges are listed in Table 7. The values were determined by regressing the observed MCH formation rate enhancement factors to their model-predicted values with two different $\omega_{x,y}$ values for loose Pt/SiO$_2$ aggregates, which are then used to determine rate enhancement factors with two different $\varphi$. The reaction-transport models based on MCHD-mediated processes react rapidly at Pt and Al$_2$O$_3$ sites thereby establishing low steady-state pressures with relatively slow rates of mass transport as a consequence. Bifunctional reactions involving these scarce and highly reactive intermediates thus influence MCH formation rates most substantially when inter-function distances (and thus the severity of gradients) are minimized. Similar bifunctional processes mediated by scarce and undetectable intermediates are plausible, more generally, for other reactions of organic molecules on composite catalysts consisting of dispersed metal, sulfide, or oxide nanoparticles densely covered by diverse bound species with a broad range of reactivity and stability that have gaseous counterparts with sufficient stability to enable their desorption and (ii) reactivity on non-innocent supports to be consequential even at low steady-state gas phase concentrations.

The hydrodesulfurization of organosulfur compounds (HDS) on supported [76–78] or unsupported [79] Mo sulfide (MoS$_2$) catalysts is promoted by the presence of a Co sulfide (CoS$_x$) catalyst prepared in a mechanical mixture [76,79] or as a “stacked bed” with Al$_2$O$_3$ or SiO$_2$-supported MoS$_2$ downstream of an Al$_2$O$_3$ or SiO$_2$-supported CoS$_x$ bed, and with a layer of SiO$_2$ to separate the two [76,78]. These promotional effects have been attributed to bifunctional processes involving (i) H$_2$-dissociation on CoS$_x$ surfaces to between Pt and Al$_2$O$_3$ sites, thus decreasing the efficiency of the scavenging processes required to confer MCH formation rate enhancements. These gradients develop because MCHD intermediates react rapidly at Pt and Al$_2$O$_3$ sites thereby establishing low steady-state pressures with relatively slow rates of mass transport as a consequence. Bifunctional reactions involving these scarce and highly reactive intermediates thus influence MCH formation rates most substantially when inter-function distances (and thus the severity of gradients) are minimized. Similar bifunctional processes mediated by scarce and undetectable intermediates are plausible, more generally, for other reactions of organic molecules on composite catalysts consisting of dispersed metal, sulfide, or oxide nanoparticles densely covered by diverse bound species with a broad range of reactivity and stability that have gaseous counterparts with sufficient stability to enable their desorption and (ii) reactivity on non-innocent supports to be consequential even at low steady-state gas phase concentrations.
form H atoms, (ii) the migration of H atoms from CoSx to MoS2 surfaces, and (iii) advantageous reactions of H atoms at MoS2 surfaces. In another study, bifunctional synergies were observed for thiophene HDS to C4 hydrocarbons on SiO2-supported Pt nanoclusters admixed with γ-Al2O3 [80]. Turnover rates were about tenfold larger on Pt nanoparticles within Na-LTA zeolites (Pt/NaLTA) than on Pt/SiO2 because LTA-encapsulated Pt particles were accessible to H2 but not to thiophene. Pt/NaLTA dilution by Al2O3 led to rate increases derived exclusively from a minority (<20%) of the Pt nanoparticles unprotected from access to thiophene because they reside outside the LTA voids. Al2O3 thus promotes HDS turnover rates only for a Pt function that is accessible to both H2 and thiophene, thereby excluding pathways that reflect solely H2 dissociation on Pt and migration of H-atoms to (and use at) an Al2O3 surface. Instead, thiophene-derived molecular shuttles must act as the species that allow chemical information to be transferred between the two functions, as reported here for toluene hydrogenation reactions. Such bifunctional processes mediated by molecular shuttles, rather than H atoms, may also account for the promotional effects of CoSx for MoS2-based HS catalysts.

3.6. Effects of Pt nanoparticle diameter on the prevalence of Al2O3-mediated rate enhancements for toluene-H2 reactions on Pt surfaces.

Rates of MCH formation on Pt/SiO2 increased more significantly when diluted with Al2O3 when the mean diameter of the Pt nanoparticles was smaller than 1.5 nm (Fig. 3). Smaller Pt nanoparticles contain surface atoms of lower mean coordination which tend to bind adsorbed species more strongly than those of higher coordination [56,81,82]. It is therefore unlikely that large, but not small, Pt nanoparticles bind MCHD molecules at strengths that preclude their desorption (and subsequent scavenging at oxide surfaces) to account for the effect of particle size on the rate enhancements.

Reported DFT calculations on Pt(1 1 1) surfaces reveal that 1,3-cyclohexadiene and 1,4-cyclohexadiene molecules can bind to Pt surfaces via overlap of the π-orbitals of each C=C group with the d-orbitals of surface Pt atoms [31]. These π-bonded structures each coordinate to two adjacent surface Pt atoms, thus permitting only Pt-site pairs as the adsorption site. Such a structure for bound 1,3-cyclohexadiene is similar to the tilted configuration of adsorbed 1,3-cyclohexadiene observed from sum-frequency generated vibrational spectra on Pt(1 1 1) surfaces [83]. Adsorbed forms of benzene on Pt(1 1 1) surfaces, on the other hand, coordinate parallel to the surface at ensembles of three or four adjacent Pt atoms [32–34]. No stable structures were reported for benzene coordinated to single or pairs of adjacent Pt atoms on these surfaces. DFT calculations on Pt clusters with 13 atoms showed, moreover, that 1-methyl-1,3-cyclohexadiene binds in its lowest energy structure at adjacent Pt-site pairs, while toluene binds at ensembles of three Pt sites [30].

Sum-frequency generated vibrational spectra of Pt(1 1 1) surfaces at typical conditions of benzene (and toluene) hydrogenation show that surfaces become saturated with benzene and co-adsorbed H-atoms [62]; such evidence suggests that low index planes of Pt surfaces are preferentially covered by molecularly-bonded forms of monoarenes in favor of their partially-hydrogenated products. Pt surfaces of large Pt nanoparticles are thus expected to be covered by toluene instead of MCHD isomers. Larger metal nanoparticles expose larger fractions of surfaces with closed-packed structures and higher coordination numbers compared to surfaces of smaller nanoparticles with higher fractions of steps, edges, and corner sites and relatively low coordination numbers [56,84]. As the abundance of surface Pt ensembles with close-packed structures decreases with particle size, so too does the fraction of threefold and fourfold ensembles that bind toluene (and benzene). The fraction of Pt surfaces containing vicinal-site pairs decreases to a lesser extent; thus, the ratio of Pt-site pairs to threefold and fourfold ensembles increases with particle size. The favorable interactions of methylcyclohexadiene isomers, but not toluene, with Pt-site pairs indicates that competitive adsorption of MCHD isomers and toluene during toluene-H2 reactions favors higher coverages of the MCHD isomers, instead of toluene, as the Pt-particle size decreases. Such higher surface coverages of MCHD isomers on smaller particles can account for the greater increase in MCH formation rate due to their hydrogenation-scavenging by oxide surfaces present within distances accessible by gas-phase diffusion.

The previous sections showed that the rates of MCH formation on Pt/SiO2 can be influenced by an oxide co-catalyst if (i) the oxide co-catalyst selectively hydrogenates prevalent MCHD intermediates (Section 3.3), (ii) sufficient amounts of this oxide are present to scavenge the intermediate at appreciable rates (Section 3.1), and (iii) the Pt and oxide sites are separated by sufficiently small distances to enable the mass transfer of molecular shuttles between the sites (Section 3.5.3). The effects of particle size on MCH formation rate enhancements conferred by Pt/SiO2 dilution with Al2O3 indicates, moreover, that not all Pt nanoparticles have surfaces covered by MCHD intermediates and thus do not all benefit from their scavenging to the same extent. These results may explain, in large part, the varying and sometimes contradictory evidence for the existence and magnitude of “hydrogen spillover” for hydrogenation reactions (as discussed by Prins [12]) when measurements on catalysts with metal nanoparticles of different size distributions are compared.

4. Conclusions

Turnover rates for methycyclohexane (MCH) formation from toluene-H2 reactants (per surface Pt site) catalyzed by the surfaces of SiO2-supported Pt nanoparticles (Pt/SiO2) with small mean diameters (<1.6 nm) increase when Pt/SiO2 is physically mixed with metal oxides (Al2O3, MgO, and TiO2). The surfaces of these Pt nanoparticles bind one or more of the bound forms of methycyclohexadiene (MCHD) isomers at high converges under reaction conditions. Some of these isomers are slow to react further to methycyclohexane (MCH); thus, their hydrogenation does not contribute significantly to the rates of MCH product formed. They do, however, inhibit the formation of more reactive intermediates that predominantly contribute to the rates of MCH formation.

These surface-bound MCHD inhibitors desorb as their gaseous molecular counterparts, which then diffuse to and hydrogenate at proximate metal oxide functions with exposed Lewis-acid-base pairs (Al2O3, MgO, and TiO2) present as physical mixtures with Pt/SiO2. Al2O3 catalyzes the hydrogenation of cyclic alkenes and alkadienes (4-methycyclohexene and 1,3-cyclohexadiene, respectively), but not toluene. These Al2O3-catalyzed hydrogenation reactions occur at rates that are insufficient to account for increased rates of MCH formation on Pt/SiO2 with admixed Al2O3 via stoichiometric hydrogenation of Pt-derived MCHD or methycyclohexene (MCHE) molecules. Al2O3-catalyzed MCHD hydrogenation does occur, however, at rates that are sufficient to compete with the rates that the prevalent MCHD inhibitors are consumed at Pt surfaces on Pt/SiO2 + Al2O3 mixtures. Such scavenging by admixed Al2O3 decreases the gaseous concentrations of these inhibitors and thus their coverages on Pt surfaces; Pt sites consequently become more available for the formation and reaction of other intermediates that produce MCH at faster rates. The selective titration of acid-base pairs by propanoic acid under conditions of toluene-H2 reactions remove any increase in rate relative to strictly monofunctional Pt/SiO2 catalysts, thus confirming the catalytic importance of these active sites on oxide surfaces and bifunctional pathways that they mediate.
The surface coverages of kinetically-relevant intermediates that form MCH isomers from bound toluene and H atoms, and that convert bound forms of MCH isomers to MCH at Pt surfaces, also involve in MCH formation from toluene occupy a greater number of adjacent Pt sites than do those involved in MCH formation from MCHE; their surface coverages (and reaction rates) thus increase disproportionately to those of the MCHE conversion steps due to the increased number of vacant Pt sites. Such disproportionate response to the scavienging of MCH inhibitors from Pt adlayers confers increased gaseous concentrations of MCH isomers at pseudo-steady state.

The spatial segregation enforced by separate Pt/SiO2 and oxide aggregates in physical mixtures requires that MCHD isomers diffuse across length scales on the order of tens of micrometers to mediate a scavenging event. Overall rates of these bifunctional reactions thus become limited by mass transport between the active sites as mean inter-function distances increase due to the significant resistance to mass transport as a consequence of these long diffusion paths and low abundance of prevalent MCH isomers. Such transport restrictions are alleviated by decreasing the mean distances between active sites at Pt and oxide surfaces by decreasing the dimensions of each aggregate.

These findings thus shed light on the mechanistic origins of bifunctional synergies between metal nanoparticles and metal oxides commonly used as their supports, which give rise to iconic rate enhancements commonly referred to as “hydrogen spillover.” Such rate enhancements are a natural consequence of the myriad hydrocarbon moieties formed on crowded metal surfaces during arene and alkene hydrogenation reactions, which invariably differ in their surface coverages and reactivities towards saturated products.

Notes. The authors declare no competing financial interest.

Data availability

Data will be made available on request.

Acknowledgement

The authors acknowledge financial support from the Chevron Energy Technology Company, and from a National Science Foundation Graduate Research Fellowship and Chevron/UC-Berkeley Graduate Research Fellowship. The authors acknowledge Drs. Prashant Ghodake, Promotion of Cobalt Fischer-Tropsch Catalysts with Noble Metals: A Review, Oil Gas Sci. Technol. - Rev. IFP, 64 (2009) 11–24, https://doi.org/10.2516/osgt.0800140.

References


