Journal of Catalysis 420 (2023) 68-88

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

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

Ari F. Fischer¹, 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- H_2 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. Al_2O_3 , SiO_2 , MgO) are ubiquitous supports for dispersed metal nanoparticles used as catalysts for hydrogenation reactions of unsaturated organic molecules [1,2], H_2 -mediated heteroatom removal processes (S,N,O) [2,3], as well as the Fischer-Tropsch synthesis and related CO_x -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

* Corresponding author.

E-mail address: iglesia@berkeley.edu (E. Iglesia).

¹ Current address: School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore 637459, Singapore. 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⁻)





JOURNAL OF CATALYSIS 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 infeasible. 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 H_2 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 TH_n^*), 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) methylcyclohexane (MCH) formation rates. Such species include various bound methylcyclohexene (MCHE) isomers, which can desorb as 1-methylcychlohexene (1MCHE), 3-methylcychlohexene (3MCHE), and 4-methylcyclohexene (4MCHE) to give pseudosteady-state gas-phase concentrations during toluene-H₂ reactions on supported Pt nanoparticles [22]. These toluene-derived species also include bound forms of methylcyclohexadiene (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- H_2 reactants.

Al₂O₃ surfaces are known to activate H–H [23,24] and C–H bonds [23] at coordinatively-unsaturated 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 1,3cyclohexadiene (13CHD) (or 4MCHE) to form benzene, 1,4cyclohexadiene, cyclohexene, and cyclohexane (or MCH and 1MCHE), 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 Al₂O₃derived 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 MCHE or MCHD, which can diffuse between non-proximate functions to complete MCH formation turnovers [29]; these distance effects of dilution extent and inter-function distance on rates are consistent with two plausible bifunctional routes, denoted here as (i) additive/sto-ichiometric hydrogenation and (ii) inhibitor-scavenging routes.

The first route involves TH_n^{*} moieties that form from toluene-H₂ mixtures on Pt, desorb, diffuse, and react with H₂ at nonvicinal Al₂O₃ sites, thus circumventing the kinetic bottlenecks prevalent at strictly monofunctional Pt surfaces and leading to higher MCH formation rates. Such TH_n* 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 TH_n^{*} species on Pt surfaces; such TH_n^{*} moieties form MCH much more slowly than other more reactive TH_n^{*} intermediates but occupy Pt surfaces thus competing with more reactive intermediates on the crowded surfaces that are ubiquitous during hydrogenation catalysis. These less competent TH_n* 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 oxide 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 pseudosteady-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 "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 model Pt surfaces at the former sites [30,31] but monoarenes do not [30,32-34], indicating a preferential coverage of small Pt nanoparticle surfaces by MCHD isomers, and thus a greater benefit from their scavenging.

The observations described as "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.

SiO₂ (Cabot (Cab-o-sil HS-5) and Sigma-Aldrich (Davisil Grade 62)), γ -Al₂O₃ (Sasol SBA200; denoted Al₂O₃-Sasol), and TiO₂ rutile (Sigma-Aldrich 99.5 %) were obtained from commercial sources. Another Al₂O₃ sample (denoted Al₂O₃-solgel) was prepared from aluminum isopropoxide (AIP; Sigma-Aldrich, 98 %) using sol–gel methods [35,36]. AIP was dissolved in deionized (DI) H₂O (resistivity \geq 17.6 megaohm-cm at ambient temperature; 10 cm³ g⁻¹ AIP) while stirring magnetically at 358 K for 1 h. HNO₃ (Sigma-Aldrich, 70 %) was then added dropwise (0.4 g⁻¹AIP) 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 2 h to form porous Al₂O₃ aggregates. A MgO sample

was prepared by treating magnesium carbonate (Fluka; basic; 40-45% Mg (as 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 SiO₂ (Pt/SiO₂) using electrostatic adsorption methods [38,39]. SiO₂ (Cab-o-sil or Davisil; washed with DI H₂O, 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(NH₃)₄(NO₃)₂ (Sigma-Aldrich, 99.995%) in DI H_2O (4 cm³ g⁻¹ SiO₂) 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 $\text{cm}^3 \text{ g}^{-1} \text{ SiO}_2$). 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 $1.7 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ 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 He (Praxair, 99.999%) at 373 K for 0.5 h; (iii) in flowing H₂ (Praxair, 99.999 %) at 1.7 cm³ 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 $2 \% O_2$ /He (Praxair) at 1.7 cm³ 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). H₂ chemisorption uptakes (Section S.1) were used to calculate saturation H coverages (denoted $\theta_{H,sat}$) 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})

$$d_{Pt} = \frac{6N_{Pt}}{2N_{H_2}} \frac{\nu_{Pt}}{a_{Pt}} \theta_{H,sat} \tag{1}$$

$$\theta_{H,sat} = 1 + 0.0364 \left(d_{Pt}^{-1} \right) + 0.735 \left(d_{Pt}^{-2} \right)$$
(2)

where 6 represent a shape factor for hemispheres, N_{Pt} is the number of Pt atoms, N_{H_2} is the number of H₂ molecules dissociatively adsorbed at the surface, v_{Pt} is the atomic volume of a Pt atom in metal (15.10 × 10⁻³ nm³), and a_{Pt} is the occupied area of a Pt atom on a bulk Pt(111) surface for an fcc lattice (6.7 × 10⁻² nm²) [41], the lowest energy crystal facet, and the 0.0364 and 0.735 coefficients are empirical parameters [40]. Dispersions were derived from $\theta_{H,sat}$ values using [40]

$$D = \frac{2N_{H_2}}{N_{Pt}} \frac{1}{\theta_{H,sat}}$$
(3)

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 (Micromeritic 3Flex Surface Analyzer) and summarized in Table S1 with adsorption and desorption isotherms shown in Figure S2. The Fe and Si content of Al₂O₃-Sasol (5.2 ppm Fe and 57 ppm Si) and Al₂O₃-solgel (139 ppm Fe and 220 ppm Si) were determined from ICP-AES. The packed densities of the SiO₂ (1.2 g cm⁻³) and γ -Al₂O₃-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.

Table 1

Pt content, fractional dispersion (*D*), mean Pt-nanoparticle diameter (d_{Pt}), air and H₂ treatment temperatures during synthesis, solids collection method,^a and SiO₂ source for Pt/SiO₂ catalysts.

Catalyst desig-nation	Pt content (% wt) ^a	Pt fractional dispersion (D) ^a	Mean Pt-nanoparticle diameter, <i>d_{Pt}</i> (nm) ^a	Treatment temperature (K): air [H ₂]	Solids collection method ^b	SiO ₂ source
Pt/SiO ₂ -1.39	0.49	0.97	1.39	573 [623]	Evaporation	Cab-o-sil
Pt/SiO ₂ -1.51	0.11	0.89	1.51	673 [623]	Evaporation	Cab-o-sil
Pt/SiO ₂ -1.67	0.17	0.81	1.67	573 [623]	Filtration	Davisil

^{a,b}Details for characterization^a and synthesis^b methods in Section 2.1.

2.2. Catalytic rate and selectivity measurements on SiO₂-supported Pt nanoparticles and oxide surfaces.

The rates of product formation from toluene-H₂ and CO-O₂ 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 guartz-diluted Pt/SiO₂ bed (denoted Al₂O₃ pre-bed) separated by a 5 mm layer of guartz 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 4methylcyclohexene (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 μ m, 53–63 μ m, 27–40 μ m, and 6–27 μ m. 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 373 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) crushing and sieving to retain aggregates with 90-130 μ m radii. Reactions of toluene-H₂ and CO-O₂ mixtures were measured using similar protocols to those used for testing singlecomponent 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 % O_2 /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⁻¹Pt/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, He, 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%), 1,3cyclohexadiene (Sigma-Aldrich, 97%), and 4-methylcyclohexene (Sigma-Aldrich, 99 %) were introduced as liquids into flowing $H_2/$ 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, 1methylcyclohexene, 4-methylcyclohexene, methylcyclohexane, benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cyclohexene, and cyclohexane were identified in the chromatographs by comparing their elution times to those of chemical standards. The elution time of 3-methylcvclohexene 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 $Pt/SiO_2 + Al_2O_3$ 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 I_H) in bifunctional routes within the pores of Pt/SiO₂ and Al₂O₃ aggregates. The concentration of I_H within pores in quasi-spherical Pt/SiO₂ aggregates is described by the following dimensionless equation derived from the conservation of mass (Section S.4):

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \xi^2 \frac{\partial}{\partial \xi} \varphi_{l_H} + \frac{\rho_{Pt} n_{Pt} R_{Pt}^2}{D_e^{Pt} [I_H]_0} r_{l_H}^{Pt} = 0$$
(4)

where ξ is the radial coordinate within Pt/SiO₂ aggregates (normalized by their mean aggregate radius; R_{Pt}), φ_{I_H} is the dimensionless I_H concentration (normalized by a reference concentration; $[I_H]_0$), ρ_{Pt} is the Pt/SiO₂ density, n_{Pt} is the number of moles of surface Pt sites per mass Pt/SiO₂, D_e^{Pt} is the effective diffusivity within the pores of the Pt/SiO₂ aggregates, and $r_{I_H}^{Pt}$ is the net I_H formation turnover rate at Pt nanoparticle surfaces. The concentration of I_H within the pores of quasi-spherical Al₂O₃ aggregates is described by a similar dimensionless equation (Section S.4):

$$\frac{1}{\varsigma^2} \frac{\partial}{\partial \varsigma} \varsigma^2 \frac{\partial}{\partial \varsigma} \varphi_{l_H} - \frac{\sigma_{Al} R_{Al}^2}{D_e^{Al} [I_H]_0} r_{l_H}^{Al} = 0$$
(5)

where ς is the radial coordinate within Al₂O₃ aggregates (normalized by their mean aggregate radii; R_{Al}), σ_{Al} is the Al₂O₃ surface area per volume, D_e^{Al} is the effective diffusivity within Al₂O₃ pores, and $r_{l_H}^{Al}$ is the areal rate of I_H formation at Al₂O₃ surfaces. The D_e^{Pt} and D_e^{Al} values were estimated from their molecular (D_b) and Knudsen (D_K) diffusivities combined as resistances in series in the Bosanquet equation [43] (Section S.4).

The radial profiles of the I_H concentration within Pt/SiO₂ and Al₂O₃ aggregates were determined by solving the coupled differential equations (Eqs (4) and (5)) with four boundary conditions: (i, ii) the derivative of the I_H concentration is zero at the center of each aggregate ($\xi = 0$ and $\varsigma = 0$) due to spherical symmetry; (iii) the net rate of I_H egress from Pt/SiO₂ aggregates into the bulk fluid is equal to the total rate of I_H ingress to Al₂O₃ aggregates from the bulk fluid:

$$W^{Pt} = -\chi \frac{\rho_{Pt}}{\rho_{Al}} W^{Al} \tag{6}$$

where W^{Pt} and W^{Al} are the rates of I_H egress (per mass catalyst) from Pt/SiO₂ and Al₂O₃ aggregates, respectively, χ is the Al₂O₃ to Pt/SiO₂ mass ratio, and ρ_{Al} is the Al₂O₃ density; and (iv) the external surfaces of Pt/SiO₂ and Al₂O₃ 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 $Pt/SiO_2 + Al_2O_3$ 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 s⁻¹; Pt_s denotes a surface Pt atom) from toluene-H₂ reactants (1.4 kPa toluene; 90 kPa H₂; 393 K) on SiO₂-supported Pt nanoparticles (Pt/SiO₂-1.39 (Table 1); 1.39 nm mean nanoparticle diameter) that are present in the reactor as intimate mixtures (Section 2.2) with (i) SiO₂, (ii) Al₂O₃ synthesized from aluminum isopropoxide using sol–gel methods (Section 2.1; denoted as Al₂O₃-solgel), or (iii) commercial γ -Al₂O₃ (Sasol SBA-200; denoted as Al₂O₃-Sasol).

MCH was the predominant product formed (>95 % selectivity) with 1-methylcyclohexene (1MCHE) and 4-methylcyclohexene (4MCHE) as the only other detectable products. 3-Methylcyclohexene (3MCHE) could not be separated from the predominant products in the chromatograms. MCH formation rates increased monotonically with the amount of Al₂O₃-Sasol mixed with Pt/SiO₂ as intimate mixtures (denoted here as the ratio of



Fig. 1. Methylcyclohexane formation turnover rates (per exposed surface Pt atom (Pt_s)) for toluene-H₂ reactions on Pt/SiO₂ (1.39 nm mean nanoparticle diameter) present as intimate mixtures (Section 2.2) with Al₂O₃-Sasol (•), Al₂O₃-solgel (•), and SiO₂ (•) and with an Al₂O₃-Sasol pre-bed (•) as a function of the oxide surface area to Pt_s ratio (β) (1.4 kPa toluene; 90 kPa H₂; 393 K). Dashed curves indicate trends. The rates for the 40 (Sasol), 470 (Sasol), and 500 (solgel) nm² Al₂O₃ Pt_s⁻¹ mixtures were extrapolated from 0.35 to 1.4 kPa toluene and for the 470 (Sasol) and 500 (solgel) nm² Al₂O₃ Pt_s⁻¹ mixtures were extrapolated from 80 to 90 kPa H₂ (supporting information; Section A.3).

the diluent surface area to the number of surface Pt atoms; β). Higher rates were also observed for mixtures with Al₂O₃-solgel; such similar rate enhancements for mixtures prepared using Al₂O₃ samples of different provenance and amounts of Si (57 (Al₂O₃-Sasol) and 220 (Al₂O₃-solgel) ppm; Section 2.1) and Fe (5.2 (Al₂O₃-Sasol) and 139 (Al₂O₃-solgel) ppm; Section 2.1) impurities suggests that rate enhancements arise from intrinsic chemical properties of Al₂O₃ surfaces and not as a consequence of adventitious impurities or of defect sites inherent in specific synthetic protocols. No products were detected from toluene-H₂ reactions on Pt-free Al₂O₃ at these conditions. MCH formation rates on Pt/SiO₂ were not affected by intimate mixing with SiO₂, 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 SiO₂ powders [44].

CO oxidation turnover rates (mole CO_2 g-atom⁻¹ Pt_s s⁻¹) on intimate Pt/SiO₂ + SiO₂ and Pt/SiO₂ + Al₂O₃-Sasol mixtures were not affected by dilution (473 K, 0.5 kPa CO, 5 kPa O₂; 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 SiO₂ supports to the Al₂O₃ 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 Al₂O₃ cannot account for the significant rate enhancements conferred by the presence of Al₂O₃ 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_2O_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_2O_3 surfaces derived from exposure to ambient air [19], thus precluding the need for (and benefit of) scavenging such impurities by Al_2O_3 diluents. The rate enhancements, evident even after such



Fig. 2. CO oxidation turnover rates (per exposed surface Pt atom (Pt_s)) during CO-O₂ reactions on Pt/SiO₂ (1.39 nm mean nanoparticle diameter) mixed with SiO₂ (\bullet) and Al₂O₃-Sasol (\blacksquare) as intimate mixtures with different oxide surface area to Pt_s ratios (β) (0.5 kPa CO; 5 kPa O₂; 473 K). The dashed line depicts the horizontal trend.

treatment protocols, indicate that any effects of Al_2O_3 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 µm (1.4 kPa toluene; 90 kPa H_2 ; 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 μ m) 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 μ m 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/SiO_2 -1.51 mixtures with TiO_2 and MgO aggregates. As in the case of Al_2O_3 , both oxides led to higher rates than for undiluted samples, with TiO_2 showing larger and MgO showing smaller rate enhancements than Al_2O_3 (for similar dilution extents). These data show that bifunctional synergies are not unique to the chemical properties



Fig. 3. Methylcyclohexane formation turnover rates (per exposed surface Pt-atom (Pt_s)) for toluene-H₂ reactions on Pt/SiO₂-1.39 mixed with Al₂O₃-Sasol as loose mixtures (Section 2.2) of 13 (\blacklozenge), 37 (\blacklozenge), and 110 (\blacktriangle) µm mean aggregate radii, and on Pt/SiO₂-1.51 mixed with Al₂O₃-Sasol (\bigtriangledown , \Box), TiO₂ (\blacklozenge), and MgO (\times) and Pt/SiO₂-1.67 mixed with Al₂O₃-Sasol (gray \blacktriangleright) as loose mixtures of 37 µm mean aggregate radii (or intimate mixtures; \Box) as a function of the oxide surface area to Pt_s ratio (β) (1.4 kPa toluene; 90 kPa H₂; 393 K). The rates for the Pt/SiO₂-1.51 + Al₂O₃ (β = 4800; 37 µm; \blacklozenge), Pt/SiO₂-1.51 + Al₂O₃ (β = 2000; \Box), Pt/SiO₂-1.51 + Al₂O₃ (β = 4200; \times) mixtures were extrapolated from 80 to 90 kPa H₂ and the Pt/SiO₂-1.51 + Al₂O₃ (β = 2000; \Box) mixture was extrapolated from 0.35 to 1.4 kPa toluene (supporting information; Section A.3).

of Al_2O_3 surfaces but reflect reactions and processes that are related to Lewis-acid-base pairs at oxide surfaces.

The rate enhancements observed on loose $Pt/SiO_2-1.39 + Al_2O_3$ mixtures decreased with increasing diameter of the Pt/SiO₂ and Al₂O₃ domains (at β = 4800 nm² Al₂O₃ g-atom⁻¹ Pt_s); 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 Lewisacid-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 (1,3cyclohexadiene (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- H_2 reactions on Pt surfaces form ensembles of bound intermediates with different numbers of H atoms (TH_n*, denoting lumped toluene-derived intermediates with *n* added H atoms). Each lumped TH_n* moiety consists of several structural isomers that differ in the position of the *n* H atoms and in the specific C atoms that are bonded to surface Pt atoms; here, *j*-TH_n* denotes each distinguishable species (in structure, stability, and reactivity) within the TH_n* ensemble. These *j*-TH_n* 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*-TH₄* ensemble includes bound forms of MCHE isomers; their ability to desorb is evident from the detection of gaseous 1MCHE and 4MCHE. The *j*-TH₂* ensemble includes the bound forms of MCHD isomers; these species can also desorb, but their equilibrium levels during toluene-H₂ reactions are below chromatographic detection limits.

 Al_2O_3 surfaces are known to activate H—H [23,24] and C—H bonds [23] on Lewis acid-base pairs consisting of coordinativelyunsaturated Al^{3+} centers and adjacent O^{2-} ; such sites may be able 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) inhibitorscavenging routes.

The first route considers hydrogenation reactions of Pt-derived MCHD or MCHE isomers at Al₂O₃ 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 Al₂O₃ 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 Al₂O₃ 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 Al_2O_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 ZrO₂ and TiO₂ surfaces that catalyze aldol condensation and ketonization reactions [51,52]; it is used here as a selective titrant of acid-base pairs at the Al_2O_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/SiO₂ during toluene-H₂ 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 H₂; 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/SiO₂ + Al₂O₃-Sasol mixture $(\beta = 470 \text{ nm}^2 \text{ Al}_2\text{O}_3 \text{ Pt}_s^{-1})$ before and during exposure to PA, and the effluent PA pressure (1.4 kPa toluene; 80 kPa H₂; 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 Al₂O₃-free monofunctional Pt/SiO₂ (0.20 mol MCH gatom⁻¹ Pt_s s⁻¹; Fig. 1). PA was nearly undetectable in the effluent stream up to \sim 4 ks and then gradually reached its inlet pressure (3.2 Pa) as binding sites on the Al₂O₃ reached saturation coverages. The total amount of PA retained by the Al₂O₃ surface that was needed to suppress increased MCH formation rates was 2.9 PA molecules per nm².

The concurrent depletion of PA from the stream and the suppression of the rate enhancements as PA titrates sites at



Fig. 4. Methylcyclohexane formation turnover rates (•; per exposed surface Pt atom (Pt_s)) and propanoic acid (PA) pressure (**■**) in the effluent as a function of time on stream during toluene-H₂ reactions with added PA on Pt/SiO₂-1.39 (a) undiluted and (b) present as an intimate mixture with Al₂O₃-Sasol (470 nm² Al₂O₃ Pt_s⁻¹) (1.4 kPa toluene; 80 kPa H₂; 3.2 Pa PA; 393 K). The rates in (b) are corrected for deactivation using a first-order deactivation trend that describes the time dependence of rates in (a).

Al₂O₃ surfaces provide compelling evidence for the role of acidbase pairs on Al₂O₃ as the catalytic function that mediates these bifunctional routes. The evidence that MCH formation rate enhancements are eliminated by selective titration of acid-base pairs during steady-state catalysis indicates that they reflect advantageous reactions that occur at steady state (i.e. bifunctional reaction pathways) instead of any processes that occur during synthesis or treatment protocols (e.g. the formation of Pt nanoparticles with unique reactive properties or the trapping of organic residues, derived from exposure to ambient air [19], by Pt/SiO₂ or Al₂O₃ surfaces).

3.3. 1,3-Cyclohexadiene and 4-methylcyclohexene reactions with H_2 on Al_2O_3 without Pt/SiO₂.

The ability of Al_2O_3 surfaces to catalyze reactions of cyclic alkadienes (13CHD) and cyclic alkenes (4MCHE) with H_2 are examined next as illustrative examples of reactions of desorb-able molecular shuttles that would enable Pt and Al_2O_3 functions to detect their respective presence and their inter-function distances in bifunctional schemes of the type introduced in Section 3.2. 13CHD was 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-H₂ reactant mixtures on Al₂O₃-Sasol led to the formation of 1,4-cyclohexadiene (14CHD), benzene, cyclohexene (CHE), and cyclohexane (CHA) as detectable products (0-100 kPa H₂; 5–70 Pa 13CHD; 393 K). Fig. 5a shows benzene, CHE, and CHA areal formation rates on Al₂O₃-Sasol at different H₂ 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 H₂ 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 H₂ pressure, while benzene formed at rates influenced only slightly by H₂ pressure (and detectable even without H₂).



Fig. 5. Areal rates of (a) 1,3-cyclohexadiene (13CHD) conversion to cyclohexane (\blacklozenge ; CHA) cyclohexene (\blacklozenge ; CHE) and benzene (\blacksquare), and H₂ consumption areal rates (\blacktriangle) as a function of H₂ pressure (393 K, 12 kPa 13CHD) and of (b) H₂ consumption (\bigstar) and H-transfer (\blacksquare) as a function of 13CHD pressure (393 K, 20 kPa H₂) on Al₂O₃-Sasol. Dashed curves indicate trends.



Scheme 1. Proposed sequence of steps for 1,3-cyclohexadiene (13CHD) hydrogenation to cyclohexene (CHE) and cyclohexane (CHA) via reaction with H_2 (H_2 consumption; steps 1a and 2a) and to CHE, CHA, and benzene via bimolecular hydrogen-transfer reactions (hydrogen transfer; steps 1b and 2b) on Al₂O₃ surfaces. Species enclosed in rectangles with sharp corners indicate reactants and with rounded corners indicate products.

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 Htransfer. The molar rates of CHE and CHA formation when H₂ was present (10-100 kPa) were much higher than benzene formation, indicative of the prevalent formation of hydrogenated products via reactions of 13CHD with H₂ (steps 1a-2a; Scheme 1) instead of only bimolecular hydrogen-transfer events. A hydrogen balance then gives the rate of H_2 consumption $(r_{-H_2}^{Al})$ from the rates of CHA (r_{CHA}^{Al}) and CHE (r_{CHE}^{Al}) formation and H-transfer (r_{HT}^{Al}) through:

$$r_{-H_2}^{Al} = 2r_{CHA}^{Al} + r_{CHE}^{Al} - r_{HT}^{Al} \tag{7}$$

Fig. 5b shows areal rates of H-transfer and H₂ consumption $(r_i^{Al}, where i$ denotes a given reaction) at different 13CHD pressures on Al₂O₃-Sasol powders (0–100 kPa H₂; 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:

$$\frac{r_i^{AI}}{S_{AI}} = \frac{\delta_i^{AI}[HC]}{1 + K_i^{AI}[HC]} \tag{8}$$

where s_{Al} is the Al₂O₃ surface area, [*HC*] is the hydrocarbon (13CHD) concentration and K_i^{Al} is the equilibrium constant for 13CHD adsorption at Al₂O₃ sites. Here, δ_i^{Al} is a pseudo-first-order rate constant containing the kinetic and thermodynamic constants and H₂

pressure dependences 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 δ_i^{Al} 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 δ_i^{Al} and K_i^{Al} 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; $K_i^{Al}[HC] \ll 1$) 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 $K_i^{Al}[HC]$ 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 (1MCHE and 3MCHE) and saturated products (MCH), without the detectable formation of MCHD isomers or toluene (toluene-3MCHE 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 1MCHE and 3MCHE) 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 δ_i^{Al} and K_i^{Al} 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; $K_i^{Al}|HC| \ll 1$) 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 $K_i^{Al}[HC]$ 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

Table 2Regressed values of coefficients K_i^{Al} and $\delta_i^{Al(a)}$ for 1,3-cyclohexadiene-H2 (13CHD-H2)and 4-methylcyclohexene-H2 (4MCHE-H2) reactions on Al2O3-Sasol (393 K).^b

Reactants	Reaction	$ \begin{array}{l} \delta_i^{Al} \left(x10^{-7} \text{ molecules } nm^{-2} \text{ Al}_2 O_3 \right. \\ \left. s^{-1} \text{ Pa}^{-1} \right) \end{array} $	K_i^{Al} (x10 ⁻² Pa ⁻¹)
13CHD-H ₂ ^(c)	H ₂ consumption	12(±1) ^{e,f}	17 ± 2
AMCHE U ^(d)	H transfer	$2.0(\pm 0.1)^{g}$	$0.21(\pm 0.03)$
4WCHE-H2	consumption	9.1(10.0)	18 1 2

^aFrom Equation (8). ^bRate data are reported in Figs. 5 and 6. The errors indicate 95 % confidence intervals. ^{c,d}20^c and 90^d kPa H₂. ^{e,g}Per H₂^(e) or 13CHD^(g) consumed. ^fThe H₂ consumption rate constant corresponds to a 13CHD consumption rate constant of $1.1(\pm 0.1) \times 10^{-6}$ 13CHD molecules nm⁻² Al₂O₃ s⁻¹ Pa⁻¹.



Fig. 6. Areal rates of H₂ consumption to methylcyclohexane (MCH; as a function of H₂ pressure on Al₂O₃-solgel ((a); **(**a) and 4-methylcyclohexene pressure (4MCHE) on Al₂O₃-solgel ((b); **(**a) and Al₂O₃-Sasol ((b); **(**b)) and isomerization to 1-methylcyclohexene (1MCHE) and 3-methylcyclohexene (3MCHE; as a function of H₂ pressure on Al₂O₃-solgel ((a); **(**)) and 4-methylcyclohexene pressure (4MCHE) on Al₂O₃-solgel ((b); **(**)) and 4-methylcyclohexene pressure (4MCHE) on Al₂O₃-solgel ((b); **(**)) and 4-methylcyclohexene pressure (4MCHE) on Al₂O₃-solgel ((b); **(**)) and Al₂O₃-Sasol ((b); **(**)) during 4MCHE-H₂ reactions on Al₂O₃ (393 K; 10–90 kPa H₂; 5–150 Pa 4MCHE). The 4MCHE pressure-dependent rate data for Al₂O₃-Sasol were collected on a regenerated catalyst with similar rates to the fresh one (Section S5). Dashed lines indicate trends.

pressures. MCH formation and 4MCHE isomerization rates on Al_2O_3 -solgel increased linearly with H_2 pressure and the former, but not the latter, approached zero as H_2 pressures decreased. The finite 4MCHE isomerization rates as H_2 pressures decreased show that this reaction can occur on Al_2O_3 without the involvement of H_2 , but the effects of H_2 pressure on these rates suggest that H_2 -mediated regio-isomerization can also occur, plausibly through bound H_2 -derived species, on Al_2O_3 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 MCHE 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



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 (γ_i) 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.

assess the role (and magnitude) of Al_2O_3 -catalyzed MCHE and MCHD hydrogenation reactions on MCH formation turnover rates for mixtures of Pt/SiO_2 and Al_2O_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 $Pt/SiO_2 + Al_2O_3$ mixtures.

The previous sections provide evidence for the ability of Al_2O_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/SiO₂ + Al_2O_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_2O_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-H₂ reactants on monofunctional Pt/SiO₂ catalysts, on which the Pt nanoparticles act as the sole mediator of toluene hydrogenation catalysis [22].

Bound toluene and the various j-TH_n^{*} species derived from toluene require ensembles of *-sites of varying size depending on the number of Pt-C bonds formed, their relative location within

molecules, and their skeletal structure and orientation. Such differences in site requirements for the binding of arenes and their partially-hydrogenated derivatives are evident from calorimetric data on Pt(111), which show that fewer molecules are required to reach saturation coverages for benzene (0.15 ML, 300 K [59]) than for CHE (0.24 ML, 100 K [60]). Toluene and TH₂* intermediates bind with the carbon ring parallel to the surface in their most stable configuration [22,31,61,62], indicative of similar ensemble size requirements, defined here by the number of adjacent surface Pt atoms (γ_{tol}). TH₄* intermediates, in contrast, bind in boat or chair conformations with the ring oriented perpendicular to the surface [22,63] in structures that resemble that of bound CHE [31]; their binding ensembles (γ_{ene}) are smaller than for toluene (γ_{tol}).

Step 1 (Scheme 2) shows quasi-equilibrated molecular adsorption of toluene at an unoccupied ensemble with γ_{tol} 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 H₂ and subsequent reaction with (i) bound toluene to form TH₂* (step 2; Scheme 2), (ii) TH₂* to form TH₄* and an ensemble of ($\gamma_{tol} - \gamma_{ene}$) adjacent vacant *-sites (step 3; Scheme 2), and (iii) TH₄* to form TH₆ and an ensemble of γ_{ene} 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 Ptderived MCHD and MCHE intermediates at Al_2O_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_2O_3 surfaces. Steps 7 and 9 (Scheme 2) show interconversions among MCHD and MCHE isomers via Al_2O_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 MCHE 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 Al_2O_3 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 Al_2O_3 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 (+ Al_2O_3).

3.4.1. Assessing contributions from additive/stochiometric methylcyclohexene hydrogenation routes to methylcyclohexane 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 react further on Pt surfaces at pseudo-steady state; they are much lower ($\sim 10^3$ -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 interconversion (9.7 ± 1.0 [64,65]; 393 K), suggesting that 3MCHE isomers (which cannot be separately detected) also form at pressures that reflect their equilibration with 1MCHE and 4MCHE isomers.

Each MCHE isomer forms MCH on $Pt/SiO_2 + Al_2O_3$ mixtures at rates ($r_{MCH,i}$) that reflect their combined rates of hydrogenation on Al_2O_3 and (of their bound precursors) on Pt surfaces on which such isomers form from toluene:

$$r_{MCH,i} = \delta^{Al}_{MCH,i} [HC]_i s_{Al} + \alpha^{Pt}_{MCH,i} \theta_{i*} L_{Pt}$$
(9)

Here, $[HC]_i$ is the gaseous concentration of a given MCHE isomer, θ_{i*} is its surface coverage at *-sites on Pt nanoparticle surfaces, and L_{Pt} is the number of exposed Pt atoms. The $\alpha_{MCH,i}^{Pt}$ coefficient is a pseudo-first-order rate constant that contains kinetic and thermodynamic parameters and H₂ pressure dependences that describe the formation and reaction of reactive intermediates involved in the conversion of each bound MCHE moiety to MCH at Pt surfaces. The $\delta_{MCH,i}^{Al}$ term represents a similar pseudo-first-order rate constant for the formation and reactions of intermediates that limit MCHE

Table 3

 1-Methylcyclohexene (1MCHE) and 4-methylcyclohexene (4MCHE) pressures in the effluent stream during toluene-H₂ reactions on Pt/SiO₂,^a their values formed in equilibrium with toluene-H₂ reactants,^b and their approach to equilibrium.^c

MCHE isomer	Measured	Equilibrium	Approach to
	pressure (Pa)	pressure (Pa) ^b	equilibrium
1MCHE 4MCHE 3MCHE	0.14 0.029 	430 44 23	3.2 x10 ⁻⁴ 7 x10 ⁻⁴

^a1.39 nm mean nanoparticle diameter. ^b80 kPa H₂, 0.7 kPa toluene, and 393 K. ^cApproach to equilibrium defined as the ratio of the observed to equilibrium MCHE pressure and evaluated using reported Δ H values for 1-methylcyclohexene [66], 3-methylcyclohexene [64], and 4-methylcyclohexene [67] with Δ S values from NIST reference tables [65].

conversion to MCH on Al₂O₃ surfaces. As with the δ_i^{Al} in Equation (8), the precise determination of all the kinetic and thermodynamic parameters and H₂ pressure dependences that determine $\alpha_{MCH,i}^{Pt}$ and $\delta_{MCH,i}^{Al}$ is not required to reach the conclusions drawn in the present study.

An expression for the MCH formation rates (per Pt_s) on Pt/ SiO₂ + Al₂O₃ mixtures can be derived by normalizing the rate equation (Eq (9)) by L_{Pt} :

$$\frac{r_{MCH,i}}{L_{Pt}} = \delta^{AI}_{MCH,i} [HC]_i \beta + \alpha^{Pt}_{MCH,i} \theta_{i*}$$
(10)

where β is the ratio of the Al₂O₃ surface area to the number of surface Pt sites ($\beta = s_{Al}/L_{Pt}$; introduced in Section 3.1). The pseudosteady-state gaseous concentrations of these MCHE isomers ($[HC]_i^{PSS}$) 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_{i*}^{PSS}) reflect the balance between their formation from bound toluene and H—S at, consumption via reactions with H—S at, and desorption from Pt surfaces. Their functional forms (derived in Section S.6) are given by:

$$[HC]_{i}^{PSS} = \frac{\alpha_{-tol,i}^{Pt} K_{tol*}[tol] \theta_{i}^{\gamma_{i}} k_{-i*}}{\delta_{MCH,i}^{Al} k_{-i*} \beta + \alpha_{MCH,i}^{Pt} \left(\delta_{MCH,i}^{Al} \beta + k_{i*} \theta_{*}^{\gamma_{i}} \right)}$$
(11)

and

$$\theta_{i*}^{\text{PSS}} = \frac{\alpha_{-tol,i}^{Pt} K_{tol*}[tol] \theta_{*}^{\gamma_{tol}} \left(\delta_{MCH,i}^{Al} \beta + k_{i*} \theta_{*}^{\gamma_{i}} \right)}{\delta_{MCH,i}^{Al} k_{-i*} \beta + \alpha_{MCH,i}^{Pt} \delta_{Al} \beta + \alpha_{MCH,i}^{Pt} k_{i*} \theta_{*}^{\gamma_{i}}}$$
(12)

Here, k_{i*} and k_{-i*} are the rate constants for the adsorption and desorption of a given MCHE species at ensembles of vicinal *-sites, respectively; θ_* is the fraction of *-sites that are unoccupied; γ_i is the number of adjacent *-sites that bind and react the MCHE isomer; and K_{tol*} is the equilibrium constant for toluene adsorption. The $\alpha_{-tol,i}^{Pt}$ term, as in the case of $\alpha_{MCH,i}^{Pt}$, is the pseudo-first-order rate constant for the formation and reactions of intermediates that limit the conversion of bound toluene to each given MCHE moiety on Pt surfaces.

The enhancement factors for MCH formation rates via the hydrogenation of a given MCHE isomer (η_i) are given by the ratio of the MCH formation rate on Pt/SiO₂ + Al₂O₃ mixtures ($r_{MCH,i}$) and on Al₂O₃-free Pt/SiO₂ catalysts (denoted as $r_{MCH,i}^0$):

$$\eta_i = \frac{r_{MCH,i}}{r_{MCH,i}^0} \tag{13}$$

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

$$\eta_i = \frac{\theta_{*}^{\gamma_{tot}}}{\theta_{*,0}^{\gamma_{tot}}} \tag{14}$$

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 (η_i) is equivalent to that of the overall MCH formation rate (η). These η values do not depend on the extent of dilution (β) or on the rate constant for MCHE hydrogenation at Al₂O₃ surfaces ($\delta_{MCH,i}^{Al}$); 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 isomers 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 supporting information (493 K; Section S.9).

3.4.2. Assessing the contributions from additive/stochiometric 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 isomer, at 393 K, 1.4 kPa toluene, 90 kPa H₂; Table S3). The quasiequilibrated nature of toluene adsorption and methylcyclohexene desorption during toluene-H₂ reactions on Pt surfaces [22] nevertheless suggests fast desorption of bound precursors to MCHD isomers from the crowded Pt surfaces present under typical toluene hydrogenation conditions. Once desorbed, their additive hydrogenation 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 $Pt/SiO_2 + Al_2O_3$ mixtures are compared next with observed MCH formation rate enhancements (Fig. 3) in order to assess whether MCHD hydrogenation rates on Al_2O_3 represent a plausible mechanism for these iconic "hydrogen spillover" rate enhancement phenomena. In such treatments, loose mixtures are considered instead of intimate ones because of their well-defined domains for the two hydrogenation functions.

Pt/SiO₂ and Al₂O₃ domains in these loose mixtures reside within distinct and separate quasi-spherical aggregates of known diameter with their inter-aggregate spaces swept by convective fluid flow. Each catalytic turnover mediated by additive/stoichiometric routes would involve MCHD isomers that form at Pt sites and which must (i) diffuse throughout the voids and reach the external surface of the Pt/SiO₂ aggregates, (ii) transfer from the Pt/SiO₂ external surfaces to the fluid phase through an external boundary layer, (iii) transfer from the fluid phase to the external surfaces of the Al₂O₃ aggregates through another external boundary layer, and (iv) react at active sites within the Al₂O₃ aggregates by diffusing through the intra-aggregate voids.

The maximum rates of such bifunctional routes (per Pt_s) would be attained when the amounts of Al₂O₃ are sufficient to react all MCHD molecules that egress from Pt/SiO₂ domains into the inter-aggregate fluid phase. These rates of egress for each MCHD isomer are driven by differences in isomer concentrations between the external surfaces of Pt/SiO₂ aggregates ($[MCHD]_i^s$; where *i* indexes over the MCHD isomers) and the fluid phase ($[MCHD]_i^b$) with transfer coefficients derived from boundary-layer theory (Section S.4). The largest rates of egress occur when $[MCHD]_i^s$ are present at equilibrium with the prevalent toluene and H₂ concentrations within Pt/SiO₂ domains ($[MCHD]_i^s = [MCHD]_i^{eq}$; where $[MCHD]_i^{eq}$ is the equilibrium value) and absent from the interaggregate fluid phase due to rapid scavenging by Al₂O₃ functions. Additive/stoichiometry MCHD hydrogenation routes can account for the observed rate enhancements only when the excess MCH formation rates (r_{MCH}^{ex} ; 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 hydrogenation rate (λ) is given (with derivation in Section S.8) as:

$$\lambda = \frac{4\pi R_{Pt}^2 k_g [MCHD]^{eq}}{r_{MCH}^{ex} N_{Pt}}$$
(15)

Here, R_{Pt} is the Pt/SiO₂ aggregate radius, k_g is the mass transfer coefficient at external surfaces of Pt/SiO₂ aggregates, $[MCHD]^{eq}$ is the total equilibrium concentration of all MCHD isomers, 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/stoichiometric MCHE hydrogenation routes cannot increase MCH formation rates (because toluene consumption, and therefore MCH formation, on Pt surfaces is limited by MCHE formation from toluene (Section 3.4)), indicate that neither MCHE nor MCHD isomers can act as molecular shuttles in additive/stoichiometric hydrogenation that are able to account for the observed bifunctional synergies. The alternate bifunctional route, involving the scavenging of less reactive species on Pt by their desorption and hydrogenation at Al_2O_3 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 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 benzene derivatives with different H content and surface attachment mode [57,72,73] as the proposed most abundant surface intermediates (MASI). These species are present at coverages that depend on their different stability as bound species, and they react at different rates as they add H atoms on their path to "desorb-able" products. Density functional theory (DFT)-derived energies for species and elementary steps involved in benzene-H₂ reactions on Pt (111) periodic models indicate that benzene-derived species, similar 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 orthohydrogenation routes) [73,74].

Table 4 Excess MCH formation turnover rates (excess rate),^a maximum rates of egress of MCHD isomers from Pt/SiO₂ aggregates (egress rate),^b and maximum MCHD egress to excess MCH formation rate ratios (λ ; Eq (15)) for loose Pt/SiO₂ + Al₂O₃ mixtures.^c

Mean aggregate radius (µm)	Excess rate (mole MCH g-atom ⁻¹ Pt _s s ⁻¹)	Egress rate (x10 ⁻⁵ mole MCHD g-atom ⁻¹ Pt _s s ⁻¹)	λ (x10 ⁻⁴)
13	0.34	23	6.6
37	0.24	13	6.9
57	0.16	8.7	5.3
110	0.068	4.7	5.6

^aDefined as the difference between the turnover rate on a given Pt/SiO₂ + Al₂O₃ mixture and Al₂O₃-free Pt/SiO₂. ^bMaximum 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. ^cRates 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 (Pt_x)⁻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 (cyclo)alkene hydrogenations on metal nanoparticles. The ability to desorb these less reactive bound species and to hydrogenate them on Al_2O_3 (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 (η) would benefit from fractional coverages of empty *-sites (θ_*) that are larger on Pt/SiO₂ + Al₂O₃ than on Pt/SiO₂. These θ_* 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:

$$1 = \theta_* + \sum_{i=1}^m \theta_{i*}$$
 (16)

where θ_{i*} denotes the *-site fractional coverage of each bound moiety. The dense hydrocarbon adlayers prevalent in arene hydrogenation lead to θ_* 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 CH₂ 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- H_2 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:

$$\theta_{i*}' = \frac{\alpha_{-tol,i}^{Pt} K_{tol*}[tol] \theta_{*}^{\gamma_{tol}}}{\alpha_{tol,i}^{Pt} \theta_{*}^{\gamma_{tol}-\gamma_{i}} + \alpha_{MCH,i}^{Pt} \theta_{*}^{\gamma_{-i}-\gamma_{i}} + \frac{k_{-i*}\delta_{MCH,i}^{Al}\beta}{\delta_{MCH,i}^{Al}\beta + k_{i*}\theta_{*}^{\gamma_{i}}}}$$
(18)

Here, γ_i and γ_{-i} are the numbers of adjacent *-sites that bind and react the hydrocarbon moiety, respectively, and the $\alpha_{-tol,i}^{Pt}$ 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 $\alpha_{tol,i}^{Pt}$ and $\alpha_{MCH,i}^{Pt}$ 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:

$$\theta_{j_*}^{\prime\prime} = \frac{\alpha_{-tol_j}^{Pt} K_{tol_*} [tol_j] \theta_*^{\gamma_{tol_*}}}{\alpha_{tol_j}^{Pt} \theta_*^{\gamma_{tol_*} - \gamma_j} + \alpha_{MCH_j}^{Pt} \theta_*^{\gamma_{-j} - \gamma_j}}$$
(19)

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_*) underpin any enhancements in MCH formation rates (η) 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'_{i*} and θ''_{j*} 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 $\theta^{\gamma_{tol}}_{*}$, thus obscuring the trends of η with β . These trends can be garnered from closed-form solutions for $\theta^{\gamma_{tol}}_{*}$ for asymptotic cases, such as when there is a single desorb-able species (denoted as I_H*) as MASI that requires a *-site ensemble for its adsorption and reactions of the same size as that for toluene ($\gamma_i = \gamma_{-i} = \gamma_{tol}$), and is formed irreversibly from toluene. The resulting expression for η (derived in Section S.10) is:

$$\eta = \frac{[tol]K_{tol*}\alpha_{-tol,i}^{Pt}}{2\alpha_{MCH,i}^{Pt}} \left(-\frac{\delta_{MCH,i}^{Al}\beta}{k_{i*}} + \frac{\alpha_{MCH,i}^{Pt}}{[tol]K_{tol*}\alpha_{-tol,i}^{Pt}} + \sqrt{\left(\frac{\delta_{MCH,i}^{Al}\beta}{k_{i*}} - \frac{\alpha_{MCH,i}^{Pt}}{[tol]K_{tol*}\alpha_{-tol,i}^{Pt}}\right)^2 + 4\delta_{MCH,i}^{Al}\beta\frac{k_{-i*} + \alpha_{MCH,i}^{Pt}}{[tol]K_{tol*}\alpha_{-tol,i}^{Pt}k_{i*}}}\right)}$$
(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:

$$\eta_0 = 1 + \beta \left(\frac{[tol] K_{tol*} \alpha_{-tol,i}^{Pt}}{2 \alpha_{MCH,i}^{Pt}} \frac{\delta_{MCH,i}^{Al}}{K_{i*} \alpha_{MCH,i}^{Pt}} \right)$$
(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_s) that I_H^{*} is formed (from gaseous toluene; $r_{-tol,i}^{Pt}$) and the turnover rate (per Pt_s) that I_H^{*} is consumed by subsequent reactions with H–S (to form MCH; $r_{MCH*,i}^{Pt}$) at the Pt surface, and (ii) the ratio of the areal rate (per nm⁻² Al₂O₃) that gaseous I_H hydrogenates (to form MCH) at Al₂O₃ surfaces ($r_{MCH,i}^{Al}$) to the turnover rate (per Pt_s) that I_H adsorbs and reacts at the Pt surface ($r_{MCH,i}^{Pt}$) to form MCH:

$$\eta_0 = 1 + \frac{\beta}{2} \left(\frac{r_{MCH,i}^{Al}}{r_{MCH,i}^{Pt}} \frac{r_{Ptol,i}^{Pt}}{r_{MCH,i}^{Pt}} \right)$$
(22)

The presence of the $(r_{MCH,i}^{Al}/r_{MCH,i}^{Pt})$ ratio in the slope of Equation (22) indicates that MCH formation rate enhancements become more significant when I_H hydrogenation areal rates at Al₂O₃ surfaces ($r_{MCH_i}^{Al}$) are large compared to I_H hydrogenation turnover rates at Pt surfaces $(r_{MCH_i}^{Pt})$. This tendency reflects the requirement that Al₂O₃ surfaces scavenge 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 $(r_{-toli}^{Pt}/r_{MCH*i}^{Pt})$ 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_{-toli}^{Pt}) are large compared to its consumption $(r_{MCH*,i}^{Pt})$. This ratio indicates that the presence of admixed Al₂O₃ 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_2O_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_2O_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 (η_{max}) obtained at large extents of Pt/SiO₂ dilution with Al₂O₃ is given by Equation (20) with $\beta \gg 1$:

$$\eta_{max} = 1 + \frac{k_{-i*}}{\alpha_{MCH,i}^{Pt}}$$
(23)

These maximum rate enhancements are independent of β , indicative of amounts of Al₂O₃ 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 ($\alpha_{MCH,i}^{Pt}$) and when Al₂O₃ surfaces are present in amounts sufficient to scavenge all desorbed I_H molecules.

MCH formation rate enhancements (η) are given by Equation (20) only for a single desorb-able intermediate with a site requirement of γ_{tol} 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 $\theta_{\gamma}^{\text{red}}$ 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_2O_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-H₂ reactions (Section 3.5) and (ii) MCHD isomers by assessing the consequences of their reactions for MCH formation rates and prevalent MCHE pseudo-steady-state pressures using kinetic and reactiontransport 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 3.3 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/SiO₂ (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-H₂-1MCHE (or toluene-H₂-4MCHE) mixtures reflect the combined rates of MCH formation from toluene consumption and from 1MCHE (or 4MCHE). 1MCHE (and 4MCHE) form irreversibly from toluene-H₂ reactions on Pt/SiO₂ (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-H₂ mixtures; as a result, the excess rates of MCH formation when MCHE isomers are added equal the rates of conversion of cofed MCHE. These measured 1MCHE and 4MCHE consumption rates (0.11 and 0.17 mol MCH g-atom⁻¹ Pt_s s^{-1} , respectively) are smaller than measured MCH formation rates (0.35 and 0.42 mol MCH g-atom⁻¹ Pt_s s⁻¹, respectively). Their differences reflect the contributions from toluene-H₂ reactions to MCH formation (0.24 and 0.25 mol MCH g-atom⁻¹ Pt_s s⁻¹); these rates are similar to measured MCH formation rates from toluene- H_2 mixtures (0.24 mol MCH g-atom⁻¹ Pt_s s⁻¹). 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 Al₂O₃ surfaces, because the gas-phase concentrations of MCHE isomers do not influence toluene-H₂ 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-H₂ reactions.

Table 5

Reactions of toluene-H₂ and toluene-H₂-methylcyclohexenes (MCHE) and the corresponding values of 1-methylcyclohexene (1MCHE) and 4-methylcyclohexene (4MCHE) pressures in the inlet and outlet streams, fractional MCHE conversion (MCHE conv.), MCH formation turnover rate (MCH TOR), and MCHE conversion turnover rate (MCHE TOR) on Pt/SiO₂.^a

Hydrocarbon reactants	1MCHE (Pa) inlet [outlet]	4MCHE (Pa) inlet [outlet]	MCHE conv.	TOR (mole MCH g-atom ⁻¹ Pt_s s ⁻¹)	
				МСН	MCHE
Toluene Toluene + 1MCHE Toluene + 4MCHE	0 [0.14] 4.5 [2.9]	0 [0.029] 0 [0.17] 3.3 [0.96]	0.36 0.71	0.24 0.35 0.42	0.11 0.17

^a0.7 kPa toluene and 80 kPa H₂ at 393 K on Pt/SiO₂ with a 1.39 nm mean Pt-nanoparticle diameter (Pt/SiO₂-1.39).

3.5.2. Site requirements for 4MCHE formation and consumption steps on Pt surfaces and their response to changes to Pt-adlayer composition.

The Al₂O₃-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-H₂ 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 MCHE from toluene-H₂ reactants at Pt surfaces (steps 2-6; Scheme 2) involve bound intermediates at ensembles containing γ_{tol} adjacent *-sites (Section 3.4). The elementary steps that govern the conversion of bound MCHE to MCH at Pt surfaces (steps 7-8; Scheme 2), in contrast, are mediated by bound intermediates requiring γ_{ene} 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 Al₂O₃-mediated scavenging of MCHD inhibitors. The larger ensembles required to form MCHE from toluene than for further MCHE 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 MCHE during toluene-H₂ reactions when Al₂O₃ is present (and leads to MCH formation rate enhancements).

The gaseous concentrations of MCHE isomers formed during toluene-H₂ reactions on Pt/SiO₂ + Al₂O₃ mixtures ($[HC]_i^{PSS}$; 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—S on Pt surfaces and by hydrogenation on Al₂O₃ surfaces) at pseudo-steady state (Section 3.4.1). A comparison between the rates of 4MCHE hydrogenation at Pt and Al₂O₃ surfaces is drawn next to assess the extent to which Pt dilution with Al₂O₃ effects pseudo-steady-state MCHE pressures.

Measured rates of 4MCHE hydrogenation on Pt-free Al₂O₃ catalyst surfaces (Section 3.3) give a pseudo-first-order rate constant (δ_i^{Al}) of 9.1 (±0.6) x10⁻⁷ 4MCHE molecules nm⁻² Al₂O₃ s⁻¹ Pa⁻¹ (Table 2; 90 kPa H₂; 393 K); this measured δ_i^{Al} value corresponds to a 4MCHE hydrogenation areal rate of 4.1 (±0.3) x10⁻⁸ 4MCHE molecules nm⁻² Al₂O₃ s⁻¹ for 4MCHE present at its pseudosteady-state pressure (on Al₂O₃-free Pt/SiO₂ ([HC]^{PSS}_{4E,0}); 0.045 Pa; Table 6). Multiplying the Al₂O₃-catalyzed areal rate by the maximum dilution extent considered for loose Pt/SiO₂ + Al₂O₃ mixtures (5400 nm² Al₂O₃ Pt⁻¹_s) gives an Al₂O₃-catalyzed 4MCHE hydrogenation rate (per Pt_s) of 2.2 (\pm 0.2) x10⁻⁴ mole MCH g-atom⁻¹ Pt_s s⁻¹. 4MCHE is hydrogenated to MCH on Pt surfaces, on the other hand, with a turnover rate of 6.7 (\pm 1.2) x10⁻² mole MCH g-atom⁻¹ Pt_s s⁻¹ (90 kPa H₂; 1.4 kPa toluene; 393 K), assuming that reactions of each MCHE isomer contribute equally to the rate that MCH is formed on Pt/SiO₂ (0.20 (\pm 0.03) mole MCH g-atom⁻¹ Pt_s s⁻¹;

Table 6

Pseudo-steady-state 4-methylcyclohexene pressures during toluene-H₂ reactions on Pt/SiO₂ present as intimate mixtures with Al_2O_3 -Sasol at different extents of dilution (β).^{a,}

β (nm ² Al ₂ O ₃ surface Pt ⁻¹)	4-Methylcyclohexene pressure (Pa)
0	0.045
470	0.056
960	0.064

 $^a1.4$ 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 Al_2O_3 -catalyzed 4MCHE hydrogenation rate on $Pt/SiO_2 + Al_2O_3$ mixtures (per Pt_s), indicating that MCHE reactions on Al_2O_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 Al_2O_3 surfaces thus simplifies to:

$$[HC]_{i}^{PSS} = \frac{\alpha_{-tol,i}^{Pt}[tol]}{\alpha_{MCH,i}^{Pt}K_{i*}} \theta_{*}^{\gamma_{tol} - \gamma_{ene}}$$
(24)

Here, K_{i*} is the equilibrium constant for the adsorption of a given MCHE isomer on Pt.

Table 6 shows 4MCHE pressures $([HC]_{4E}^{PSS})$ during toluene-H₂ reactions on Pt/SiO₂ mixed with different amounts of Al₂O₃-Sasol (1.4 kPa toluene; 90 kPa H₂; 393 K; 0–960 nm² Al₂O₃ Pt_s⁻¹). 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 $[HC]_{4E}^{PSS}$ (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 MCHE ($\theta_*^{\gamma_{tol}-\gamma_{ene}}$) and (ii) a coefficient ($\alpha_{-tol,4E}^{Pt}[tol]/\alpha_{MCH,4E}^{Pt}K_{4E*}$; where 4E replaces i in the subscripts to denote 4MCHE) that contains lumped kinetic parameters ($\alpha_{-tol,4E}^{Pt}$ and $\alpha_{MCH,4E}^{Pt}$), a toluene pressure dependence, and the 4MCHE adsorption equilibrium constant (K_{4E*}). This coefficient depends only on the nature of the Pt nanoparticle surface without any effects of Al₂O₃ 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 Al₂O₃ surfaces. These same increased coverages of vacant *-site ensembles are next shown to underpin MCH formation rate enhancements (η).

 $[HC]_i^{PSS}$ values (Eq (24)) are related to the enhancement factor (η) for MCH formation rates from toluene-H₂ reactants by replacing the θ_* term with its functional form from Equation (14):

$$[HC]_{i}^{PSS} = \frac{\alpha_{-tol,i}^{Pt}[tol]}{\alpha_{MCH\,i}^{Pt}K_{i*}} \left(\eta \theta_{*,0}^{\gamma_{tol}}\right)^{1-\omega_{ene}}$$
(25)

In this equation, ω_{ene} is defined as the ratio of the numbers of adjacent *-sites required to bind MCHE isomers (γ_{ene}) and toluene (γ_{tol}):

$$\omega_{ene} = \frac{\gamma_{ene}}{\gamma_{tol}} \tag{26}$$

The $\alpha_{-tol,i}^{Pt}$, $\alpha_{MCH,i}^{Pt}$, K_{i*} , $\theta_{*,0}^{\gamma_{tol}}$, and ω_{ene} 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/ SiO₂ + Al₂O₃ mixture ($[HC]_i^{PSS}$; Eq (23)) to that on Pt/SiO₂ ($[HC]_{i,0}^{PSS}$; Eq (23) with η = 1), denoted as ζ_i , therefore becomes a singlevalued function of the rate enhancement factor for MCH formation:

$$\zeta_i = \eta^{1 - \omega_{ene}} \tag{27}$$

Fig. 7 depicts values of the 4MCHE pressure enhancement factor (ζ_{4E}) and η for loose and intimate mixtures (Pt/SiO₂-1.39; 1.4 kPa toluene; 90 kPa H₂; 393 K) with different dilution extents and mean aggregate radii. These ζ_{4E} values increased monotonically with increasing η ; the observed trends correspond to a ω_{ene} value of 0.62 ± 0.02, which agrees well with that measured on catalyst Pt/SiO₂-1.39 (ω_{ene} = 0.7 ± 0.02) from the effects of toluene pressure on pseudo-steady-state 4MCHE pressures in the absence of Al₂O₃ [22].

 $ζ_{4E}$ and η vary in a manner consistent with the mechanismbased inhibitor-scavenging model (Eq (27)), indicating that increased MCH formation rates and MCHE pressures can both be attributed to a greater abundance of vacant *-site ensembles caused by Al₂O₃-mediated scavenging of desorb-able inhibitors. This mechanistic origin of Al₂O₃-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 Al₂O₃ (and other metal oxide) co-catalyst provides an additional route for the consumption of desorb-able species with high metal surface coverages and low reactivities, thereby uncovering the active sites that catalyze reactions of other



Fig. 7. 4-Methylcyclohexene (4MCHE) concentration enhancement factor (ζ_{4E} ; Eq (27)) at different MCH formation turnover rate enhancement factors (η ; Eq (12)) for toluene-H₂ reactions on Pt/SiO₂-1.39 (90 kPa H₂, 1.4 kPa toluene, 393 K) achieved by dilution with Al₂O₃-Sasol in loose (\blacksquare ; 4800 nm² Al₂O₃ surface Pt⁻¹; 10–110 µm mean aggregate radius) and intimate (\bullet ; denoted as "int"; dilution extent of 400–1000 nm² Al₂O₃ surface Pt⁻¹⁻¹) mixtures. The solid curve indicates a fit to the functional form of Equation (27).

intermediates with higher reactivities towards the ultimate products.

3.5.3. Effects of Pt/SiO₂ and Al_2O_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/SiO₂ + Al₂O₃ mixtures would require the diffusion of MCHD isomers between Pt and Al₂O₃ 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-H₂ reactants $(2-30 \times 10^{-15} \text{ mole cm}^{-3}$, depending on the particular isomer; 1.4 kPa toluene; 90 kPa H₂ 393 K (Table S3)). MCHD diffusion within porous aggregates of Pt/SiO₂ and Al₂O₃ 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/SiO₂ and Al₂O₃ aggregates (at similar extents of dilution; Fig. 3).

The spatial segregation enforced by separate Pt/SiO₂ and Al₂O₃ aggregates in loose mixtures (and by the less well-defined boundaries among constitutive Pt/SiO₂ and Al₂O₃ regions in intimate mixtures) causes MCHD concentrations to be highest within Pt/ SiO₂ aggregates and lowest within Al₂O₃ aggregates. Such concentration profiles of MCHD inhibitors across the radial dimensions of Pt/SiO₂ and Al₂O₃ aggregates are depicted in Scheme 3 for loose mixtures with mean aggregate radii between 13 and 106 µm. 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/SiO₂ and Al₂O₃ domains). The coverages of the surface-bound counterparts of these MCHD isomers are related to their gaseous concentrations $([HC]_i)$ 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 (η ; Eq (14)). MCH formation rate enhancements at a given position within the Pt/SiO₂ 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 Al₂O₃ aggregates. These local rate enhancements thus exhibit gradients across the dimensions of the Pt/SiO₂ aggregate voids.

The effects of gradients in local MCH formation rate enhancements across the dimensions of Pt/SiO₂ aggregates on overall rate enhancements are determined by averaging their values across the aggregates' volumes. These volume-averaged rate enhancement factors (denoted as $\langle \eta \rangle$) are determined by integrating the local rate enhancement factor (η ; Eq (14)) across the radial coordinate of the quasi-spherical Pt/SiO₂ aggregates (assuming that MCHD concentrations are uniform in the angular dimensions):

$$\langle \eta \rangle = \frac{3}{R_{Pt}^3} \int_0^{R_{Pt}} \frac{\theta_{\star}^{\gamma_{tot}}}{\theta_{\star,0}^{\gamma_{tot}}} R^2 dR$$
(28)

Here, R is the radial coordinate of the Pt/SiO₂ 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 θ_{i}^{2nd} are known at each radial position within Pt/SiO₂ aggregates. There are five distinct gaseous MCHD isomers, all of



Scheme 3. Concentration profiles (φ_{lH}) of prevalent methylcyclohexadiene inhibitors (I_H) across radial dimensions of quasi-spherical Pt/SiO₂ (ξ) and $A_{2}O_{3}$ (ς) aggregates formed during toluene- H_2 reactions on loose Pt/SiO₂ + $A_{2}O_{3}$ mixtures (13–106 μ m radii). Dimensionless I_H concentrations (φ_{lH}) are normalized by a reference concentration (I_{H})₀ (Section 2.3). Dimensionless radii are normalized by the mean Pt/SiO₂ aggregate radius (R_{pt} ; Section 2.3). Profiles are obtained from Equation (28) with $\theta_{+}^{\gamma_{tol}}$ values from Equation (30) and φ_i from the solution to coupled differential Equations (4) and (5), using regressed parameter values (Table 7).

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 $\theta_{*}^{\gamma_{tol}}$. These gaseous MCHD isomers differ in their Gibbs free energy of formation from toluene and H₂ 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/SiO₂ and Al₂O₃ 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-H₂ 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 $Pt/SiO_2 + Al_2O_3$ 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/SiO₂-1.39 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:

$$1 = \theta_{I_H} \tag{29}$$

where $\theta_{l_{H}}$ 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 $\theta_{l_{H}}$ term in Equation (29) to give:

$$1 = \frac{\alpha_{-tol,I_{H}}^{Pt} K_{tol*}[tol]}{k_{I_{H^{*}}[I_{H}]_{0}}} \left(\widetilde{\theta}_{*} - \widetilde{\theta}_{*}^{(\omega_{-I_{H}}-1)} \right) + \varphi_{I_{H}} \widetilde{\theta}_{*}$$
(30)

where the dimensionless vacant *-site coverage (θ_*) is defined as:

$$\widetilde{\theta}_* = \left(\frac{k_{I_H*}[I_H]_0}{k_{-I_{H*}}}\right) \theta_*^{\gamma_{tol}}$$
(31)

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

The $\varphi_{l_{H}}$ and θ_{*} values at each radial position within quasispherical Pt/SiO₂ and Al₂O₃ 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/SiO₂ (Eq (4)) and Al₂O₃ (Eq (5)) domains (Section 2.3). These equations contain terms for the net rate of MCHD formation from Pt surfaces ($r_{l_{H}}^{Pt}$) and reaction at Al₂O₃ surfaces ($r_{l_{H}}^{Al}$) (derivation details in Section S.10):

Table 7

Values of coefficients from reaction-transport models^a determined by regressing the observed methylcyclohexane formation rate enhancement factors to their model-predicted values with two different ω_{JH}^{b} values for loose Pt/SiO₂ + Al₂O₃ mixtures.^{c,d}

Coefficients	cients ω_{-IH}	
	1	ω _{ene}
$k_{-l_{H}*}/[l_{H]_{0}}[MCHD Pt_{s}^{-1} Pa^{-1} MCHD s^{-1}] \\ \delta^{Al}_{MCH,l_{H}}[MCHD nm^{-2} Pa^{-1} MCHD s^{-1}] \\ \alpha^{Pt}_{tol,l_{H}}K_{tol*}[tol]/k_{l_{H}*}[l_{H}]_{0} [n.u.]$	2 (±100) ^e 5 (±7) x10 ⁻⁵ 1 (±50) x10 ^{-2 e}	1 (±6000) x10 ^{3 e} 5 (±4) x10 ⁻⁵ 3 (± 10000) x10 ^{-5 e}

^aFrom Equation (28) with θ_{i}^{ad} from Equation (30) and φ_{i} from the solution to coupled differential Equations (4) and (5). ^bRatio of the number of adjacent *-sites that mediates I_{H}^{*} hydrogenation and binds toluene ($\omega_{-IH} = \gamma_{-IH} \gamma_{tol}$), taken to be ω_{ene} (0.62; Fig. 7) or 1. ^c1000–5000 nm² Al₂O₃ Pt_s⁻¹ and 13–110 µm mean aggregate radii (Fig. 3). ^dErrors indicate 90 % confidence intervals for parameter estimates. ^eThe large uncertainties indicate that the model is not sensitive to both ($k_{-I_{H}*}/[I_{H}]_{0}$) and ($\alpha_{-Iol,I_{H}}^{Pt} K_{tol*}[Iol]/k_{I_{H}*}[I_{H}]_{0}$) parameters.

$$\mathbf{r}_{I_{H}}^{Pt} = k_{-I_{H}*} \left(1 - \varphi_{I_{H}} \widetilde{\theta}_{*} \right)$$
(32)

$$r_{I_H}^{Al} = \delta_{MCH,I_H}^{Al} [I_H]_0 \varphi_{I_H}$$
(33)

The resulting coupled differential equations (Eqs (4) and (5)) are combined with Equation (30) and solved, subject to the boundary condition enumerated in Section 2.3, to obtain $\varphi_{l_{H}}$ and $\tilde{\theta}_{*}$ at each radial location within Pt/SiO₂ aggregates, which are then used to determine rate enhancement factors ($\langle \eta \rangle$; Eq (28)) for each mixture.

The kinetic and thermodynamic parameters and $[I_H]_0$ and [tol]terms in Equations (30), 31, and 33 can be grouped into three unique coefficients that are enumerated in Table 7. Their values were determined by regressing the observed MCH formation enhancement factors to those determined from the reactiontransport models for loose mixtures with dilution extents ranging from 1000 to 5000 nm² Al₂O₃ Pt_s⁻¹ and mean aggregate radii ranging from 13 to 110 µm (90 kPa H₂; 1.4 kPa toluene; 393 K). Two sets of coefficients were determined using different $\omega_{-l_{H}}$ values that reflect (i) equivalent ensembles of adjacent *-sites that are required to hydrogenate $I_{H}^{*}(\gamma_{-l_{H}})$ and to adsorb $I_{H}(\gamma_{tol})$ $(\omega_{-I_{H}} = 1)$ and (ii) a smaller ensemble of adjacent *-sites (which resembles that which binds MCHE isomers $(\gamma_{-I_H} = \gamma_{ene}))$ that is required to hydrogenate I_{H}^{*} than is required for I_{H} adsorption $(\omega_{-l_{H}} = \omega_{ene})$. Their values and uncertainty ranges are listed in Table 7. Fig. 8 shows a plot of parity comparing measured MCH formation rate enhancements to those predicted from the reactiontransport models. The experimental trends were better described by the reaction-transport model with $\omega_{-l_H} = \omega_{ene}$ than $\omega_{-l_H} = 1$ as indicated by the smaller sum of squared errors (SSE) for the former (0.470) than the latter (0.449). Their linear correlation indicates excellent agreement between these measured and predicted values, demonstrating that gradients in the concentrations of prevalent MCHD intermediates across Pt/SiO₂ and Al₂O₃ domains account for the effects of inter-function distances in these mixtures.

The δ_{MCH,l_H}^{Al} term reflects the pseudo-first-order rate constant for Al₂O₃-catalyzed hydrogenation of the MCHD intermediate in the prevalent inhibitor-scavenging route. Its regressed values (5 (±7) and 5 (±4) x10⁻⁵ MCHD molecules nm⁻² Al₂O₃ Pa⁻¹ s⁻¹ for $\omega_{-l_H} = 1$ and $\omega_{-l_H} = \omega_{ene}$, respectively; Table 7) are similar in magnitude to that for 13CHD hydrogenation on Al₂O₃ (5.0 (±0.5) x10⁻⁶ 13CHD molecules nm⁻² Al₂O₃ s⁻¹ Pa⁻¹; 393 K; 90 kPa H₂ (Table 2)). Such similarity shows that Al₂O₃ surfaces can hydrogenate cyclic alkadienes at the rates required for MCHD scavenging and for the concomitant rate enhancements mediated by such inhibitor scavenging routes on Pt/SiO₂ + Al₂O₃ mixtures.

The reaction-transport models based on MCHD-mediated inhibitor-scavenging routes explored in this section reveal that $Pt/SiO_2 + Al_2O_3$ mixtures with larger aggregates impose radial gradients in the concentrations of desorb-able MCHD isomers



Fig. 8. Methylcyclohexane (MCH) formation turnover rate enhancement factors (η) for Pt/SiO₂ + Al₂O₃ mixtures predicted from inhibitor-scavenging routes (Eqs (4), 5, 28, and 30; coefficients in Table 7) with a single desorb-able intermediate (I_H*) and a site ratio (ω_{-IH}) equal to one (\blacklozenge) or ω_{ene} (0.62 (Fig. 7); \spadesuit) as a function of the measured values at the same conditions (90 kPa H₂; 1.4 kPa toluene; 393 K).

between Pt and Al₂O₃ 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 Al₂O₃ 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 (i) 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 (MoS₂) 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 Al₂O₃ or SiO₂-supported MoS₂ downstream of an Al₂O₃ or SiO₂supported CoS_x bed, and with a layer of SiO₂ to separate the two [76,78]. These promotional effects have been attributed to bifunctional processes involving (i) H₂-dissociation on CoS_x surfaces to

form H atoms, (ii) the migration of H atoms from CoS_x 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 CoS_x for MoS₂-based HDS catalysts.

3.6. Effects of Pt nanoparticle diameter on the prevalence of Al₂O₃mediated rate enhancements for toluene-H₂ reactions on Pt surfaces.

Rates of MCH formation on Pt/SiO_2 increased more significantly when diluted with Al_2O_3 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(111) surfaces reveal that 1,3cyclohexadiene 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 requiring 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(111) surfaces [83]. Adsorbed forms of benzene on Pt(111) 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 [32]. 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(111) surfaces at typical conditions of benzene (and toluene) hydrogenation show that surfaces become saturated with benzene and co-adsorbed Hatoms [62]; such evidence suggests that low index planes of Pt surfaces are preferentially covered by molecularly-bound 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. Large metal nanoparticles expose larger fractions of surfaces with close-packed structures and high coordination numbers compared to surfaces of smaller nanoparticles with higher factions 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 hydrogenative 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-catalysts 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 methylcyclohexane (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 methylcyclohexadiene (MCHD) isomers at high converges under reaction conditions. Some of these isomers are slow to react further to methylcyclohexane (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-acidbase pairs (Al₂O₃, MgO, and TiO₂) present as physical mixtures with Pt/SiO₂. Al₂O₃ catalyzes the hydrogenation of cyclic alkenes and alkadienes (4-methylcyclohexene 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 methylcyclohexene (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 MCHE isomers from bound toluene and H atoms, and that convert bound forms of MCHE isomers to MCH at Pt surfaces, also increase as MCHD inhibitors are scavenged. Those intermediates involved in MCHE 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 scavenging of MCHD inhibitors from Pt adlayers confers increased gaseous concentrations of MCHE isomers at pseudo-steady state.

The spatial segregation enforced by separate Pt/SiO_2 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 MCHD 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 Deshlahra and Zhijie Wu for performing the coupled-cluster and CBS-QB3 thermodynamic calculations and Extreme Science and Engineering Discovery Environment (XSEDE; Project Number TG-CTS150005) for providing computational resources. The authors also thank Drs. Zhijie Wu, Xueyi Zhang, and Edwin Yik for their helpful insights and their underpinning initial studies of these effects and Drs. Edwin Yik, Jorge Quesada, Shashikant Kadam, and Sai Chen for the careful review of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2022.11.013.

References

- M. Boudart, Catalysis by Supported Metals. Adv. Catal. (1969), 20, 153–166, https://doi.org/10.1016/S0360-0564(08)60271-0.
- [2] G. Busca, Structural, surface, and catalytic properties of aluminas, in: Adv. Catal, 1st ed., Elsevier Inc., 2014, pp. 319–404, https://doi.org/10.1016/B978-0-12-800127-1.00003-5.

- [3] J. Hancsók, G. Marsi, T. Kasza, D. Kalló, Hydrogenation of the aromatics and olefins in FCC gasoline during deep desulphurisation, Top. Catal. 54 (16-18) (2011) 1102–1109, https://doi.org/10.1007/s11244-011-9731-9.
- [4] F. Diehl, A.Y. Khodakov, 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/ogst:2008040.
- [5] M.V. Twigg, Catalytic control of emissions from cars, Catal. Today. 163 (2011) 33–41, https://doi.org/10.1016/j.cattod.2010.12.044.
- [6] J.H. Sinfelt, P.J. Lucchesi, Kinetic evidence for the migration of reactive intermediates in surface catalysis, J. Am. Chem. Soc. 85 (1963) 3365–3367, https://doi.org/10.1021/ja00904a012.
- [7] S. Čeckiewicz, B. Delmon, Cooperative action of Pt/γ-Al₂O₃ catalyst and γ-Al₂O₃ diluent in the hydrogenation of benzene, J. Catal. 108 (1987) 294–303, https:// doi.org/10.1016/0021-9517(87)90179-5.
- [8] M. Choi, S. Yook, H. Kim, Hydrogen spillover in encapsulated metal catalysts: New opportunities for designing advanced hydroprocessing catalysts, ChemCatChem. 7 (2015) 1048–1057, https://doi.org/10.1002/cctc.201500032.
- [9] H. Shin, M. Choi, H. Kim, A mechanistic model for hydrogen activation, spillover, and its chemical reaction in a zeolite-encapsulated Pt catalyst, Phys. Chem. Chem. Phys. 18 (2016) 7035–7041, https://doi.org/10.1039/c5cp05536a.
- [10] P. Antonucci, N. van Truong, N. Giordano, R. Maggiore, Hydrogen spillover effects in the hydrogenation of benzene over Pt γ-Al₂O₃ catalysts, J. Catal. 75 (1982) 140–150, https://doi.org/10.1016/0021-9517(82)90129-4.
- [11] S.S.M. Konda, S. Caratzoulas, D.G. Vlachos, Computational insights into the role of metal and acid sites in bifunctional metal/zeolite catalysts: A Case study of acetone hydrogenation to 2-propanol and subsequent dehydration to propene, ACS Catal. 6 (2016) 123–133, https://doi.org/10.1021/acscatal.5b01686.
- [12] R. Prins, Hydrogen spillover. Facts and fiction, Chem. Rev. 112 (2012) 2714– 2738, https://doi.org/10.1021/cr200346z.
- [13] J.E. Benson, H.W. Kohn, M. Boudart, On the reduction of tungsten trioxide accelerated by platinum and water, J. Catal. 5 (1966) 307–313, https://doi.org/ 10.1016/S0021-9517(66)80013-1.
- [14] R.B. Levy, M. Boudart, The kinetics and mechanism of spillover, J. Catal. 32 (1974) 304–314, https://doi.org/10.1016/0021-9517(74)90080-3.
- [15] R. Prins, V.K. Palfi, M. Reiher, Hydrogen spillover to nonreducible supports, J. Phys. Chem. C. 116 (2012) 14274–14283, https://doi.org/10.1021/jp212274y.
- [16] W.C.J. Conner, J.L. Falconer, Spillover in Heterogeneous Catalysis, Chem. Rev. 95 (1995) 759–788, https://doi.org/10.1021/cr00035a014.
- [17] V.V. Rozanov, O.V. Krylov, Hydrogen spillover in heterogeneous catalysis, Russ. Chem. Rev. 66 (1997) 107–119, https://doi.org/10.1070/ RC1997v066n02ABEH000308.
- [18] M. Xiong, Z. Gao, Y. Qin, Spillover in heterogeneous catalysis: New insights and opportunities, ACS Catal. 11 (2021) 3159–3172, https://doi.org/10.1021/ acscatal.0c05567.
- [19] J.C. Schlatter, M. Boudart, Hydrogenation of ethylene on supported platinum, J. Catal. 24 (1972) 482–492, https://doi.org/10.1039/tf9625801761.
- [20] G.C. Bond, P.B. Wells, The mechanism of the hydrogenation of unsaturated hydrocarbons on transition metal catalysts, Adv. Catal. (1965) 91–226, https:// doi.org/10.1016/S0360-0564(08)60554-4.
- [21] G.C. Bond, Metal-catalysed reactions of hydrocarbons, Springer (2005), https:// doi.org/10.1016/s1351-4180(06)71746-9.
- [22] A. Fischer, Mechanistic Insights into Metal-Catalyzed Hydrogenations and the Role of Metal Oxide Co-catalysts (Doctoral thesis), University of California, Berkeley (2021).
- [23] R. Wischert, P. Laurent, C. Coperet, F. Delbecq, P. Sautet, γ-Alumina: The essential and unexpected role of water for the structure, stability, and reactivity of "defect" sites, J. Am. Chem. Soc. 134 (2012) 14430–14449, https://doi.org/10.1021/ja3042383.
- [24] Y. Amenomiya, Adsorption of hydrogen and H_2-D_2 exchange reaction on alumina, J. Catal. 22 (1971) 109–122, https://doi.org/10.1016/0021-9517(71) 90271-5.
- [25] U. Rodemerck, E.V. Kondratenko, T. Otroshchenko, D. Linke, Unexpectedly high activity of bare alumina for non-oxidative isobutane dehydrogenation, Chem. Commun. 52 (2016) 12222–12225, https://doi.org/10.1039/c6cc06442f.
- [26] M. Dixit, P. Kostetskyy, G. Mpourmpakis, Structure-Activity Relationships in Alkane Dehydrogenation on γ-Al₂O₃: Site-Dependent Reactions, ACS Catal. 8 (2018) 11570–11578, https://doi.org/10.1021/acscatal.8b03484.
- [27] H. Zhang, Y. Jiang, G. Wang, N. Tang, X. Zhu, C. Li, H. Shan, In-depth study on propane dehydrogenation over Al₂O₃-based unconventional catalysts with different crystal phases, Mol. Catal. 519 (2022), https://doi.org/10.1016/j. mcat.2022.112143.
- [28] S. Wang, K. Goulas, E. Iglesia, Condensation and esterification reactions of alkanals, alkanones, and alkanols on TiO₂: Elementary steps, site requirements, and synergistic effects of bifunctional strategies, J. Catal. 340 (2016) 302–320, https://doi.org/10.1016/j.jcat.2016.05.026.
- [29] P.B. Weisz, Polyfunctional Heterogeneous Catalysis, Adv. Catal. (1962) 137– 190, https://doi.org/10.1016/S0360-0564(08)60287-4.
- [30] W. Zhao, C. Chizallet, P. Sautet, P. Raybaud, Dehydrogenation mechanisms of methyl-cyclohexane on Γ-Al₂O₃ supported Pt13: Impact of cluster ductility, J. Catal. 370 (2019) 118–129, https://doi.org/10.1016/j.jcat.2018.12.004.
- [31] C. Morin, D. Simon, P. Sautet, Intermediates in the hydrogenation of benzene to cyclohexene on Pt(111) and Pd(111): A comparison from DFT calculations, Surf. Sci. 600 (2006) 1339–1350, https://doi.org/10.1016/j.susc.2006.01.033.
- [32] C. Morin, D. Simon, P. Sautet, Density-Functional Study of the Adsorption and Vibration Spectra of Benzene Molecules on Pt(111), J. Phys. Chem. B. 107 (2003) 2995–3002, https://doi.org/10.1021/jp026950j.

- [33] K.M. Bratlie, M.O. Montano, L.D. Flores, M. Paajanen, G.A. Somorjai, Sum frequency generation vibrational spectroscopic and high-pressure scanning tunneling microscopic studies of benzene hydrogenation on Pt(111), J. Am. Chem. Soc. 128 (2006) 12810–12816, https://doi.org/10.1021/ja0626032.
- [34] S. Haq, D.A. King, Configurational transitions of benzene and pyridine adsorbed on Pt{111} and Cu{110} surfaces: An infrared study, J. Phys. Chem. 100 (1996) 16957–16965, https://doi.org/10.1021/jp960814v.
- [35] I.H. Cho, S. Bin Park, S.J. Cho, R. Ryoo, Investigation of Pt/γ-Al₂O₃ catalysts prepared by sol-gel method, J. Catal. 173 (1998) 295–303, https://doi.org/ 10.1006/jcat.1997.1949.
- [36] S. Lee, K. Lee, J. Im, H. Kim, M. Choi, Revisiting hydrogen spillover in Pt/LTA: Effects of physical diluents having different acid site distributions, J. Catal. 325 (2015) 26–34, https://doi.org/10.1016/j.jcat.2015.02.018.
- [37] J.K. Bartley, C. Xu, R. Lloyd, D.I. Enache, D.W. Knight, G.J. Hutchings, Simple method to synthesize high surface area magnesium oxide and its use as a heterogeneous base catalyst, Appl. Catal. B Environ. 128 (2012) 31–38, https://doi.org/10.1016/j.apcatb.2012.03.036.
- [38] S. Soled, W. Wachter, H. Wo, Use of zeta potential measurements in catalyst preparation, Stud. Surf. Sci. Catal. 175 (2010) 101–107, https://doi.org/10.1016/S0167-2991(10)75013-8.
- [39] J.P. Brunelle, Preparation of catalysts by metallic complex adsorption on mineral oxides, Pure Appl. Chem. 50 (1978) 1211–1229, https://doi.org/ 10.1351/pac197850091211.
- [40] A.S. Almithn, D.D. Hibbitts, Supra-Monolayer Coverages on Small Metal Clusters and Their Effects on H2 Chemisorption Particle Size Estimates, AIChE J. 64 (2018) 3109–3120, https://doi.org/10.1002/aic.16110.
- [41] W.P. Davey, Precision Measurements of the Lattice Constants of Twelve Common Metals, Phys. Rev. 25 (1925) 753-761, https://doi.org/10.1103/ PhysRev.25.753.
- [42] W.A. Dietz, Response factors for gas chromatographic analyses, J. Chromatogr. Sci. 5 (1967) 68–71, https://doi.org/10.1093/chromsci/5.2.68.
- [43] N. Wakao, J.M. Smith, Diffusion in catalyst pellets, Chem. Eng. Sci. 17 (1962) 825-834, https://doi.org/10.1016/0009-2509(62)87015-8.
- [44] R.J. Madon, M. Boudart, Experimental criterion for the absence of artifacts in the measurement of rates of heterogeneous catalytic reactions, Ind. Eng. Chem. Fundam. 21 (4) (1982) 438–447, https://doi.org/10.1021/i100008a022.
- [45] A.D. Allian, K. Takanabe, K.L. Fujdala, X. Hao, T.J. Truex, J. Cai, C. Buda, M. Neurock, E. Iglesia, Chemisorption of CO and mechanism of CO oxidation on supported platinum nanoclusters, J. Am. Chem. Soc. 133 (2011) 4498–4517, https://doi.org/10.1021/ja110073u.
- [46] C.H. Hu, C. Chizallet, C. Mager-Maury, M. Corral-Valero, P. Sautet, H. Toulhoat, P. Raybaud, Modulation of catalyst particle structure upon support hydroxylation: Ab initio insights into Pd13 and Pt13/γ-Al₂O₃, J. Catal. 274 (2010) 99–110, https://doi.org/10.1016/j.jcat.2010.06.009.
- [47] M. Tang, W.A. Larish, Y. Fang, A. Gankanda, V.H. Grassian, Heterogeneous Reactions of Acetic Acid with Oxide Surfaces: Effects of Mineralogy and Relative Humidity, J. Phys. Chem. A. 120 (2016) 5609–5616, https://doi.org/ 10.1021/acs.jpca.6b05395.
- [48] M.A. Hasan, M.I. Zaki, L. Pasupulety, Oxide-catalyzed conversion of acetic acid into acetone: an FTIR spectroscopic investigation, Appl. Catal. A Gen. 243 (2003) 81–92, https://doi.org/10.1016/S0926-860X(02)00539-2.
- [49] A.R. Barron, The interaction of carboxylic acids with aluminium oxides: Journeying from a basic understanding of industrial and humanitarian applications, Dalt. Trans. 43 (2014) 8127–8143, https://doi.org/10.1039/c4dt00504j.
- [50] S.R. Tong, L.Y. Wu, M.F. Ge, W.G. Wang, Z.F. Pu, Heterogeneous chemistry of monocarboxylic acids on α-Al₂O₃ at different relative humidites, Atmos. Chem. Phys. 10 (2010) 7561–7574, https://doi.org/10.5194/acp-10-7561-2010.
- [51] S. Wang, E. Iglesia, Experimental and theoretical assessment of the mechanism and site requirements for ketonization of carboxylic acids on oxides, J. Catal. 345 (2017) 183–206, https://doi.org/10.1016/j.jcat.2016.11.006.
 [52] S. Wang, E. Iglesia, Experimental and Theoretical Evidence for the Reactivity of
- [52] S. Wang, E. Iglesia, Experimental and Theoretical Evidence for the Reactivity of Bound Intermediates in Ketonization of Carboxylic Acids and Consequences of Acid-Base Properties of Oxide Catalysts, J. Phys. Chem. C. 121 (2017) 18030– 18046, https://doi.org/10.1021/acs.jpcc.7b05987.
- [53] R. Wischert, C. Copøret, F. Delbecq, P. Sautet, Optimal Water Coverage on Alumina: A Key to Generate Lewis Acid-Base Pairs that are Reactive Towards the C-H Bond Activation of Methane, Angew. Chemie - Int. Ed. 50 (2011) 3202– 3205, https://doi.org/10.1002/anie.201006794.
- [54] J.E. Rekoske, R.D. Cortright, S.A. Goddard, S.B. Sharma, J.A. Dumesic, Microkinetic analysis of diverse experimental data for ethylene hydrogenation on platinum, J. Phys. Chem. 96 (1992) 1880–1888, https://doi.org/10.1021/j100183a067.
- [55] R.D. Cortright, S.A. Goddard, J.E. Rekoske, J.A. Dumesic, Kinetic study of ethylene hydrogenation, J. Catal. 127 (1991) 342–353, https://doi.org/10.1016/ 0021-9517(91)90230-2.
- [56] M. Boudart, G. Djega-Mariadassou, Kinetics of Heterogeneous Catalytic Reactions, Princeton University Press, Princeton, N. J., 1984.
- [57] S.D. Lin, M.A. Vannice, Hydrogenation of aromatic hydrocarbons over supported Pt catalysts: II. Toluene hydrogenation, J. Catal. 143 (1993) 554– 562, https://doi.org/10.1006/jcat.1993.1298.
- [58] L.P. Lindfors, T. Salmi, S. Smeds, Kinetics of toluene hydrogenation on a supported Ni catalyst, Chem. Eng. Sci. 48 (1993) 3813–3828, https://doi.org/ 10.1016/0009-2509(93)80224-E.
- [59] H. Ihm, H.M. Ajo, J.M. Gottfried, P. Bera, C.T. Campbell, Calorimetric measurement of the heat of adsorption of benzene on Pt(111), J. Phys. Chem. B. 108 (2004) 14627–14633, https://doi.org/10.1021/jp0401590.

- [60] O. Lytken, W. Lew, J.J.W. Harris, E.K. Vestergaard, J.M. Gottfried, C.T. Campbell, Energetics of cyclohexene adsorption and reaction on Pt(111) by lowtemperature microcalorimetry, J. Am. Chem. Soc. 130 (2008) 10247–10257, https://doi.org/10.1021/ja801856s.
- [61] S.J. Carey, W. Zhao, C.T. Campbell, Energetics of adsorbed benzene on Ni(111) and Pt(111) by calorimetry, Surf. Sci. 676 (2018) 9–16, https://doi.org/ 10.1016/j.susc.2018.02.014.
- [62] K.M. Bratlie, L.D. Flores, G.A. Somorjai, In situ sum frequency generation vibrational spectroscopy observation of a reactive surface intermediate during high-pressure benzene hydrogenation, J. Phys. Chem. B. 110 (2006) 10051– 10057, https://doi.org/10.1021/jp0612735.
- [63] M. Yang, K.C. Chou, G.A. Somorjai, The structures and reactions of linear and cyclic C6 hydrocarbons adsorbed on the Pt(111) crystal surface studied by sum frequency generation vibrational spectroscopy: Pressure, temperature, and H₂ coadsorption effects, J. Phys. Chem. B. 108 (2004) 14766–14779, https://doi.org/10.1021/jp048238n.
- [64] I.A. Yursha, G.Y. Kabo, D.N. Andreevskii, Equilibriums and thermodynamics of the isomerization of methylcyclohexenes, Neftekhimiya. 14 (1974) 688–693.
- [65] K. Kroenlein, C. Muzny, A. Kazakov, V. Diky, R. Chirico, J. Magee, I. Abdulagatov, M. Frenkel, NIST/TRC Web Thermo Tables (WTT) NIST Standard Reference Subscription Database 3 -, Professional Edition Version 2 (2011).
- [66] M. Peereboom, B. van de Graaf, J.M.A. Baas, Experimental and calculated thermodynamic data for the isomeric methylcyclohexenes and methylenecyclohexane, Recueil. J. R. Netherlands Chem. Soc. 101 (1982) 336–338, https://doi.org/10.1002/recl.19821011003.
- [67] A. Labbauf, F.D. Rossini, Heats of Combustion, Formation, and Hydrogenation of 14 Selected Cyclomonoolefin Hydrocarbons, J. Phys. Chem. 65 (1961) 476– 480, https://doi.org/10.1021/j100821a022.
- [68] R.B. Moyes, P.B. Wells, The Chemisorption of Benzene, Adv. Catal. 23 (1973) 121–156, https://doi.org/10.1016/S0360-0564(08)60300-4.
- [69] M. Saeys, M. Neurock, G.B. Marin, T. Hall, V. Charlottes, Density functional theory analysis of benzene (de)hydrogenation on Pt(111): Addition and removal of the first two H-atoms, J. Phys. Chem. B. 107 (2003) 3844–3855, https://doi.org/10.1021/jp022166n.
- [70] M. Saeys, M.F. Reyniers, M. Neurock, G.B. Marin, Ab initio reaction path analysis of benzene hydrogenation to cyclohexane on Pt(111), J. Phys. Chem. B. 109 (2005) 2064–2073, https://doi.org/10.1021/jp049421j.
- [71] M. Saeys, M.F. Reyniers, M. Neurock, G.B. Marin, Adsorption of cyclohexadiene, cyclohexene and cyclohexane on Pt(111), Surf. Sci. 600 (2006) 3121–3134, https://doi.org/10.1016/j.susc.2006.05.059.
- [72] S.D. Lin, M.A. Vannice, Hydrogenation of aromatic hydrocarbons over supported Pt catalysts: I. Benzene hydrogenation, J. Catal. 143 (1993) 539– 553, https://doi.org/10.1006/jcat.1993.1297.
- [73] T. Bera, J.W. Thybaut, G.B. Marin, Single-Event microkinetics of aromatics hydrogenation on Pt/H-ZSM22, Ind. Eng. Chem. Res. 50 (2011) 12933–12945, https://doi.org/10.1021/ie200541q.
- [74] M.K. Sabbe, G. Canduela-Rodriguez, M.F. Reyniers, G.B. Marin, DFT-based modeling of benzene hydrogenation on Pt at industrially relevant coverage, J. Catal. 330 (2015) 406-422, https://doi.org/10.1016/j.jcat.2015.08.003.
- [75] M. Saeys, M. Reyniers, J. Thybaut, M. Neurock, G. Marin, First-principles based kinetic model for the hydrogenation of toluene, J. Catal. 236 (1) (2005) 129–138, https://doi.org/10.1016/j.jcat.2005.09.019.
 [76] J. Ojeda, N. Escalona, P. Baeza, M. Escudey, F.J. Gil-Llambías, Synergy between
- [76] J. Ojeda, N. Escalona, P. Baeza, M. Escudey, F.J. Gil-Llambías, Synergy between Mo/SiO2 and Co/SiO2 beds in HDS: A remote control effect?, Chem Commun. 3 (2003) 1608–1609, https://doi.org/10.1039/b301647c.
- [77] H. Knöuzinger, Specific Poisoning and Characterization of Catalytically Active Oxide Surfaces, Adv. Catal. 25 (1976) 184–271, https://doi.org/10.1016/S0360-0564(08)60315-6.
- [78] C. Navarrete, R. García, C. Sepulveda, F.J. Gil-Llambias, J.L.G. Fierro, N. Escalona, Deep hydrodesulphurization via hydrogen spillover, Catal. Letters. 141 (2011) 1796–1802, https://doi.org/10.1007/s10562-011-0717-9.
- [79] M. Karroua, P. Grange, B. Delmon, Existence of synergy between "CoMoS" and Co9S8. New proof of remote control in hydrodesulfurization, Appl. Catal. 50 (1) (1989) L5–L10, https://doi.org/10.1016/S0166-9834(00)80849-0.
- [80] E.-S.-L. Yik, Hydrodesulfurization on Transition Metal Catalysts: Elementary Steps of C-S Bond Activation and Consequences of Bifunctional Synergies (Doctoral thesis), University of California, Berkeley, 2015.
- [81] B. Hammer, J.K. Nørskov, Electronic factors determining the reactivity of metal surfaces, Surf. Sci. 343 (1995) 211–220, https://doi.org/10.1002/ 9783527809080.cataz15812.
- [82] L.M. Falicov, G.A. Somorjai, Correlation between catalytic activity and bonding and coordination number of atoms and molecules on transition metal surfaces: Theory and experimental evidence, Proc. Natl. Acad. Sci. 82 (1985) 2207–2211, https://doi.org/10.1073/pnas.82.8.2207.
- [83] X. Su, K.Y. Kung, J. Lahtinen, Y.R. Shen, G.A. Somorjai, 1,3- and 1,4-cyclohexadiene reaction intermediates in cyclohexene hydrogenation and dehydrogenation on Pt(111) crystal surface: A combined reaction kinetics and surface vibrational spectroscopy study using sum frequency generation, J. Mol. Catal. A Chem. 141 (1999) 9–19, https://doi.org/10.1016/S1381-1169(98)00245-3.
- [84] M.P.C. Van Etten, B. Zijlstra, E.J.M. Hensen, I.A.W. Filot, Enumerating active sites on metal nanoparticles: Understanding the size dependence of cobalt particles for CO dissociation, ACS Catal. 11 (2021) 8484–8492, https://doi.org/ 10.1021/acscatal.1c00651.