



# Theoretical and kinetic assessment of the mechanism of ethane hydrogenolysis on metal surfaces saturated with chemisorbed hydrogen



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## ABSTRACT

Ethane hydrogenolysis involves C–C bond rupture in unsaturated species in quasi-equilibrium with gaseous reactants and H<sub>2</sub> on metal clusters, because C–C bonds weaken as C-atoms replace hydrogen with exposed metal atoms from catalyst surfaces. The nature and reactivity of such adsorbed species are probed here using kinetic data and density functional theory (DFT) for the case of Ir surfaces, but with conclusions that appear to be general to hydrogenolysis on noble metals. On surfaces saturated with chemisorbed H-atoms (H\*), theory and experiments indicate that C–C cleavage occurs predominantly via an  $\alpha,\beta$ -bound \*CHCH\* species that forms via sequential dehydrogenation of adsorbed ethane; all other intermediates cleave C–C bonds at much lower rates (>10<sup>7</sup>-fold). Measured activation energies (213 kJ mol<sup>-1</sup>) and free energies (130 kJ mol<sup>-1</sup>) reflect the combined values for quasi-equilibrated steps that desorb H\*, adsorb C<sub>2</sub>H<sub>6</sub>, form C<sub>2</sub>-intermediates by dehydrogenation, and form the transition state from \*CHCH\* species. DFT-derived activation energies (218 kJ mol<sup>-1</sup>) and free energies estimated from these values and statistical mechanics treatments of reaction and activation entropies (137 kJ mol<sup>-1</sup>) are in excellent agreement with measured values. The removal of four H-atoms in forming the kinetically-relevant \*CHCH\* intermediates, taken together with measured effects of H<sub>2</sub> pressure on hydrogenolysis rates, show that 2–3 H\* must be removed to bind this intermediate and the transition state, as expected from the structure of the proposed adsorbed species and H\* adsorption stoichiometries on Ir surface atoms that vary slightly with surface coordination on the non-uniform surfaces of metal clusters. Theory and experiments combine here to provide mechanistic insights inaccessible to direct observation and provide compelling evidence for reaction pathways long considered to be plausible for hydrogenolysis on noble metals. The extent of unsaturation in the single relevant intermediate and its C–C cleavage rates will depend on the identity of the metal, but the elementary steps and their kinetic relevance appear to be a general feature of metal-catalyzed hydrogenolysis.

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## 1. Introduction

Hydrogenolysis of C–C bonds on metals is the reaction of choice for decreasing the chain length of acyclic molecules and for opening rings in cyclic hydrocarbons [1–12]. It is also responsible, however, for yield losses during hydrocarbon reforming and isomerization [13,14], making mechanistic models of hydrogenolysis reactivity and selectivity useful in practice [15]. C–C bond rupture has been widely used to probe the effects of cluster size [9,10,16–26], elemental identity, and alloying [27–37] in catalysis. Early studies recognized that hydrogenolysis requires the progressive weakening of C–C bonds through the formation of unsaturated intermediates

that replace C–H bonds with C–metal bonds on surfaces [9,11,16,38–41]. The structure and degree of unsaturation of these species on metal surfaces have been inferred indirectly from measured effects of H<sub>2</sub> pressure on hydrogenolysis rates [29,38–40] and from isotopic exchange data [42–44], because they lack distinguishable spectroscopic signatures required for their direct interrogation and, therefore, can only be assessed using theoretical methods [35,45–48].

Our recent studies have addressed the enthalpic and entropic barriers that govern reactivity and selectivity in hydrogenolysis of C<sub>2</sub>–C<sub>10</sub> n-alkanes [49] and isoalkanes [50] on supported Ir clusters. Here, we combine hydrogenolysis turnover rates and their kinetic interpretation on Ir clusters saturated with chemisorbed hydrogen (H\*) with density functional theory (DFT) treatments on the Ir(111) surface in order to infer mechanistic details for the hydrogenolysis of ethane. This study shows that C–C bond cleavage occurs via a specific reactive intermediate (\*CHCH\*) that

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forms by the loss of four H-atoms (as H<sub>2</sub>) through the sequential dehydrogenation of adsorbed ethane molecules. These findings and the DFT-derived activation barriers agree well with measured turnover rates and activation energies on Ir clusters. They confirm the essential role of unsaturation in the cleavage of C–C bonds in ethane [45,46,48] and, by inference, in larger n-alkanes, isoalkanes, and cycloalkanes [7,8,16,35,47], for which similar kinetic dependences and activation barriers have been observed. The identification of the reactive species that cleave C–C bonds shows also how their concentrations depend on H<sub>2</sub> pressures and temperatures and can, therefore, inform the choice of reaction conditions and catalysts for processes that deliberately, or inadvertently, involve hydrogenolysis reactions.

## 2. Methods

### 2.1. Synthesis and characterization of Ir–SiO<sub>2</sub>

Ir–SiO<sub>2</sub> (3.0 wt.%) was prepared by incipient wetness impregnation using reported methods [49]. Samples were heated to 393 K at 0.017 K s<sup>−1</sup> in flowing dry air (Praxair, 99.99%, 5.0 cm<sup>3</sup> g<sup>−1</sup> s<sup>−1</sup>) and held for 8 h and subsequently heated at 0.033 K s<sup>−1</sup> to 1123 K and held for 12 h. The sample was cooled to ambient temperature and then heated at 0.033 K s<sup>−1</sup> to 1173 K in flowing 50% H<sub>2</sub>/He (Praxair, 99.999%, 1.0 cm<sup>3</sup> g<sup>−1</sup> s<sup>−1</sup>) and held for 8 h. The sample was again cooled to ambient temperature and passivated in flowing 0.5% O<sub>2</sub>/He (Praxair, 99.99%, 1.0 cm<sup>3</sup> g<sup>−1</sup> s<sup>−1</sup>) for 3 h. The number of exposed Ir atoms (I<sub>r,s</sub>) was determined from volumetric uptakes of H<sub>2</sub>, O<sub>2</sub>, and CO at 298 K [49,51] and the mean Ir cluster diameter (<d<sub>chem</sub>>) was estimated by assuming hemispherical crystallites and the atomic density of bulk Ir (70.7 atoms nm<sup>−3</sup>) [52,53]. Ir fractional dispersions from H<sub>2</sub>, O<sub>2</sub>, and CO chemisorption were 0.13, 0.15, and 0.13, respectively, the average of which indicates that the mean diameter of the Ir clusters was 7 nm. Distribution of cluster sizes was determined by transmission electron microscopy (TEM) in bright-field mode (Philips, CM200F) using samples applied as a fine dust onto lacey carbon-coated Cu grids. Surface-averaged cluster diameters were calculated using the following:

$$\langle d_{\text{TEM}} \rangle = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where  $n_i$  is the number of clusters with a diameter  $d_i$  (1029 clusters) [54]. Values of <d<sub>TEM</sub>> (14.4 nm) and <d<sub>chem</sub>> (7 nm) indicate that the majority of the Ir exists in aggregates of ~10<sup>4</sup> atoms. We must conclude that, in this case, distributions of detected cluster sizes overestimate the mean cluster diameter because TEM does not detect a significant numbers of small ( $d < 0.6$  nm) clusters that are represented in chemisorption experiments. Thus, we conclude that the chemisorption measurements most accurately represent the average size of the clusters, 7 nm, and the corresponding number of I<sub>r,s</sub> is used to calculate hydrogenolysis turnover rates. The Ir content was measured by inductively-coupled plasma optical emission spectroscopy (Galbraith Laboratories, Inc.). The Supporting Information summarizes the synthesis and characterization of the 7 nm Ir–SiO<sub>2</sub> catalyst (Table S1) and contains a representative TEM image and cluster size distribution for the Ir–SiO<sub>2</sub> catalyst (Fig. S1).

### 2.2. Ethane hydrogenolysis rate measurements

Ethane hydrogenolysis rates were measured in a flow packed-bed stainless steel tubular reactor (3/8" O.D.) with plug-flow hydrodynamics from 553 to 663 K with ethane ((C<sub>2</sub>H<sub>6</sub>)) and hydrogen ((H<sub>2</sub>)) pressures from 10 to 80 kPa and from 0.6 to 1.8 MPa, respectively. The reactor was placed within a three-zone resistively-heated

furnace, and the bed temperature was measured with a type K thermocouple held within a 1/16" stainless steel sheath aligned axially along the bed. The Ir–SiO<sub>2</sub> catalyst was mixed with additional SiO<sub>2</sub> (Cab–O–Sil HS-5, washed with deionized water and treated in flowing dry air at 793 K for 5 h) to avoid any axial or radial temperature gradients. Pressure was controlled using a dome-loaded regulator (Mity-Mite, S91XW). The catalyst was treated in flowing H<sub>2</sub> (Praxair, 99.999%) at ambient pressure (50 cm<sup>3</sup> g<sup>−1</sup> s<sup>−1</sup>) by heating to 673 K at 0.083 K s<sup>−1</sup> and holding for 2 h. The composition of the reactant stream was set using electronic mass flow controllers (Parker, 201) to meter the flow rates of H<sub>2</sub> (Praxair, 99.999%), and ethane (5% ethane, 10% Ar, 85% He, Praxair, certified-grade). CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> effluent concentrations were measured by gas chromatography (Agilent GC, 5890) using a methyl silicone capillary column (HP-1, 50 m × 0.32 mm × 1.05 μm) and a flame ionization detector. No other hydrocarbons were detected. All rates are reported at differential conversions (<5%) to avoid consequential axial gradients in reactant concentrations. Turnover rates are reported as moles of ethane consumed per unit time normalized by the number of surface metal atoms determined by chemisorption, and reported uncertainties represent two-standard deviations (95% confidence intervals).

### 2.3. Computational methods

Periodic plane-wave DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [55–58]. The plane-waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 396 eV [59,60]. The revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used to determine exchange and correlation energies [61–63]. Calculations of gaseous species were computed using 18 × 18 × 18 Å unit cells. The catalyst surface was modeled as a 4 × 4 Ir(111) closed-packed periodic lattice with a lattice parameter of 3.84 Å; it consists of four layers in the z-direction with the bottom two layers fixed in their bulk positions and the other two allowed to relax to their minimum energy structures. Wavefunctions were converged to within 10<sup>−6</sup> eV and forces were computed using a fast Fourier transform (FFT) grid with a cutoff of twice the planewave cutoff and a 3 × 3 × 1 Monkhorst–pack sampling of the first Brillouin zone (k-point mesh) [64]. For optimizations, the structures were relaxed until the force on unconstrained atoms was <0.05 eV/Å. After geometric convergence, a single-point calculation with a 6 × 6 × 1 k-point mesh was performed to optimize energy minima of reactant, product, and transition states.

Transition state (TS) structures were obtained for each elementary reaction by using the nudged elastic band (NEB) method [65,66] and the dimer method [67]. The NEB method was carried out using 16 images, and wavefunctions were converged to within 10<sup>−4</sup> eV using a 3 × 3 × 1 k-point mesh and an FFT grid size of 1.5 times the planewave cutoff. The maximum force on each atom was converged to <0.3 eV/Å. These protocols provided an estimate of the reaction path and a starting point for the structure and the reactive vibrational mode for each transition state. The dimer algorithm was then used with wavefunctions converged to within 10<sup>−6</sup> eV using a 3 × 3 × 1 k-point mesh and an FFT grid size of 2 times the planewave cutoff. For dimer calculations, the maximum force on each atom was converged to <0.05 eV/Å. As with optimizations of reactant and product states, the energy of the TS was then determined using a single-point calculation with 6 × 6 × 1 k-point mesh. Zero-point energy and thermal corrections were implemented using vibrational frequencies for reactants, transition states and products involved in each elementary step to estimate enthalpies and entropies of each state (details in Supporting information). For transition states, these frequency

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