Supra-Monolayer Coverages on Small Metal Clusters and Their Effects on H₂ Chemisorption Particle Size Estimates

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Published online February 14, 2018 in Wiley Online Library (wileyonlinelibrary.com)

H₂ chemisorption measurements are used to estimate the size of supported metal particles, often using a hydrogen-to-surface-metal stoichiometry of unity. This technique is most useful for small particles whose sizes are difficult to estimate through electron microscopy or X-ray diffraction. Undercoordinated metal atoms at the edges and corners of particles, however, make up large fractions of small metal clusters, and can accommodate multiple hydrogen atoms leading to coverages which exceed 1 ML (supra-monolayer). Density functional theory was used to calculate hydrogen adsorption energies on Pt and Ir particles (38–586 atoms, 0.8–2.4 nm) at high coverages (≤ 3.63 ML). Calculated differential binding energies confirm that Pt and Ir (111) single-crystal surfaces saturate at 1 ML; however, Pt and Ir clusters saturate at supra-monolayer coverages as large as 2.9 ML. Correlations between particle size and saturation coverage are provided that improve particle size estimates from H₂ chemisorption for Pt-group metals. © 2018 American Institute of Chemical Engineers AIChE J, 64: 3109–3120, 2018

Keywords: density functional theory, chemisorption, coverage effects, coadsorbate interactions, transition metals

Introduction

Noble metal catalysts are used extensively for many thermo-, electro-, and photochemical reactions, including hydrogenation, dehydrogenation, and oxidation of hydrocarbons, CO oxidation and hydrogenation, oxygen reduction on anode surfaces, and light-induced H₂ evolution. The size of the supported metal particles of these catalysts has a significant impact on process economics because only surface metal atoms can interact with reagents. Previous studies show that metal particle size has a significant effect on coke formation and catalytic deactivation during reforming processes. Furthermore, particle size can have an impact on the rate per surface metal atom (turnover rate) for “structure-sensitive” reactions; metal particles of different sizes expose surface ensembles with unique structures. Therefore, accurate assessment of the size of supported metal particle catalysts is critical for characterization of these materials.

Molecular hydrogen (H₂) is a common reagent in metal-catalyzed reactions, such as the hydrogenation of unsaturated C=C bonds and the reduction of CO, NO, or N₂. It is also used to cleave C=C bonds in alkane hydrogenolysis, C=O bonds in hydrodeoxygenation, and C=S bonds in hydrodesulfurization. H₂ readily dissociates on most noble metal catalysts, including Pt and Ir, at ambient or near-ambient conditions. Dissociative chemisorption of H₂ has therefore been widely used as a chemical titration to estimate the dispersion of supported metal particles, which is the fraction of metal atoms present at particle surfaces and therefore accessible to reagents. H₂ isotherms are generated to determine the amount of strongly bound (chemisorbed) H* adsorbed at “saturation” (the H* coverage in equilibrium with the highest pressure used in the isotherms) while excluding weakly bound (physisorbed) H₂. Metal dispersions are then calculated by assuming a H* to surface-metal (H:Mₛ) stoichiometry at saturation (θₛₐₜ, often assumed to be unity), and particle sizes can be estimated from dispersion for a given particle shape (e.g., hemispherical, spherical). X-ray diffraction (XRD) and transmission electron microscopy (TEM) can confirm these particle size estimates; however, small metal particles (<1 nm in diameter) are difficult to observe in standard TEM instruments and their sizes are inaccurately estimated using XRD. For these highly dispersed noble metal catalysts, the most common estimate of their size is given by H₂ chemisorption, which requires an accurate estimate of saturation H* coverages during chemisorption experiments.

Surface science studies suggest θₛₐₜ values of unity on the (111) plane of FCC metal crystals (such as Ir and Pt) at H₂ chemisorption conditions. The (111) plane represents >90% of the surface of large metal particles (>4 nm) and, therefore, the assumption that θₛₐₜ is unity is reasonable for large particles. The Brunauer-Emmett-Teller (BET) method has been used to estimate the H:Mₛ stoichiometry for unsupported metal particles by measuring the monolayer volume of an inert gas (e.g., N₂) physisorbed on the surface. Spenadel and Boudart found that the surface area measured from H₂ chemisorption on unsupported platinum particles (430 nm) agrees well with its BET surface area and concluded that H:Ptₜ is indeed unity; however, these particles are ~100 times larger...
than those typical of supported catalysts. Other studies used electron microscopy and small angle X-ray diffraction to measure the particles dispersion independently and also confirmed a $\theta_{\text{sat}}$ of unity for particles $>5$ nm in diameter.$^{35-37,42-44}$ Average particle sizes calculated from H$_2$ chemisorption on Ir/Al$_2$O$_3$ by assuming $\theta_{\text{sat}}$ of 1 (2.2 nm) were slightly smaller than the average size observed directly by TEM (2.9 nm).$^{45}$ Values of unity for $\theta_{\text{sat}}$ are often assumed, based on these studies, for other metals that are catalytically similar to Pt and Ir, such as Ru and Pd, which are studied less extensively.$^{46-48}$

Saturation coverages, however, have been shown to exceed unity on several metal catalysts, especially at low metal loadings; $\theta_{\text{sat}}$ values of 1.3–2.0, 1.2–1.98, and 1.24–3.0 have been reported for Pt,$^{49,50}$ Rh,$^{50,51}$ and Ir$^{45,50}$ respectively, using TEM (for particles $>0.6$ nm) and XRD (for particles $>5$ nm). Extended X-ray absorption fine structure (EXAFS) is also used in conjunction with chemisorption measurements, which estimates particle size by measuring the average coordination number of metals within nanoparticles (which increases with increasing particle size);$^{52}$ $\theta_{\text{sat}}$ of 1.14 and 2.68 for Pt and Ir particles ($<4$ nm), respectively, have been reported by comparing EXAFS and H$_2$ chemisorption data.$^{50}$

These high $\theta_{\text{sat}}$ values have been attributed to H* spillover to the support (artificially inflating H:M ratios).$^{52}$ H* diffusion into the bulk, $^{54}$ or to the ability of under-coordinated metal atoms present at the edges and corners of supported particles to bind more than one H*,$^{45,50,51}$ Al$_2$O$_3$-supported Pt, Rh, and Ir particles show different $\theta_{\text{sat}}$ values, and the $\theta_{\text{sat}}$ values for Ir/Al$_2$O$_3$ and Ir/SiO$_2$ are independent of the support,$^{50}$ both of which indicate that hydrogen spillover is an unlikely explanation for supra-monolayer coverages.$^{55,56}$ Subsurface hydrogen has been observed on Pd, which can form hydrides and act as a hydrogen storage medium.$^{57}$ The solubilities of H* into bulk Pt, Rh, and Ir, however, are low$^{58}$ and it is unlikely that significant amounts of subsurface H* exist in these materials. Recent DFT studies$^{15,59}$ and infrared experiments$^{60}$ for CO* chemisorption on Ru clusters confirm the formation of bridge-bound geminal dicarbonyl species on low-coordinated corner and edge atoms, which lead to supra-monolayer coverages (CO* : Ru$^+$ $> 1$). An assumed $\theta_{\text{sat}}$ value of unity in chemisorption measurements could lead to underestimated particle sizes for metals that can reach supra-monolayer coverages because the larger H$_2$ uptake will be inaccurately attributed to a larger dispersion. A 1 nm Ir particle that can reach 2 ML coverage, for example, would be described as a 0.5 nm particle by chemisorption if a value of unity is used for $\theta_{\text{sat}}$.

Here, we use density functional theory calculations (DFT) to provide a quantitative description of how H* covers Ir and Pt nanoparticles ranging from 38 to 586 atoms (0.80–2.4 nm average diameter) by examining symmetrically-covered sub- and supra-monolayer H* adlayers at a wide range of coverages ($\theta_1 = 0.09–3.63$ ML). Our results indicate that under-coordinated edge and corner atoms, present on all clusters to different extents, uptake multiple H* atoms, leading to supra-monolayer coverages. H* prefers to adsorb to surface sites rather than subsurface sites even at very high coverages (1.84–3.63 ML, depending on particle size), ruling out H* ingress as an explanation for supra-monolayer coverages on Ir and Pt particles. This study attempts to establish correlations between saturation coverages and particles size that can be used to improve estimates of particle size from H$_2$ chemisorption.

### Methods

Periodic, planewave density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP).$^{61,62}$ Planewaves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 396 eV.$^{63-65}$ The revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used to describe exchange and correlation energies.$^{66,67}$ Wavefunctions were converged until electronic energies varied less than 10$^{-6}$ eV. Forces on all atoms were determined using a fast Fourier transform (FFT) grid with a cutoff equal to twice the planewave cutoff and structures were geometrically optimized until the forces on all atoms were less than 0.05 eV Å$^{-1}$.

Gas-phase H$_2$ was modeled within an $18 \times 18 \times 18$ Å unit cell of empty space. Ir (111) and Pt (111) surfaces were modeled as 4 × 4 closed-packed periodic lattices with four layers orthogonal to the surface and 10 Å of vacuum separating slabs; the bottom two layers were fixed in their bulk positions and the top two layers were relaxed. A $3 \times 3 \times 1$ Monkhorst-pack sampling of the first Brillouin zone (k-point mesh) was used during geometric convergence, and after geometric convergence, a single-point calculation with a $6 \times 6 \times 1$ k-point mesh was performed to determine the electronic energy.

Symmetric cubo-octahedral Ir and Pt particles (38–586 atoms, 0.80–2.4 nm diameter) were examined, which include sites with different metal-atom coordination (Figure 1). For particle calculations, the Brillouin zone was sampled only at the Γ-point. Cubo-octahedral particles consist of eight hexagonal (111) terraces and six square (100) terraces connected by edge and corner atoms. The sizes of these particles can be described by the length of the edges connecting adjacent (111) terraces (h) and by the length of the edges connecting adjacent (111) and (100) terraces (s). The surface composition and details of all particles examined in this study are shown in Table 1.

H* preferably binds in an atop position on low-index Ir and Pt surfaces$^{69,70}$ and metal atoms in the (111) and (100) terraces of these particles were modeled as either bare or occupied by a single atop H* atom ($t_{111}$ and $t_{100}$ in Figure 1). Edge atoms, which have lower coordination numbers (CN = 7), may bind up to 2 atop H* atoms ($e_{111}$ and $e_{100}$ in Figure 1); corner atoms (CN = 6) may bind up to 3 atop H* atoms (c in Figure 1). The edges of these nanoparticles, as previously observed for CO* on Ru,$^{15,59,60}$ may also bind a H* atom in their bridging sites (be in Figure 1). The total number of different H* configurations is computationally intractable as coverage increases up to and beyond 1 ML, even if only these sites are considered. Generally, in this work we calculate energies of fully symmetric H* adlayers, in which all sites of each type have equivalent H* occupancies. The particles were filled with H* to find the minimum energy pathway from a bare surface to a surface with three atop H* per corner, two atop H* per edge, one atop H* per terrace, and one bridging H* for every edge site (designated as “3c,2e,1t,1b” in this work, 1.84–3.63 ML, depending on particle size). The average adsorption energy ($\Delta E_{\text{avg}}$) of all n H* on a particle is defined as the energy to form the n-H*-covered particle from a stoichiometric amount of gas-phase H$_2$ and a bare surface

$$\Delta E = E[n\text{H*}] - 0.5n \cdot E[\text{H}_2] - E[\text{M}]$$

(1)

The average binding energy of adding an extra x H* to a surface (x > 1) containing n H* is defined as the average differential binding energy ($\Delta E_{\text{diff}}$).
energies and determine where hydrogen would first adsorb on a bare particle. The cubo-octahedral metal particles expose atoms with four distinct coordination numbers (CN = 6, 7, 8, and 9), associated with exposed corners, edges, (100) terraces, and (111) terraces, respectively. Previous studies showed that on Ir and Pt(111) surfaces, \( H^* \) preferably binds atop metal atoms, which is confirmed here for the Ir\(_{201}\) and Pt\(_{201}\) particle (Figure 3); the binding energy for \( H^* \) atop Ir (111) terraces is at least 10 kJ mol\(^{-1}\) stronger than that for \( H^* \) in threefold and bridging sites, and at least 8 kJ mol\(^{-1}\) stronger on Pt (111) terraces. Therefore, only the atop binding mode was considered on the (111) terraces for all other particles.

There are six unique \( M_i \) atoms on a M\(_{201}\) cubo-octahedral particle (Figure 1b), which have six distinct atop sites (1 H–M bond), eight bridge sites (2 H–M bonds), six threefold sites (3 H–M bonds), and one fourfold site (4 H–M bonds) where \( H^* \) can bind (Figure 2). The average \( H^* \) binding energy on the Ir\(_{201}\) particle is \(-42 \text{ kJ mol}^{-1}\) across all atop sites, \(-30 \text{ kJ mol}^{-1}\) across all bridge sites, \(-16 \text{ kJ mol}^{-1}\) across all threefold sites, and \(-9 \text{ kJ mol}^{-1}\) at the fourfold site, showing a

### Results and Discussion

**Effect of binding mode and metal atom coordination number on \( H^* \) binding energy**

The adsorption energy of a single \( H^* \) atom was calculated for different binding modes and locations, shown in Figure 2, to probe the effect of metal atom coordination on adsorption energies and determine where hydrogen would first adsorb on a bare particle. The cubo-octahedral metal particles expose atoms with four distinct coordination numbers (CN = 6, 7, 8, and 9), associated with exposed corners, edges, (100) terraces, and (111) terraces, respectively. Previous studies showed that on Ir and Pt(111) surfaces, \( H^* \) preferably binds atop metal atoms, which is confirmed here for the Ir\(_{201}\) and Pt\(_{201}\) particle (Figure 3); the binding energy for \( H^* \) atop Ir (111) terraces is at least 10 kJ mol\(^{-1}\) stronger than that for \( H^* \) in threefold and bridging sites, and at least 8 kJ mol\(^{-1}\) stronger on Pt (111) terraces. Therefore, only the atop binding mode was considered on the (111) terraces for all other particles.

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### Table 1. Size and Surface Composition of all Metal Particles Examined in this Study

<table>
<thead>
<tr>
<th>( N^a )</th>
<th>( h )</th>
<th>( s )</th>
<th>( d_{avg} ) (nm)</th>
<th>( \bar{E}_n )</th>
<th>( E_{\text{sat}} )</th>
<th>( \theta_{\text{HE}} ) (ML) max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>Pt</td>
<td>( M_i )</td>
<td>( t_{111} )</td>
<td>( t_{100} )</td>
<td>( c_{11} )</td>
<td>( c_{10} )</td>
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<tr>
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<td>2</td>
<td>1.11</td>
<td>1.13</td>
<td>60</td>
<td>0.76</td>
</tr>
<tr>
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<td>3</td>
<td>1.28</td>
<td>1.31</td>
<td>78</td>
<td>0.67</td>
</tr>
<tr>
<td>124</td>
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<td>2</td>
<td>1.35</td>
<td>1.37</td>
<td>84</td>
<td>0.68</td>
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<td>201</td>
<td>3</td>
<td>3</td>
<td>1.59</td>
<td>1.62</td>
<td>122</td>
<td>0.61</td>
</tr>
<tr>
<td>314</td>
<td>4</td>
<td>3</td>
<td>1.91</td>
<td>1.94</td>
<td>174</td>
<td>0.55</td>
</tr>
<tr>
<td>405</td>
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<td>4</td>
<td>2.09</td>
<td>2.13</td>
<td>204</td>
<td>0.50</td>
</tr>
<tr>
<td>586</td>
<td>4</td>
<td>4</td>
<td>2.40</td>
<td>2.45</td>
<td>272</td>
<td>0.46</td>
</tr>
</tbody>
</table>

*Total number of atoms.
*Number of exposed atoms on the surface.
*Number of bridging sites on the edges of the particle.
*Maximum coverage (\( H^*/M_i \)) examined in this study.
observed in DFT studies of CO* chemisorption on Ru,60 Pt,71 bonds with increasing metal coordination numbers was also simple bond-order-conservation concepts.74 The most stable binding site for H* on Ir201 is a bridge site between a corner of electrons from the metal atoms to the adsorbed H*,73 or by general preference for H* to bind atop Ir as previously shown for (111) terraces.69 Similarly for Pt201, H* binds with an energy of −32, −30, −17, and −8 kJ mol−1 at atop, bridging, threefold, and fourfold sites, respectively. For each type of binding mode (atop, bridging, threefold) on Ir201, a clear trend exists between the average CN of the metal atoms at the site (CN) and ΔE (Figure 3a). The weakening of M−adsorbates bonds with increasing metal coordination numbers was also observed in DFT studies of CO* chemisorption on Ru,60 Pt,74 and Au clusters,72 and can be attributed to the back donation of electrons from the metal atoms to the adsorbed H*73 or by simple bond-order-conservation concepts.74 The most stable binding site for H* on Ir201 is a bridge site between a corner and edge atom along the (111)−(100) edge (CN = 6.5, ΔE = −58 kJ mol−1). H* binds atop the (111)−(100) edge (−46 kJ mol−1) more strongly than it binds atop the (111)−(111) edge (−35 kJ mol−1) despite those atoms having identical coordination numbers (CN = 7). Similarly, H* bridges atoms along the (111)−(100) edge (−58 kJ mol−1) more strongly than it binds to bridge sites along the (111)−(111) edge (−38 kJ mol−1, both sites CN = 6.5). These differences in binding energies for sites of identical CN demonstrate the inadequacy of coordination numbers as a descriptor for H* binding energies, as previously noted for CO* and O* on Au.75 H* adsorption energies on Pt201 change weakly with increasing CN (Fig. 3b) and the atop terrace (111) site is slightly more favorable (CN = 9, ΔE = −38 kJ mol−1) than other atop sites, in contrast to the strong trend with CN for atop-bound H* observed on Ir201; despite these differences, H* is also most stable when bridging atoms along the (111)−(100) edge of Pt201 (CN = 6.5, ΔE = −45 kJ mol−1), similar to Ir201. These results for Ir201 and Pt201 indicate that H* does not preferentially bind at threefold or fourfold sites; for other particle sizes, we focus on atop sites and bridging sites along particle edges.

Increasing or decreasing Ir particle size also affects H* binding energies, even for identical sites. Ir38 particles bind H* very strongly compared to larger particles for all sites considered, while increasing the particle size from Ir79 to Ir586 slightly strengthens H* binding. For example, H* binds atop a corner atom with a binding energy of −63 kJ mol−1 on an Ir38 particle, but that weakens to −42 kJ mol−1 on an Ir79 particle, and then strengthens slightly to −50 kJ mol−1 on an Ir586 particle. This is consistent with previous reports that the adsorption energy of CO* on the atop site of the (111) terrace becomes weaker with increasing particle size from Au13 to Au309, above which particle size effects disappear and CO* adsorption energy becomes identical to that obtained from a periodic flat surface.72 Here, the dramatic differences in binding energy between the Ir38 and larger particles may be caused by nanoparticle effects in which small metal clusters (<40 atoms) cease to behave like the bulk metal as a result of the decrease in the valence and conductivity bands.76 Overall, H* binds most strongly to bridge sites between two corner/edge atoms and most weakly atop a (111) terrace atom on all Ir particles studied. Increasing CN of the binding site weakens binding (Figure 5a), while increasing particle size slightly strengthens binding from Ir79 to Ir586, while H* binds most strongly to Ir38 (Figure 4a).

H* binds strongly to the Pt38 particle, but increasing Pt particle size has a less dramatic effect on ΔE values than is observed on Ir particles. ΔE is a weak function of particle size from Pt79 to Pt586 (Figure 4b). H*, for example, binds to the bridging site with −58 kJ mol−1 in Pt38, and that weakens to −45 kJ mol−1 in Pt201 and then strengthens to −56 kJ mol−1 in Pt586. The binding energy of a terrace H* (CN = 9) weakens from −60 to −38 kJ mol−1 with increasing particle size from Pt38 to Pt586, approaching the calculated value for Pt (111)
observed in DFT studies of CO* chemisorption on Ru, Pt, and Au clusters, and can be attributed to the back donation for (111) terraces. Similarly for Pt, H* binds with an energy of threefold, and fourfold sites, respectively. For each type of CN atoms along the (111)–(100) edge (58 kJ mol$^{-1}$), eight bridge sites, six threefold sites, and one fourfold site).

Figure 3. The adsorption energy of a single H* atom as a function of the average metal coordination number of the adsorbates (which are comprised almost entirely of low-index terraces). The critical H* adsorption energy ($\Delta E_{\text{diff}}^\text{crit}$) could therefore lie between $-9$ and $+4$ kJ mol$^{-1}$ based on calculated $\Delta E_{\text{diff}}$ values and prior observations that $\theta_{\text{sat}}$ is unity for (111) surfaces. The errors associated with DFT calculations of pathways to fill a bare particle is inefficient and computationally intractable; on a M$_{301}$ particle, for example, there are 21 distinct sites where the first H* atom can adsorb and 148 possible sites for the second atom, thus requiring a total of 3108 different calculations to rigorously determine the most favorable ground state of just a pair of H*.

Covering the particles with H*

Here, we examine how H* covers Ir and Pt particles by systematically adding H* atoms to the particles as depicted in Scheme 1. As described in the second section, we consider up to three H* atop each corner atom, up to two H* atop each edge, up to one H* atop each terrace, and up to one H* bridging between each corner/edge atom. Chemisorbed species on metal clusters alter the binding properties of coadsorbates through a combination of through-space and through-surface interactions. Through-space interactions of H* atoms are expected to be weak because the Bohr radius of a hydrogen atom (0.0529 nm) is much smaller than the M–M bond distances of 0.27 and 0.28 nm for Ir and Pt, respectively, rendering direct through-space interactions implausible. Adsorbed H* atoms, instead, can interact locally through the metal surface by binding to the same metal atoms (metal-atom-sharing) or can interact nonlocally by electron withdrawing effects. Therefore, H* atoms adsorb on the surface in a manner that minimizes unfavorable interactions with coadsorbed species, as such, H* may partially cover bridging sites around the particle then start filling the terrace atoms to avoid metal-atom-sharing on bridge sites. Rigorous analysis of all possible

Figure 4. The adsorption energy of a single H* atom on different binding sites as function of particle size for (a) Ir and (b) Pt clusters.

Figure 5. The adsorption energy of a single H* atom as a function of coordination number for (a) Ir and (b) Pt particles.
using the RPBE exchange-correlation functional, which is known to underestimate binding energies (by 10–20 kJ mol$^{-1}$) compared to other functionals$^{77}$ and neglects attractive dispersive forces between coadsorbed species.$^{13}$ Furthermore, recent studies (García-Díezeguez M, Hibbitts D, Iglesia E. Hydrogen chemisorption on Pt clusters at catalytic temperatures: Langmuir and two-dimensional gas models revisited. In preparation)$^{78}$ have demonstrated that vibrational frequency analysis can severely underestimate entropies of adsorbed species, such as H*.

Taken together, these uncertainties and the results on Ir and Pt (1 1 1) surfaces suggest that an RPBE-calculated $\Delta E_{\text{diff}}$ value of $-5$ kJ mol$^{-1}$ is a reasonable estimate of the weakest-bound H* that remains on the surface at the near-ambient conditions used in H$_2$ chemisorption.

Less than half of the Ir$_{201}$ particle surface is made up of (1 1 1) terrace atoms, and the presence of undercoordinated edge and corner atoms significantly alters how adsorption occurs and at what coverage the particle surface is saturated in H* during H$_2$ chemisorption. Scheme 1 shows average binding energies of 24 H* adsorbed atop all corner atoms of Ir$_{201}$ (1c, $-43$ kJ mol$^{-1}$), 36 H* atop all edge atoms (1e, $-40$ kJ mol$^{-1}$), 62 H* atop all terrace atoms (1t, $-30$ kJ mol$^{-1}$), and 72 H* bridging between corner/edge atoms (1be, $-52$ kJ mol$^{-1}$). The most favorable site to initially fill is therefore bridging between corner/edge atoms, as was the case for a single H* ($-58$ kJ mol$^{-1}$) (Figure 7a). Once these sites are filled, 24 H* can then bind atop all corners (1c,1be) with an average differential binding energy of $-24$ kJ mol$^{-1}$ (Eq. 2), 36 H* can bind atop all edges (1e,1be; $-17$ kJ mol$^{-1}$), and 62 H* can bind atop all terrace atoms (1t, $-29$ kJ mol$^{-1}$), the last of which is most favorable (Figure 7b). At each state, we consider binding additional H* to each site (up to each site’s limit) and we follow the path with the most favorable average differential binding energy (Scheme 1) until the particle has three H* atop every corner, two H* atop every edge, and one H* between every pair of corner and edge atoms (3c,2e,1t,1be) (Figure 7g). With increasing $\theta$, $\Delta E_{\text{diff}}$ weakens, first from $-52$ kJ mol$^{-1}$ to $-29$ kJ mol$^{-1}$ at $\theta = 0.59$ ML, and then gradually to $-20$ kJ mol$^{-1}$ at 1.59 ML, before increasing more rapidly to 21 kJ mol$^{-1}$ at 2.28 ML. Coverages above 1.59 ML correspond to $\Delta E_{\text{diff}}$ values $\geq 5$ kJ mol$^{-1}$ ($\Delta E_{\text{crit}}$) and are unlikely to occur at near-ambient conditions in the Ir$_{201}$ particle because they will have large, positive adsorption free energies once zero-point and entropy effects are considered. Here, based on the assumed value for $\Delta E_{\text{crit}}$ of $-5$ kJ mol$^{-1}$, we estimate 1.59 ML as the saturation coverage for Ir$_{201}$ (Figure 7d), consistent with the reported supra-monolayer coverages on Ir.$^{45,50}$

Small particles (Ir$_{38}$–124) fill with slightly different sequences than the Ir$_{201}$ particle (Supporting Information Schemes S1–S7), and these differences reflect the different number of sites of each type as the particle size varies. On the Ir$_{38}$ particle, the eight terrace atoms are first occupied ($\Delta E_{\text{diff}} = -69$ kJ mol$^{-1}$), as they lack coadsorbate interactions, unlike the undercoordinated bridge sites that are filled next (36 H*, $-46$ kJ mol$^{-1}$). No edge atoms are present on M$_n$ particles (all undercoordinated atoms are corners), and so the remainder of the particle is filled by sequential adsorption of H* to the 24 corner sites until all corners have three atop H* (3c, 1t, 1be). Adsorption above 2.88 ML ($\Delta E_{\text{diff}} = +36$ kJ mol$^{-1}$) is very unlikely at H$_2$ chemisorption conditions (Figure 6), indicating that Ir$_{38}$ saturates at 2.88 ML (2c, 1t, 1be). For the Ir$_{79}$–124 particles, $\Delta E_{\text{diff}}$ values suggest that coverages saturate between 2 and 2.2 ML.
These adsorption energies are calculated that coverages never exceed 30% on Pt (111), also in stark dictation with earlier reports. In fact, using these adsorption near-ambient conditions (300 K, 100 kPa H2), in direct contra-

positive adsorption free energy would predict that the Pt and Ir saturation coverages, thus we assume here a

gives an adsorption entropy of

Neglecting these errors, one can estimate an adsorption free
1.3 ML correspond to $\Delta E_{\text{diff}}$ values $\geq -5$ kJ mol$^{-1}$ ($\Delta E_{\text{crit}}^{\text{diff}}$) and are unlikely to occur at near-ambient conditions, indicating that Pt$_{201}$ saturates at 1.3 ML while Ir$_{201}$ saturates at 1.79 ML, consistent with previous reports of higher coverages on Ir than on Pt.$^{45,50}$ Similar to Ir$_{38}$, terrace atoms are first filled in Pt$_{38}$ with an average binding energy of $-68$ kJ mol$^{-1}$ before H* atoms fill the bridging sites with $\Delta E_{\text{diff}}$ value of $-28$ kJ mol$^{-1}$. H* is then added sequentially to the corners up to two H* atoms per each corner at 2.88 ML (2c, 1t, 1be; $\Delta E_{\text{diff}} = +35$ kJ mol$^{-1}$) before surface reconstruction occurs at 3.63 ML (3c, 1t, 1be). $\Delta E_{\text{diff}}$ values increase from $-20$ to $+35$ kJ mol$^{-1}$ at 2.13 ML, indicating that Pt$_{38}$ saturates at this coverage while Pt$_{116}$ and Pt$_{124}$ particles saturate at 1.46 and 1.43 ML, respectively. Large particles (Pt$_{314-586}$) reach saturation between 1.21 and 1.13 ML with one H* atom on bridge, terrace, and corner sites (1c, 1t, 1be).

High coverages of larger adsorbates, as reported previously for CO* on Ru nanoparticles, $^{15,59,60}$ increase the lateral compression of surface adlayers and weaken the bonds between adsorbed species and surface atoms, thus increasing the reactivity and desorption rate of bound species to create vacant sites required to adsorb reactants or dissociate species. Through-space coadsorbate interactions are, however, expected to be weak for small species like hydrogen but such species can also interact through the metal surface. The binding energy of a terrace H* atom changes weakly in Ir but more rapidly in Pt with increasing H* coverage on corner and edge metal atoms (see Supporting Information Section S5), indicating that local through-surface interactions are stronger in Pt than in Ir. Notably, the average surface metal-metal bond (M$_x$–M$_y$) distance increases with increasing H* coverage in Ir and Pt clusters, in contrast to single-crystal (111) surfaces (discussed in Supporting Information Section S6). These

Figure 8. Saturation coverages at $\Delta E_{\text{diff}}^{\text{crit}}$ for selected Ir (a–c) and Pt (d–f) particles.

Shown beneath each image are $\Delta E$ (red) and $\Delta E_{\text{diff}}$ (blue) in kJ mol$^{-1}$. Images for all other particles can be found in the Supporting Information (Figures S9 and S10). [Color figure can be viewed at wileyonlinelibrary.com]
relaxation effects with increasing coverage in metal clusters weaken M–M bonds, leading to greater back-donation and stronger metal-adsorbate bonds.

**Adding an extra H* atom**

An extra H* atom was added to the atop, threefold, or sub-surface sites in the terraces to examine the binding behavior of extra H* atoms above the “fully covered” states of Ir particles (3c,2e,1t,1be, 1.84–3.63 ML) and Pt particles (2c,2e,1t,1be, 1.75–2.88 ML) (Figure 9). The threefold sites preferentially bind the extra H* atom on larger particles with ∆E_diff from −11 to +12 kJ mol⁻¹ for Ir and from +4 to +19 kJ mol⁻¹ for Pt. Two H* atoms can also share a terrace metal atom in an atop binding mode with a less favorable ∆E_diff (Ir: −8 to +20 kJ mol⁻¹, Pt: +21 to +65 kJ mol⁻¹) than the threefold sites, on average. H* diffusion into a subsurface position (followed by readsorption of a surface H* atom) has much larger ∆E_diff values (Ir: +73 to +94 kJ mol⁻¹, Pt: +49 to +70 kJ mol⁻¹), indicating that the existence of subsurface H* atoms is unlikely, even at these extremely high surface coverages (1.75–3.63 ML).

**How supra-monolayer H* coverages affect chemisorption measurements of particle size**

Dissociative chemisorption of H₂ is extensively used to estimate the dispersion and thus the crystallite size of metal catalysts dispersed on a support. Chemisorption measurements are especially important for highly dispersed catalysts because their size is difficult to measure using standard TEM instruments and XRD. The measurement of the amount of chemisorbed H* at near ambient conditions gives the metal surface area and the metal dispersion for a known saturation coverage (θ_sat). The metal dispersion D is given by

\[
D = \frac{2N_{hl}}{N_M} \theta_{sat}^{-1}
\]

where \(N_M\) and \(N_{hl}\) are the total number of moles of metal in the catalyst sample and H₂ chemisorbed (as 2 H*), and \(\theta_{sat}\) is the saturation coverage. Surface-averaged chemisorption diameters can be calculated from this dispersion as

\[
d_{chem} = \frac{f_{shape}}{D} \frac{\nu_m}{\sigma_m}
\]

where \(f\) is a particle shape correction factor (six for spherical particles), \(\nu_m\) and \(\sigma_m\) are the volume and surface area of a metal atom. Typically, \(\theta_{sat}\) is assumed to be unity during H₂ chemisorption experiments.

The number of H* atoms chemisorbed by a catalyst sample depends on the H*-content of many sites on, within, and off the metal cluster. For example, H* can exist within the bulk of metal nanoparticles, where \(\theta_{bulk}\) is the fractional content (coverage) of bulk sites, whose number \((N_{bulk})\) is proportional to the volume of the particle (i.e., it is of \(O(d^3)\)). Similarly, we must account for H* adsorbed to terrace \((\theta_h N_h = O(d^2))\), edge \((\theta_e N_e = O(d))\), and corner \((\theta_c N_c = O(d))\) sites of the particle surface, as well as any possible H* spillover by including terms that account for H* adsorbed to the support near the metal-support interface \((\theta_{int} N_{int} = O(d^1))\) and away from that interface \((\theta_{supp} N_{supp} = O(d^0))\)

\[
n_{sat} = \theta_{bulk} N_{bulk}(d^3) + \theta_h N_h(d^2) + \theta_e N_e(d^1) + \theta_c N_c(d^0)
\]

where the dependence of the number of each type of site on the particle diameter is given (e.g., the number of terrace atoms is given by a second-order polynomial). For large particles (>6 nm), the higher order terms will dominate this expression, and the H* content in the bulk and on the low-index terraces which prevail on such surfaces will dictate H* uptake values. Pt and Ir particles are not expected to form bulk H*, as indicated by the very low H* solubilities in those materials, especially in contrast to Pd, which can form hydrides at reasonable conditions. Here, we calculated differential adsorption energies for H* in bulk positions near surface atoms, and found very large, endothermic adsorption energies for all sizes of Ir and Pt particles examined, indicating that \(\theta_{bulk} = 0\) for both materials (Figure 9). As described above, the dependence of \(\theta_{sat}\) on the identity of the metal for Rh, Pd,
and Ir supported on Al₂O₃ and the independence of θ_sat for Ir supported on Al₂O₃ and SiO₂ suggest that H* spillover effects are minimal, such that θ_inter ≈ 0 and θ_supp ≈ 0. The remaining terms of Eq. 5 represent H* adsorbed to surfaces, and for large particles, the H* coverage at terrace sites will dictate the overall H* uptake, and this explains the agreement between predicted and measured θ_sat values near unity for single crystal surfaces. Unsupported metal particles (>400 nm) and large supported metal particles (>6 nm) are minimal, such that H* spillover effects are neglected, and here we use the differential adsorption energies calculated for H* on surfaces of Ir and Pt particles (0.8–2.4 nm, Figure 6) to estimate the fractional coverages of such sites (θ_e, θ_f, and θ_t) and to predict θ_sat(d), and we also discuss the errors associated with the common assumption of unity for θ_sat.

Figure 6 shows, for multiple Ir and Pt particles, the coverage at which H* binds weaker than the ∆E_diff value of −5 kJ mol⁻¹, which is our estimate of the weakest binding energy of H* that would adsorb at the near-ambient conditions used in the practice of H₂ chemisorption. This estimate is based on the calculated ∆E_diff values on Ir and Pt (111) surfaces, which are known to saturate at 1 ML, providing bounds (−9 and +5 kJ mol⁻¹) on ∆E_diff. Because it arises from the calculated ∆E_diff of a known surface, this estimate of ∆E_diff does not require an accurate estimate of the entropy of adsorbed H* or of the systematic errors in ∆E_diff caused by our use of an “underbinding” exchange-correlation functional (RPBE) or by the lack of dispersive coadsorbate interactions in our DFT models. Estimated θ_sat values for Ir and Pt particles of increasing size are shown in Figure 10a, and as particle size increases to infinity, θ_sat approaches the saturation coverage of (111) terraces (1 ML). Correlations between θ_sat and d_real for Ir and Pt particles, based on the saturation coverages at ∆E_diff = −5 kJ mol⁻¹, are given by

\[ \theta_{\text{sat}} = \frac{\theta_e N_e(d_e^2 - d_i^2) + \theta_f N_f(d_f^2 - d_i^2) + \theta_t N_t(d_t^2)}{N_{\text{surf}}(d_i^2)} \]  

(6)

where the dependence of the number of each type of site on the particle diameter is given. From these expressions for the number of sites, we can get an expression for θ_sat that depends on the coverage of terrace, edge (including bridging-edge sites), and corner sites, and how much of the surface is occupied by each site (fi)

\[ \theta_{\text{sat}} = \theta_e(1 - f_e - f_i) + \theta_f f_e (d_i^{-1} - d_e^{-2}) + \theta_t f_e (d_i^{-1} - d_t^{-2}) \]  

(7)

From this general formula, a semiempirical relationship can be described

\[ \theta_{\text{sat}} = 1 + \alpha (d_{\text{real}}^{-1} - d_{\text{crit}}^{-1}) + \beta (d_{\text{real}}^{-2} - d_{\text{crit}}^{-2}) \]  

(8)

where α is related to the excess coverage of edge H*, and β relates to a weighted difference between the excess coverages of corner H* and edge atop H* atoms. This equation can be used to fit the critical coverages estimated for Ir (α ≈ 1.21; β ≈ 0.203) and Pt (α ≈ 0.0364; β ≈ 0.735), and gives good agreement with those values, as shown in Figure 10a. These estimates of saturation coverage can be used to improve H₂ chemisorption analysis by substituting Eq. 8 into Eqs. 3 and 4

\[ d_{\text{chem}} = \frac{N_M f_{\text{shape}}}{2N_{H_2}} \frac{v_m}{a_m} \left(1 + \alpha (d_{\text{real}}^{-1} - d_{\text{crit}}^{-1}) + \beta (d_{\text{real}}^{-2} - d_{\text{crit}}^{-2})\right) \]  

(9)

Figure 10b shows the average diameters of all metal particles examined in this study compared to the particle sizes that would be estimated from H₂ chemisorption assuming a θ_sat of unity (d_{\text{unity}}). Particle sizes would be underestimated by a factor of 2–4 for M₃₈ particles (estimates of 0.2 nm for Ir and 0.4 nm of Pt compared to real sizes near 0.8 nm), whereas M₄₈₆ particles (2.4 nm) would be underestimated by 43% for Ir (1.37 nm estimated) and 12% for Pt (2.16 nm estimated) if a θ_sat value of unity were used. Extrapolating our correlation (Eq. 9) to a 5 nm particle, we obtain θ_sat values of 1.25 for Ir and 1.04 for Pt, indicating that d_{\text{unity}} would be 4 nm for Ir and 4.8 nm for Pt. These deviations depend not only on the size of the particle, but also on the metal because different metals have different affinities for H*, particularly at undercoordinated sites, and we are currently repeating this study on other transition metals to extend the correlations provided here (Eq. 8 and Figure 10) that can improve H₂ chemisorption measurements.

![Figure 10. (a) Saturation coverages at ∆E_diff as a function of particle size for Ir (blue) and Pt (green) particles. (b) Deviation of estimated particles size using chemisorption measurements from the actual size. Dashed lines represent second-order fits using Eq. 8. Shadings represent 90% confidence intervals. [Color figure can be viewed at wileyonlinelibrary.com]](image-url)
Conclusions

Differential adsorption energies for H* chemisorption on Ir and Pt particles (38–586 atoms, 0.80–2.45 nm) were calculated using DFT by modeling systematic increases in H* coverage (up to 3.63 ML) to determine the origin of supramonolayer coverages previously observed,45,50 to estimate the saturation coverage (\(\theta_{\text{sat}}\)) of H* at the near-ambient conditions used in H\(_2\) chemisorption measurements, and to evaluate the accuracy of the common assumption that \(\theta_{\text{sat}}\) is unity for particle size estimates from H\(_2\) chemisorption isotherms.

Sequential H* adsorptions on Ir and Pt (111) surfaces weaken gradually as coverage increases from 1/16 to 1 ML, and then dramatically with the addition of one more H* atom, indicating that H* coverage would not exceed 1 ML on a single crystal (111) terrace, confirming earlier reports.31,40 The presence of undercoordinated edge and corner atoms in metal nanoparticles, however, significantly alters how particles fill and at what coverages they saturate. Undercoordinated metal atoms can accommodate multiple H* atoms giving rise to supramonolayer coverages. \(\Delta E_{\text{diff}}\) values suggest that H* continues to adsorb beyond 1 ML and saturation coverages of up to 2.9 ML on Ir and 2.1 ML on Pt are plausible, consistent with prior experimental studies.45,49,50 H* adsorption on surfaces remains more favorable than H* diffusion into the bulk at very large coverages (1.8–3.6 ML depending on the metal size), indicating that the existence of subsurface H* atoms is unlikely for Ir and Pt catalysts. Chemisorption measurements using an assumed H:M of unity underestimate the particle sizes of highly dispersed particles by up to 75% (i.e., a 1 nm particle will appear to be 0.25 nm by H\(_2\) chemisorption). This deviation decreases with increasing particle size as the highly coordinated terrace sites dominate the surfaces of large particles, but remains relevant even for 5 nm Ir particles (which would be estimated as 4 nm if \(\theta_{\text{sat}}\) is assumed to be unity). Correlations are presented for Ir and Pt which give estimates of \(\theta_{\text{sat}}\) as a function of particle diameter, and these can be used to improve particle size estimates from H\(_2\) chemisorption by recognizing that multiple H* can adsorb to undercoordinated metal atoms that make up a significant fraction of the surface of highly dispersed metals.

Acknowledgments

David Hibbitts acknowledges Prof. David Flaherty (University of Illinois, Urbana-Champaign) and Enrique Iglesia (University of California, Berkeley) for helpful discussions. Abdurahman Almithn acknowledges Saudi Arabian Cultural Mission (SACM) and King Faisal University, Saudi Arabia, for funding his graduate studies and research. Manuscript reviews and proofreading from Alex Hoffman and Pavlo Kravchenko (University of Florida) are gratefully acknowledged.

Literature Cited
