Intermetallic Compounds as an Alternative to Single-atom Alloy Catalysts: Geometric and Electronic Structures from Advanced X-ray Spectroscopies and Computational Studies

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Pt–Fe intermetallic compound (IMC) catalysts, including Pt₃Fe, PtFe and PtFeₓ, are shown to have advantageous catalytic properties similar to those reported for single-atom alloy catalysts. Suppression of the Pt ensembles responsible for hydrogenolysis results in high olefin selectivity during propane dehydrogenation. In situ resonant inelastic X-ray scattering (RIXS) results and density functional theory calculations show that these changes are associated with a decrease in the average energy of the filled 5d states of Pt in the Pt–Fe intermetallic compound structures compared to monometallic Pt, accompanied by an increase in the average energy of the unfilled valence bands. The decrease in energy of the filled Pt 5d orbitals increases with increasing Fe content in the IMC, i.e. PtFeₓ > PtFe > Pt₃Fe. These results demonstrate that by altering the stoichiometry of IMC catalysts it is possible to control both the ensemble size and electronic properties of active sites, which affords another mechanism for tuning catalytic properties, in addition to changing promoter metals. The present study demonstrates the potential of ordered intermetallic compounds as an alternative to traditional solid-solution single-atom alloys to serve as catalysts with well-defined and uniform active sites.

Introduction

Economic and environmental factors are causing the energy and chemical industries to seek to utilize light-gas and renewable resources, rather than crude oil, as raw materials.[1] Such factors have created a need for improved catalytic materials suitable for the selective transformation of these new feedstocks. To accelerate materials discovery, it is necessary to possess an atomistic understanding of the role of catalysts during chemical reactions. However, there are often multiple potentially active species in heterogeneous catalysts, which are utilized in approximately 90% of industrial processes,[2] making the study of such materials inherently complex. To help circumvent this challenge there has been growing interest in atomically precise heterogeneous single-atom catalysts, which are comprised of isolated active metal atoms, ions, or complexes on a support.[3–10] These materials, similar to homogenous catalysts, possess well-defined and uniform active sites. This allows for clearer interpretations of catalytic functionality and has the potential to greatly aid in the rational design of new materials.

Single-atom alloys (SAA’s) are a class of single-atom catalysts that are comprised of a catalytically active metal atomically dispersed in a less-catalytic metal host. This results in active sites having well-defined and uniform local coordination environments and catalytic properties unique from the individual components. SAA catalysts have been shown to be active and selective for both the hydrogenation and dehydrogenation of various hydrocarbons and oxygenates.[7–11] Several SAA’s have also been reported to be resistant to poisoning by CO due to greatly reduced adsorption enthalpies on the isolated atoms compared to pure metal surfaces.[12–13] In all studies, the enhanced catalytic function has been attributed to the unique geometric and electronic properties of the isolated metal atoms. In reported SAA’s, Ni, Pd, or Pt has commonly been isolated at random throughout the host lattice; so high host-to-catalyst atomic ratios are required to ensure complete isolation of active sites.
Binary intermetallic compounds (IMC’s) are a type of alloy wherein the two components occupy fixed positions within the crystal lattice, resulting in each metal having a well-defined and uniform local coordination environment. This structural uniformity has led to a growing interest in the use of IMC’s in heterogeneous catalysis. It is hypothesized that an IMC phase with an appropriate crystal structure in which the catalytic atoms are isolated by the second “host” metal could result in active sites with unique properties similar to those reported for SAA’s. In addition, a much higher density of the active sites can be achieved with IMC’s instead of SAA’s, where in the latter a large amount of the host limits the density of surface active sites. The ordered structure of IMC’s allows for precise control over the geometric and electronic structures of the active sites, and controls the distance between neighboring active Pt sites. With advanced spectroscopic characterizations combined with theory, it will eventually be possible to build structure-activity relationships to tune catalyst electronic structure, and in turn, better design materials for optimal performance.

Herein, we demonstrate this approach with a nanoparticle IMC catalyst, using Pt as the active metal and Fe as the host, in which the PtFe$_2$ phase was formed. Isolation of Pt atoms and long-range atomic ordering were confirmed by in situ extended X-ray absorption fine structure (EXAFS) and synchrotron X-ray diffraction (XRD) measurements. The isolated active sites were found to be highly olefin selective for propane dehydrogenation compared to Pt nanoparticles (NP’s). IMC phases with contiguous Pt atoms in Pt$_x$Fe and PtFe were synthesized for comparison and showed similar olefin selectivity and dehydrogenation rates to the completely isolated active sites in PtFe$_2$. Relative shifts in Pt valence electronic structure calculated from density functional theory (DFT) agreed with those measured by in situ resonant inelastic X-ray scattering (RIXS) and provide insight into the adsorptive properties of the IMC catalysts. This approach demonstrates the potential of ordered IMC’s as an alternative to solid-solution SAA’s for use as catalysts in selective chemical transformations.

Results and discussion

As shown in the phase diagram (Figure 1) there are three Pt–Fe intermetallic compound phases: Pt$_x$Fe (Cu$_3$Au structure type), PtFe (Cu$_3$Au), and PtFe$_2$ (Cu$_3$Au). Unlike the post-transition metals commonly used as promoters in IMC catalysts, Fe has an unfilled d-shell in the metallic state, which likely results in Pt–Fe alloys having different electronic properties due to stronger interactions between Pt–Fe $d$ states as opposed to Pt–Pt $d$ states.

Silica supported Pt–Fe IMC NP’s with nominal Fe:Pt atomic ratios of 0.7, 2.9, and 4.4 were synthesized by sequential incipient wetness impregnation and are designated by their nominal composition. Monometallic Pt and Fe catalysts were prepared using similar methods for comparison (detailed synthetic procedures can be found in the methods section of the Supplemental Information).

In situ X-ray absorption spectroscopy measurements were performed to investigate the local coordination environment of Pt in the catalysts, and the $\lambda_{pp}$ edge EXAFS are shown in Figure 2a. The EXAFS of the Pt catalyst shows three prominent peaks at 1.94, 2.39, and 2.86 Å (phase uncorrected distances) characteristic of Pt–Pt scattering. The Pt–Pt CN was determined to be 8.8 at a distance of 2.75 Å, values typical of small NP’s. A single peak is observed in the EXAFS of the Pt–Fe(4.4), catalyst, which is characteristic of scattering from a 3d metal (i.e. Fe). There is no evidence of Pt–Pt scattering in the first coordination, and fitting results (Table 1) confirm Pt has only Fe first nearest-neighbors (8.6 at 2.66 Å). To confirm that Pt isolation resulted from structural ordering, rather than by dilution within a solid solution, in situ synchrotron powder XRD patterns were collected. Figure 2b. shows the XRD patterns of the reduced catalysts after subtraction of the scattering from the reaction cell and silica support. The diffraction pattern of the mono-metallic Pt catalyst is characteristic of fcc Pt with peaks at 2.973° and 3.415°, corresponding to the (111) and (200) reflections, respectively. The lower angle of the diffraction peaks is due to the high synchrotron X-ray energy (106.257 keV) compared to laboratory XRD. The lattice constant calculated from Bragg’s law is 3.92 Å. Two distinct sets of peaks are observed in the pattern of the Pt–Fe(4.4) catalyst, indicating the presence of two separate phases. The broad peaks at 3.099°, 3.527°, 5.056°, and 5.904° are characteristic of an fcc structure. However, the peaks are shifted to higher 20 values compared to the Pt catalysts, indicating a decreased lattice parameter.

| Table 1. Pt $L_{III}$ edge XANES and EXAFS fitting parameters after reduction at 550 ºC. |
|--------------------------------|-----------------|----------------|--------------|-----------------|-----------------|-----------------|
| Catalyst | $L_{III}$ Energy [keV] | Scattering Pair | CN | R [Å] | $\Delta\sigma$ [eV] | $E_o$ [eV] |
| Pt       | 11.5640          | Pt–Pt          | 8.8 | 2.75 | 2.0            | −0.2           |
| Pt–Fe    | 11.5642          | Pt–Pt          | 6.1 | 2.73 | 2.0            | −1.3           |
| (0.7)    | 11.5644          | Pt–Fe          | 2.2 | 2.64 | 5.0            | −3.2           |
| Pt–Fe    | 11.5644          | Pt–Pt          | 5.0 | 2.74 | 2.0            | −1.7           |
| (2.9)    | 11.5646          | Pt–Fe          | 4.6 | 2.64 | 5.0            | −2.0           |
| Pt–Fe    | 11.5646          | Pt–Fe          | 8.6 | 2.66 | 5.0            | −0.5           |
pattern is consistent with that reported for the PtFe IMC phase, with a AuCu₃ structure type and calculated lattice parameter of 3.76 Å, confirming the formation of an ordered structure in which Pt atoms are isolated by Fe and are only surrounded by Fe atoms in the first coordination shell. Sharp peaks are also observed in the pattern of the Pt–Fe(4.4) catalyst at 3.311°, 4.687°, and 5.742°. These peaks match those of monometallic Fe and are consistent with large agglomerates of bcc α-Fe. This indicates that not all the reduced Fe in the sample forms the IMC structure. A lattice constant of 2.87 Å was calculated from the position of the (110) peak at 3.311° and matches that reported for bulk α-Fe. This indicates that Pt is not present in significant levels in the Fe phase, which would lead to lattice expansion, and suggests that the isolated Pt atoms observed by EXAFS are solely in the PtFe IMC structure.

Propane dehydrogenation was used as a model reaction to study the ability of the isolated Pt atoms in the PtFe IMC to selectively activate C–H bonds, since there is growing interest in selectively activating C–H rather than C–C bonds, as new routes are sought to more efficiently utilize light alkanes from shale gas. The geometric structure of catalysts can be an important factor in dictating selectivity for such reactions, as a single atom is all that is required for dehydrogenation, while larger ensembles are reported to be necessary for hydrogenolysis. Recently, a Pt–Cu SAA was shown to facilitate hydrogen – deuterium exchange in butane and avoid coke formation, which deactivated the monometallic Pt catalyst used for comparison. Similarly, Pt having only Cu nearest-neighbors has been reported to be highly selective for propane dehydrogenation compared to monometallic catalysts. In these studies, isolation of the active Pt atoms was concluded to be responsible for the increased catalytic selectivity. Elimination of large Pt ensembles suppressed structure sensitive reactions (i.e. coke formation and hydrogenolysis); while, the isolated atoms maintained the structure insensitive dehydrogenation reaction.

In addition to olefin selectivity, catalyst stability is a major issue during propane dehydrogenation. However, the dilute gas concentrations used in the reported catalyst tests are far from industrially relevant conditions so long-term stability was not a focus of the current study. Furthermore, since propylene selectivity was of primary interest and catalysts become more selective as they deactivate, short times on stream were used to compare the performance of Pt and the IMCs.

The effect of conversion on the propylene selectivity of the PtFe catalysts is shown in Figure 3. Under these conditions, the monometallic Fe catalyst showed no propane conversion, consistent with the much lower reported activity compared to Pt. When tested with a feed containing 2.5 % C₃H₈ in N₂, the PtFe catalyst was 98 % selective towards propylene at 10 % conversion, constituting a significant improvement over Pt, which was 90 % selective (Figure 3a). As the propane conversion increased, there was an even larger difference in selectivity between the two catalysts; the PtFe catalyst maintained high propylene selectivity (94 %) while that of Pt decreased to 55 %. We note that, as the propane conversion increases, so does the partial pressure of hydrogen in the reactor. The small decrease in propylene selectivity at high conversion observed for the PtFe catalyst suggests that even in the presence of hydrogen, hydrogenolysis is suppressed by the formation of the IMC structure. This is in contrast to Pt, which showed a large decrease in dehydrogenation selectivity in the presence of hydrogen.

To further investigate the competition between dehydrogenation and hydrogenolysis, a stoichiometric ratio of C₃H₈ and H₂ was fed to the reactor. The PtFe catalyst was essentially unaffected by the presence of H₂ in the feed, with propylene selectivities of 97 and 94 % at conversions of 10 and 40 %, respectively (Figure 3b). Unlike the PtFe IMC catalyst, with H₂ added to the propane, the Pt catalyst was less selective for dehydrogenation. The propylene selectivity decreased from 75

Figure 2. a. Magnitudes of the Fourier transform of the k²-weighted Pt L₃ edge EXAFS of Pt (black), Pt–Fe(0.7) (red), Pt–Fe(2.9) (green), and Pt–Fe(4.4) (blue). (Δk = 3.00–11.40 Å⁻¹). b. Background subtracted XRD patterns at 35 °C of the catalysts after reduction at 550 °C (Pt – black, Pt–Fe(0.7) – red, Pt–Fe(2.9) – green, Pt–Fe(4.4) – blue, and Fe – magenta) and simulated patterns of identified phases (Pt – dashed black, Pt–Fe – dashed red, PtFe – dashed green, PtFe(3.3) – dashed blue, and α-Fe – dashed magenta).
to 48% as the conversion was increased from 10 to 30%, comprising changes of 15 and 7% compared to only feeding propane. These results further confirm that even in the presence of H₂, the IMC structure remains selective for dehydrogenation; while, Pt shows an increased propensity for hydrogenolysis.

The increased olefin selectivity of the PtFe₃ catalyst can be attributed, in part, to the isolated nature of the active Pt atoms. As discussed above, formation of the ordered IMC structure results in Pt atoms with only Fe nearest neighbors. Owing to its much lower activity than Pt, Fe behaves essentially as a diluent in the IMC structure, similar to Cu in the reported SAA catalysts. The isolated atoms are capable of dehydrogenation, while elimination of Pt ensembles suppresses hydrogenolysis. The results presented here for propane dehydrogenation demonstrate the ability to synthesize catalysts containing metals in isolated geometries, analogous to those found in SAA’s, by forming ordered IMC’s.

In the Pt NP’s, there are only Pt atoms; while in the PtFe₃ catalysts, Pt is surrounded by only Fe neighbors. To obtain a more complete understanding of the structure-activity relationship, it is also important to look at the catalysts in which Pt has both Pt and Fe neighbors in the first coordination shell and contain small ensembles of three or fewer active atoms. With fine tuning of the synthetic conditions, phase-pure Pt₃Fe and PtFe catalysts were obtained and denoted with the nominal Pt/Fe molar ratios, Pt–Fe(0.7) and Pt–Fe(2.9), respectively. The phase purity of the reduced catalysts was confirmed by in situ XRD and XAS, Table 1 and Figure 2b.

The EXAFS spectrum of Pt–Fe(0.7) shows three peaks similar to monometallic Pt; however, the second and third peaks are shifted to 2.35 and 2.84 Å, the first peak has become a shoulder on the leading edge of the second, and there is a change in peak ratios. The changes in the spectrum of Pt–Fe(0.7) are consistent with the presence of non-Pt neighbors, and a good fit was obtained by including contributions from Pt–Pt and Pt–Fe scattering. The Pt–Fe CN is 2.2 at a distance of 2.64 Å and the Pt–Pt CN is 6.1 at a distance of 2.73 Å, shorter than the Pt–Pt distance in monometallic Pt NP’s. Pt–Fe(0.7) has a similar diffraction pattern to the monometallic Pt catalyst, but all the peaks are shifted to higher 2°, indicating a decrease in the lattice constant. The diffraction pattern matches that of the PtFe alloy with a Cu₃Au structure type. The most intense peaks at 3.021° and 3.449° correspond to the (111) and (200) reflections and the lattice constant calculated from Bragg’s law is 3.86 Å.

The EXAFS of Pt–Fe(2.9) show an asymmetric peak at 2.29 Å with a shoulder at 2.84 Å, consistent with Pt having Pt and non-Pt neighbors like Pt–Fe(0.7). The Pt–Pt CN is 5.0, lower than Pt–Fe(0.7). However, the bond distance is 2.74 Å, similar to Pt–Fe(0.7). The Pt–Fe CN of Pt–Fe(2.9) is 4.6, larger than Pt–Fe(0.7), and at an equivalent distance of 2.64 Å. The diffraction pattern of Pt–Fe(2.9) is similar to Pt–Fe(0.7), but the peak positions of the four most intense peaks are shifted. The first and third peaks are shifted to higher angle (3.040° and 4.961°) while the second and fourth peaks are shifted to lower angle (3.432° and 5.786°) compared to Pt–Fe(0.7). The pattern of Pt–Fe(2.9) matches that of the PtFe alloy with a AuCu structure type with the peaks at 3.040° and 3.432° corresponding to the (101) and (110) reflections. The shift to higher angle of the first and third peaks and to lower angle of the second and fourth peaks is due to PtFe having a tetragonal unit cell, rather than a fcc cell like the Pt, Fe phase. The lattice constants a and c determined from Bragg’s law are 2.77 and 3.67 Å.

The phase-pure Pt–Fe intermetallic compound catalysts provide an opportunity to study the effect of the crystal structure (geometric structure) on the catalytic selectivity and activity. At 10% propane conversion, Pt₃Fe and PtFe are 97% and 98% selective for propylene, similar to PtFe, at 98%. At 40% propane conversion, the three alloy catalysts were 91, 95, and 94% selective, much higher than monometallic Pt. The large difference in selectivity between the Pt and Pt–Fe catalysts at high conversion indicates that all alloys are more olefin selective than Pt. Pt₃Fe and PtFe were also tested for
propane dehydrogenation with a feed containing equal molar amounts of H₂ and C₃H₈ (1.7% H₂, 1.7% C₃H₈, balance N₂). At 10% conversion with H₂ in the feed, Pt₃Fe (94%) and PtFe (96%) maintained high selectivity for propylene, similar to that of PtFe₃ (97%). Even at 40% conversion, the three alloy catalysts were 90%, 93%, and 94% selective, which is only a slight decrease compared to 10% conversion. Thus, alloy catalysts maintain selectivity even with co-fed H₂.

Traditionally, CO chemisorption measurements are used to determine the fraction of exposed Pt atoms to determine turnover rates (TOR). However, Fe may also chemisorb CO.\[30-34\] Pt surface areas can also be measured by O₂-H₂ titration.\[35\] However, in these alloys both Pt and Fe are oxidized. Therefore, to determine selectively the Pt dispersion, the increase in the Pt \( I_{\text{XANES}} \) XANES white line intensity after oxidation was determined. The changes can be isolated by taking the difference of the XANES spectra of oxidized and reduced catalysts. This approach has been used to determine the surfaces coverages on Pt of various adsorbed species during water-gas shift chemical reactions.\[37\] The intensity of the difference spectrum is proportional to the amount of surface oxidized Pt. Using monometallic Pt NP’s of different sizes, the correlation between dispersion and \( \Delta I_{\text{XANES}} \) intensity was determined. Figure 4 shows the \( \Delta I_{\text{XANES}} \) spectra of the three alloy catalysts and the XANES fits, and TOR’s (based on propylene production) are in Table S5. The TOR of Pt and the 3 PtFe IMC are very similar, ca. 0.5 ± 0.2 sec⁻¹, suggesting little change due to alloy formation with Fe.

**Electronic characterization.** Chemical bonding between the constituents in alloys alters the valence electronic states that are responsible for the catalytic behavior of the metals. Experimental and theoretical works have shown that the unique isolated geometries of metals in SAA’s can lead to electronic perturbations, which can in turn lead to changes in adsorption enthalpies and reaction barriers.\[12,27,37-39\] To determine the effect of atomic ordering on the valence states of Pt, in situ RIXS measurements and DFT calculations were performed. The 2-D RIXS planes show the incident photon energy (x-axis) and energy loss (y-axis) versus the intensity of emitted photons (Figure 5). The position of the maximum intensity along the incident energy axis corresponds to the average energy of the unfilled valence states of Pt. The energy loss axis gives the energy difference between the incident and emitted photons, which equals the energy difference between the unfilled and filled valence states, and the location of the maximum intensity can be used to determine the average energy of the filled 5d states.

The maximum RIXS intensity of the Pt catalyst occurs at an incident energy of 11564.2 eV and an energy loss of 3.1 eV. When the Pt₃Fe phase is formed, the maximum RIXS intensity shifts to slightly higher incident energy, 11564.4 eV, and energy loss, 3.4 eV. Further increases in the incident energy and energy loss to 11564.5 and 3.6 eV, respectively, are observed when the PtFe phase is formed. The PtFe₃ structure shows the maximum incident energy, 11564.6 eV, and energy loss, 3.8 eV, of the four catalysts. RIXS measurements show that the valence electronic states of Pt are dependent upon the composition of the alloy, as summarized in Table 2. As the Fe content of the alloy increases, there is a continual upward shift of the unfilled 5d states. This is accompanied by an increase in the energy loss due to a decrease in the energy of the filled states.

To corroborate the experimentally observed shifts in electronic states, and to provide additional insights into the electronic structure of alloyed platinum, ground state periodic DFT simulations of RIXS spectra were performed. The calculated RIXS planes capture the broad characteristics of the experimental spectra (Figure 6), and the maximum intensity peak position (Table 2) is also qualitatively comparable to the experimental results (note that the electronic densities of states, as calculated, correspond to 0 K, and hence broadening of the experimental scattering signal compared to the calculations is observed). To further quantify the calculated peak positions, Gaussian functions were fit to obtain maxima, due to the broadness of the observed peaks. Calculated incident and energy loss peaks correlate closely with experimental spectra for Pt and Pt₃Fe. However, although the calculated results for the two alloys with the highest Fe compositions follow the same trends as the experimental spectra, the magnitude of the calculated changes relative to Pt is larger for both incident energy and energy loss than what is seen experimentally. This discrepancy in the absolute shift in energies may be a result of several uncertainties. First, although all spin configurations were simulated for

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**Table 2. Position of most intense feature in RIXS planes of Pt and Pt–Fe alloy catalysts.**

| Catalyst | Experimental Data | DFT Calculated Data |
|----------|-------------------|---------------------|
|          | Incident Energy [eV] | Energy Loss [eV] | Incident Energy [eV] | Energy Loss [eV] |
| Pt       | 11564.2            | 3.1                | 0.7               | 3.3             |
| Pt₃Fe    | 11564.4            | 3.4                | 0.9               | 3.4             |
| PtFe₃    | 11564.5            | 3.6                | 1.2               | 4.2             |
| PtFe₅    | 11564.6            | 3.8                | 1.4               | 5.0             |

[a] Incident Energy is relative to the Fermi energy.
each alloy, and the lowest total energy configuration was used, there may be higher order electron correlations between Pt and Fe electrons that are not captured at the GGA level. Such effects would be more apparent in the unoccupied states, which are likely more sensitive to the choice of DFT functional, although we note that the influence of such states on RIXS spectra will be only modest since RIXS only considers those states which lie close to the Fermi energy (~10 eV). Additional tests for electronic structure convergence were performed using smaller core pseudopotentials, which did not significantly change the trends reported. The results were also largely independent of the cutoff energy and number of unoccupied bands chosen, so long as they are sufficient to sample the unoccupied states of interest in the RIXS simulation (approximately 10 eV). Another possible explanation for the quantitative discrepancy is that, to simplify the analysis, only the closest-packed low index planes of each alloy were analyzed in the simulations. The experimental spectra will obviously include an averaged contribution from Pt atoms with different coordination numbers corresponding to all crystallographic planes of a given particle. The size of the particles will further influence the strain exerted across the particle, which may further affect the $d$ electronic states. This strain effect is well-discussed in literature for alloy films.\textsuperscript{[41]} Despite the quantitative differences, the relative accuracy of the predicted shifts replicates the correct trend in electron energies, even for compositional changes of the same alloying metal. The modest level of theory required to simulate spectra of this accuracy indicates it could be possible to screen across a large number of alloys computationally, which is more feasible than synthesizing and performing RIXS measurements on every IMC composition.

The Pt densities of states (DOS) used to model each spectrum are shown in Figure 7. For NP catalysts, the experimental DOS is difficult to acquire. However, if the RIXS for theory and experiment show good qualitative agreement, then the calculated DOS from theory can be used to better understand the experimental electronic structure. Thus, the RIXS provides another approach for connecting chemical intuition from DFT to synthesized catalysts. The DOS shows a shift in the occupied and unoccupied Pt $d$-electrons upon formation of the IMC structure. When Pt is surrounded by Fe, there is an upward shift in the mean energy levels of the unoccupied electronic states with a corresponding downward shift in the mean energy levels of the occupied electronic states. The observed changes in energy of the Pt valence states further change the energetic overlap of the metal orbitals with those of adsorbates and chemical intermediates, thereby altering binding energies and reaction barriers.

Figure 5. Lu$_3$ RIXS planes of Pt (top left), Pt–Fe(0.7) (Pt$_3$Fe, top right), Pt–Fe(2.9) (PtFe, bottom left), and Pt–Fe(4.4) (PtFe$_3$, bottom right).
It has been reported that CO, a common model adsorbate, binds weakly on several SAA's as compared to the monometallic catalytic element.\textsuperscript{12,13} The Blyholder model suggests that the dominant factor dictating the chemisorption of CO to metal surfaces is the back donation of electrons from the valence d-states to the $\pi^*$ orbital of CO.\textsuperscript{42} It is hypothesized that lowering the energy of the filled 5d states of Pt would reduce back donation, resulting in weaker heats of adsorption. GGA levels of DFT are known to poorly capture the back-donation in CO, however, the shifts in orbital energies should be sufficient for GGA DFT to capture a change in binding energy. The binding energy of CO on Pt and the three Pt–Fe IMC surfaces were calculated from DFT to test this prediction (Table 3). The results show decreasing Pt–C bond strengths with increasing Fe content of the alloy, as would be expected from the RIXS results which indicate a reduction in the energy of the filled 5d Pt states. For the PtFe\textsubscript{3} low index surfaces, the binding energy to Pt top sites is reduced to the point that adsorption onto other Pt–Fe ensembles becomes thermodynamically favorable. For a comparison that is solely due to the alloying effect, the PtFe\textsubscript{3} top site binding energy is reported here; however, the Supporting Information includes CO binding energies at other sites for each alloy, as well as more discussion of CO binding to the PtFe\textsubscript{3} alloy.

Figure 6. DFT calculated RIXS maps of Pt (top left), Pt\textsubscript{3}Fe (top right), PtFe (bottom left), and PtFe\textsubscript{3} (bottom right). The x-axis of each plot is the incident energy with respect to the Fermi edge of Pt in eV. The y-axis of each plot is the energy loss in eV.

Figure 7. Projected density of states for Pt d electrons in Pt and the three Pt–Fe intermetallic compound phases. Pt – dashed black, Pt\textsubscript{3}Fe – solid red, PtFe – solid green, PtFe\textsubscript{3} – solid blue.
The increased olefin selectivities observed for the Pt–Fe catalysts are consistent with previously reported IMC alkane dehydrogenation catalysts. It has been proposed that the increased olefin selectivity arises from the elimination of large active-metal ensembles by incorporation of the noncatalytic promoter metals into the active surface. Segregation of the active atoms reduces hydrogenolysis, which is thought to require ensemble active sites. The local coordination geometries of Pt in PtFe, PtFe, and PtFe are equivalent to those in the highly selective IMC catalysts. Although Pt and Fe both perform dehydrogenation and hydrogenolysis, Fe catalyzes the reactions at much lower rates than Pt. Due to this large difference in the activity of the two metals, Fe behaves as a diluent, similar to the non-catalytic post-transition elements, resulting in the small Pt ensembles in the IMC structures being highly selective for dehydrogenation. These considerations support the proposal that geometric effects have a strong influence on the olefin selectivities in alkane dehydrogenation reactions.

While geometric effects are believed to play an important role in increasing the olefin selectivity, alloying also changes the electronic properties of metals. The observed changes with alloy composition indicates changes to the Pt 5d states, which are responsible for the activation of reactants and bonding with intermediates. In situ XANES show there is an upward shift in the average energy of the unfilled 5d states of Pt (Figure S1); while, the RIXS spectrum shows a corresponding downward shift in the average energy of the filled valence states. As the Fe content of the phase is increased (i.e. Pt–Pt bonds are lost and Pt–Fe bonds are formed), larger changes in the valence states are observed. Upon formation of PtFe, there is a small shift in the valence states, followed by a slightly larger shift in PtFe, and finally the largest change in PtFe. The decrease in the energy of the filled Pt 5d orbitals in these PtFe IMC’s, however, is significantly smaller than those for the PtZn,.[43] The DFT RIXS planes calculated from the projected DOS of Pt show a similar trend to the experimental results. Inspection of the DOS shows that as the Fe content is increased, there is a reduction in the number of filled and unfilled states near the Fermi edge, as well as increases in the number of lower and higher energy states. Integration of the Pt d-DOS shows no large change in the number of Pt d-electrons (Table S7). It is believed that this change in the average energy of the 5d-states, rather than the typically proposed transfer of electrons, is the dominant electronic effect on Pt of alloying. Such changes are in part responsible for the changes in adsorbate bond energies and reactant surface coverages, which also affect the catalytic properties. Reduction of the heats of adsorption of hydrogen, for example, would lead to changes in surface coverage and likely lead to lower hydrogenolysis selectivity and higher olefin selectivity.

**Conclusions**

Pt–Fe intermetallic compound catalysts were synthesized in which active Pt atoms have varying numbers of Fe nearest-neighbors. Experimental and theoretical results revealed that the Pt–Fe IMC’s have advantageous catalytic properties similar to those reported for SAAs. Elimination of the Pt ensembles responsible for hydrogenolysis via isolation of active atoms by less-catalytic Fe in the IMC structure yielded high olefin selectivity during propane dehydrogenation. Interestingly, even partial removal of Pt-Pt bonds in the PtFe and PtFe structures also improved selectivity significantly. In situ RIXS measurements agreed with the valence electronic structure calculated by DFT, which showed a decrease in the average energy of the filled 5d states of Pt in the IMC structures compared to monometallic Pt. The observed decrease of the filled 5d states was accompanied by an increase in the average energy of the unfilled valence bands. Using CO as a probe molecule, DFT calculations show that the perturbations to the valence states of Pt results in weaker metal – adsorbate bonds, suggesting that electronic effects also influence the catalytic properties. These results show that by altering the stoichiometry of IMC catalysts, it is possible to control both the ensemble size and electronic properties of active sites, which affords another mechanism for catalyst tunability in addition to changing promoter metals. The presented study demonstrates the potential of ordered intermetallic compounds as an alternative to traditional solid-solution single-atom alloys for synthesizing catalysts with well-defined and uniform active sites.

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Conflict of Interest

The authors declare no conflict of interest.

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