

Synthesis of Pt₃Y and Other Early–Late Intermetallic Nanoparticles by Way of a Molten Reducing Agent

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Supporting Information

ABSTRACT: Early-late intermetallic phases have garnered increased attention recently for their catalytic properties. To achieve the high surface areas needed for industrially relevant applications, these phases must be synthesized as nanoparticles in a scalable fashion. Herein, Pt₃Y-targeted as a prototypical example of an early-late intermetallic-has been synthesized as nanoparticles approximately 5-20 nm in diameter via a solution process and characterized by XRD, TEM, EDS, and XPS. The key development is the use of a molten borohydride (MEt₃BH, M = Na, K) as both the reducing agent and reaction medium. Readily available halide precursors of the two metals are used. Accordingly, no organic ligands are necessary, as the resulting halide salt byproduct prevents sintering, which further permits dispersion of the nanoscale intermetallic onto a support. The versatility of this approach was validated by the synthesis of other intermetallic phases such as Pt₃Sc, Pt₃Lu, Pt₂Na, and Au₂Y.

T he late transition metals readily alloy with elements that have much more negative reduction potentials such as the alkali, alkaline-earth, and rare-earth metals and form a range of intermetallic (IM) phases.¹ Recently, a number of papers have predicted—and experimental work has confirmed—that some of these early–late IM phases have exceptional catalytic activity and/or stability. Nørskov and co-workers predicted that Pt₃Y would be more active than pure Pt in the oxygen reduction reaction (ORR) on the basis of computations of the oxygen adsorption energy for a Pt overlayer on the IM.² Indeed, bulk polycrystalline electrodes of Pt₃Y were 6–10 times more active than pure Pt at 0.9–0.87 V vs RHE.² Other Pt IM phases such as Pt₅Tb, Pt₅Gd, and Pt₅Ca are also good ORR catalysts.³ Outside of catalysis, IMs of the alkali metals with Au are predicted to be good candidates for plasmonic applications.⁴

Exploration of the potential applications of these materials would be greatly facilitated by a scalable synthesis of the IM

phases in nanoparticle (NP) form. Pt/Y IM NPs have been synthesized, but only by two low-throughput microgram-scale physical means: a cosputtering technique⁵ and a gas aggregation technique.⁶ Other reports of Pt/Y NPs synthesized by chemical means do not have firm evidence of a Pt_nY IM phase.⁷

A solution-phase chemical synthesis of early metal IMs is difficult because of the early metals' extreme oxygen affinity and very negative reduction potentials: -2.37 V for Y^{3+}/Y as opposed to +1.2 V for Pt²⁺/Pt. Indeed, a recent review described it as "almost impossible".8 The strict absence of oxygen and water-or any protic solvent, making the wellstudied polyol process⁹ unworkable—is an absolute necessity, and only the strongest reducing agents can work. For example, *n*BuLi can be added to Au NPs to form Au₃Li,¹⁰ and KEt₃BH is strong enough to reduce TiCl₄ with PtCl₄ together in tetrahydrofuran (THF) to form Pt₃Ti NPs after annealing.¹¹ Another challenge is the high temperature sometimes needed to achieve the structural ordering of the active IM phase rather than the disordered alloy; this rules out organic surfactants during the annealing step, as they will decompose and potentially contaminate the NP surfaces. Rather, salt¹² and oxide¹³ matrices can be used to prevent sintering and control the particle size during annealing.

We initially targeted alkali metal triethylborohydrides as strong reducing agents for their ability to reduce early metal halides such as TiCl₄ in THF¹⁴ and its success for other Pd and Pt IM phases.^{11,12,15} In our hands, YCl₃ could not be reduced with KEt₃BH in THF, and if PtCl₄ was included in the reaction, only pure Pt was observed. This is consistent with the past characterization of an Y³⁺ complex with two Et₃BH⁻ ligands.¹⁶ In searching for more extreme reducing conditions, we noted that the melting points of the solvent-free triethylborohydrides are quite low: 30° and 95 °C for the Na and K salts, respectively. Although only commercially available as solutions in THF or toluene, they can be isolated as white, crystalline

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Scheme 1. Process Scheme for the Synthesis of Pt₃Y Nanoparticles



powders if handled carefully.¹⁷ Therefore, we hypothesized that a molten triethylborohydride salt could be the extremely reducing environment that could (1) reduce yttrium and (2) afford NPs. Molten salt "solvents" have been used to great effect in the synthesis and processing of NPs.¹⁸ Moreover, as long as halide salts of platinum and yttrium were used, the byproduct NaX or KX salts would stabilize the newly formed Pt/Y NPs toward sintering and growth as observed for similar Pt/M NPs in an excess of KCl.^{12,19}

Mixing PtCl₄, YCl₃, and KEt₃BH as solids at room temperature affords no reaction: the orange color of PtCl₄ does not change. However, heating the mixture past the melting point of KEt₃BH turns the mixture black, consistent with metal NP formation (Scheme 1; see the Supporting Information (SI) for experimental details). The molten salt solution is then heated to 200 °C for 30-60 min to ensure completion. After cooling, liquid BEt₃ is observed above a black precipitate. The excess borohydride and byproduct borane are washed away with thoroughly dried THF and hexane under strictly air- and water-free conditions. The resulting gray or black powder is sealed in a quartz tube under vacuum and annealed at 650 °C for 2 h. The resulting Pt₃Y NPs are released from the salt matrix by washing with water in the presence of a carbon support, affording supported Pt₃Y NPs. Any Y₂O₃ formed from the excess YCl₃ is removed with acid.

Transmission electron microscopy (TEM) images of the NPs show their sizes to be between 5 and 20 nm, with some larger agglomerates (Figure 1). Collection of energy-dispersive X-ray spectroscopy (EDS) spectra on multiple areas of the TEM grid confirm a Pt/Y ratio of 3:1 (Figure S1). High-resolution TEM (HRTEM) images show a lattice spacing of ~2.35 Å, more consistent with Pt₃Y (111 at 2.35 Å) than Pt (111 at 2.27 Å) (Figure 1c,d). The polydispersity observed is consistent with those of other salt-stabilized IM particles that had only a small excess of salt—15 KCl per Pt₃Fe afforded similarly polydisperse particles in past literature.¹² On the basis of the stoichiometry of our system—21 KCl formed per Pt₃Y—some polydispersity is therefore expected.

Crystalline IM Pt₃Y was also confirmed by powder X-ray diffraction (PXRD) (Figure 2). The PXRD pattern could be indexed left-shifted from the pure Pt reference, indicating an expansion of the unit cell of pure metallic Pt stemming from the higher atomic radius of Y (180 pm) compared with Pt (135 pm). In detail, the 111 reflection is observed at $2\theta = 44^{\circ}$, compared with $2\theta = 46.5^{\circ}$ for pure Pt (Figure 2; Co X-ray source, $\lambda = 1.79$ Å). Most tellingly, the presence of the 100, 110, 210, 211, 221, and 310 reflections confirms the formation of the ordered IM Pt₃Y phase in the cubic Cu₃Au structure type (space group $Pm\overline{3}m$) rather than a disordered alloy. One should note that the observed diffraction patterns are shifted from those found in the databases for Pt₃Y, representing an increase of ~1% in the unit cell edge from a = 4.069(3) Å



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Figure 1. (a, b) TEM images of Pt_3Y NPs (black particles) dispersed onto a carbon support (gray matrix). (c) HRTEM image of a Pt_3Y NP (scale bar = 2 nm) and (d) its corresponding FFT image.



Figure 2. PXRD patterns of Pt₃M and Pt NPs synthesized in molten NaEt₃BH and KEt₃BH, respectively. The blue, green, red, and purple lines represent database patterns for Pt₃Y (PDF 03-065-5161), Pt₃Lu (PDF 03-065-5757), Pt₃Sc (PDF 03-065-8049), and Pt (PDF 00-004-0802). The gray line is a guide to show the smaller Pt₃Lu, Pt₃Sc, and Pt unit cells compared with that of Pt₃Y. The insets emphasize the presence of reflections for the ordered IM $Pm\overline{3}m$ Pt₃M phases. The peak at 30° is from the carbon support. $\lambda = 1.79$ Å (Co K α).

(PDF 03-065-5161) to a = 4.126(2) Å. Others have observed similar unit cell expansions in IM NPs. Sun and co-workers observed an expansion in PtFe NPs after annealing at 750 °C to form the face-centered tetragonal IM phase¹³—citing NP surface effects and imperfect phase formation—as did Peter and co-workers in their synthesis of Pd₂Ge—citing Ge deficiency.¹⁵ Another possible explanation is interstitial hydride: as the reducing agent is a hydride donor, platinum and yttrium hydride intermediates are likely, and residual hydride may be present even after annealing. The Pt-only control experiment afforded Pt⁰ NPs with no unit cell expansion (Figure 2), suggesting that Y is responsible for the imperfect phase formation and/or inclusion of hydride. Similar unit cell expansions have been observed in the nickel—metal hydride literature for substoichiometric interstitial hydride.²⁰

X-ray photoelectron spectroscopy (XPS) characterization²¹ confirmed the presence of Y⁰. A low photon energy of 350 eV-kinetic energy of 190 eV for the Y 3d region-probes 0.6 nm into the surface²² and shows Y_2O_3 at 158.5 and 160.5 eV with a small Y⁰ peak at 155.8 eV (Figure 3a). A higher photon energy of 760 eV (KE = 600 eV) probes 1 nm into the surface, and the Y⁰ signal becomes more pronounced (Figure 3b). This depth profiling suggests oxidation of Y⁰ from the surface layers and retention of Y^0 below ca. 1 nm, as has been seen in the literature for bulk Pt/Y IM.²³ Both photon energies show pure Pt⁰ (Figure S2). These observations are consistent with EDS mapping of the Pt_xY NPs synthesized by gas aggregation, which showed a Pt overlayer of ~ 1 nm over the IM phase containing the Y^{0.6a} After a further, unoptimized acid treatment at 80 °C, the Y_2O_3 decreases relative to the Y^0 (Figure S3), suggesting that further optimization of the acid treatment could lead to a clean NP surface, which is key for future applications. Also of note for catalyst applications is the fact that across multiple samples no peaks in the chloride 2p region were observed.

After verification that Pt_3Y was successfully formed, optimization of the process was undertaken. Initially, a large excess of borohydride was used—ca. 4–5-fold excess—for the practical reason that stirring was poor without enough molten salt. Much of the excess (now only 1.5-fold needed) could be replaced with a small amount of an inert, high-boiling liquid such as dioctyl ether, 1,3-diisopropylbenzene, or trioctylamine. This helped stirring and afforded a cleaner product (Figure S4). NaEt₃BH was also found to work well; notably, in control experiments without YCl₃, Pt₂Na was observed with NaEt₃BH, while only Pt⁰ was observed with KEt₃BH, consistent with Pt/K alloy formation being thermodynamically disfavored (Figure S5).¹

TEM and XRD characterization before and after annealing gives some insight into the mechanism of the reaction. After the heating to 200 °C and washing with THF/hexanes but before the 650 °C annealing, NaCl or KCl is the only phase observed by XRD, with very broad Pt⁰ visible in some cases (Figure S6).No crystalline yttrium-containing phases are visible, suggesting that they either remain amorphous or are already incorporated into the Pt as a disordered alloy (Pt,Y, in Scheme 1). It is clear that the yttrium does react in some way, for if it remained as YCl₃ it would be washed away with the THF. As proposed for the Pt₃Ti and Pt₃V syntheses in the literature,¹¹ an yttrium hydride intermediate is likely $(YH_x \text{ and } Pt_xY_yH_z \text{ in }$ Scheme 1). TEM shows small (<4 nm) particles in the salt matrix, consistent with the very broadened XRD pattern (Figure S7). After annealing to 650 °C under vacuum, Pt₃Y, KCl or NaCl, and Y_2O_3 are observed by XRD (Figure S6). It is



Figure 3. XPS spectra of Pt_3Y NPs drop-cast onto a gold substrate, focused on the Y 3d region. Photon energies of (a) 350 and (b) 760 eV were used and referenced to the Au $4f_{7/2}$ peak (84.0 eV) at each respective photon energy. See the SI for fitting parameters.

not clear how the excess yttrium in the reaction is converted to the oxide; possibly trace oxygen impurities are introduced during the tube sealing process. Also of note in Figure S6 is the clear broadening of the Pt_3Y peak relative to the sharp KCl peaks; Scherrer analysis gives crystalline domain diameter as ca. 10–15 nm, consistent with TEM of the particles dispersed in the salt matrix (Figure S7) and after acid treatment.

Pt₃Sc and Pt₃Lu were also synthesized, affording similar particle sizes (Figure S8) and correspondingly smaller unit cells as observed by XRD (Figure 2). Like Pt₃Y, the unit cell edge expands ~1% (Table S1). EDS confirmed the presence of Sc and Lu after acid washes (Figure S9, S10). When PtCl₄ is replaced with AuCl₃, Au₂Y is observed with a Au₂Na impurity (Figure S11).

In conclusion, the trialkylborohydride molten salt has proven itself as a highly reducing reaction medium, affording the first chemical synthesis of the Pt₃Y IM phase in nanoparticle form. The NPs are 5-20 nm in diameter, with some larger agglomerates, and the process can be generalized to other difficult early-late IM phases. Incorporation of additional salt matrix to help control the particle size is a crucial further point for improvement, as is leaching of the particles from the salt and stabilization as a colloidal suspension by organic ligands for further processing. We predict that this method will be applicable to not only other difficult-to-reduce metals and metal combinations but also other chemistries that need a polar, harshly reducing environment as supplied by the trialkylborohydride molten salt. Increasing the scale, optimization of the particle/support system, and incorporation into electrochemical and gas-phase reactors are ongoing for catalyst applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01366.

Procedures for NP formation and support incorporation and further TEM, XRD, EDX, and XPS analysis (PDF)

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Notes

The authors declare no competing financial interest.

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