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, Pt₃Na, and Au₃Y.

The 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. 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. Norskov 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. Indeed, bulk polycrystalline electrodes of Pt₃Y were 6–10 times more active than pure Pt at 0.9–0.87 V vs RHE. Other Pt IM phases such as Pt₃Tb, Pt₃Gd, and Pt₃Ca are also good ORR catalysts. Outside of catalysis, IMs of the alkali metals with Au are predicted to be good candidates for plasmonic applications.

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 technique and a gas aggregation technique. Other reports of Pt/Y NPs synthesized by chemical means do not have firm evidence of a Pt₃Y IM phase.

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 Y³⁺/Y as opposed to +1.2 V for Pt²⁺/Pt. Indeed, a recent review described it as “almost impossible.” The strict absence of oxygen and water—or any protic solvent, making the well-studied polyl process unworkable—is an absolute necessity, and only the strongest reducing agents can work. For example, nBuLi can be added to Au NPs to form Au₃Li, and KEt₃BH is strong enough to reduce TiCl₄ with PtCl₄ together in tetrahydrofuran (THF) to form Pt₃Ti NPs after annealing. 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, salt and oxide 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 THF and its success for other Pd and Pt IM phases. 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. 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...
powders if handled carefully.

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.

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.

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.

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 2θ = 44°, compared with 2θ = 46.5° for pure Pt (Figure 2; Co X-ray source, λ = 1.79 Å). Most tellingly, the presence of the 100, 110, 210, 211, and 310 reflections confirms the formation of the ordered IM Pt₃Y phase in the cubic Cu₃Au structure type (space group Fm3m) 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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samples no peaks in the chloride 2p region were observed.
note for catalyst applications is the fact that across multiple
that further optimization of the acid treatment could lead to a
alloy formation being thermodynamically disfavored (Figure
incorporated into the Pt as a disordered alloy (Pt
suggesting that they either remain amorphous or are already
form the face-centered tetragonal IM phase 13

X-ray photoelectron spectroscopy (XPS) characterization 21
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 surface 22 and shows Y2O3 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 Y0 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
coloring of the Pt3Y NPs synthesized by gas aggregation, which
showed a Pt overlayer of ~1 nm over the IM phase containing
the Y0. 6a After a further, unoptimized acid treatment at 80
°C, the Y0 overlayer decreases relative to the Y0 (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 Pt3Y 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.
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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, Au3Y is observed with a Au3Na 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
cult-to-reduce metals and

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)

ASSOCIATED CONTENT
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Diagrams

Figure 3. XPS spectra of Pt3Y 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 4f7/2 peak (84.0 eV) at each respective photon energy. See the SI for fitting parameters.

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5674
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5674
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