

Synthesis and Reactivity of Volatile Compounds for Materials Applications

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Elemental boron is a highly attractive fuel for propellants and explosives.^{1,2} Of all the chemical elements, boron has the highest volumetric heat of combustion (33.4 kcal/cm³) and the third highest gravimetric heat of combustion (14.1 kcal/g), after H₂ and Be. These values are over 3 times higher per unit volume, and 1.4 times higher per unit mass, than those of hydrocarbon fuels.^{3,4} In order to increase the rate of energy release during the combustion of boron and make it a more attractive fuel for propellants and explosives, it is advantageous to prepare it in a nanoparticulate form.

Boron nanoparticles were prepared by gas phase pyrolysis of decaborane. The particles are >97 % boron and free of hydrogen as judged by combustion analysis. Typical recovered yields are 40 %. In order to incorporate nanoparticles into larger assemblies and to stabilize them for long term storage under ambient conditions, it is desirable to functionalize their surfaces. Treatment of the boron nanoparticles with a ~6 mol percent benzene solution of XeF₂ (a convenient fluorinating agent), yields boron particles whose surfaces are fluoride terminated.

Thermogravimetric analyses (TGA) conducted in pure oxygen show that surface fluorination of the boron nanoparticle causes an increase in the onset temperature of oxidation and increases the overall yield of oxidation products (Figure 1).

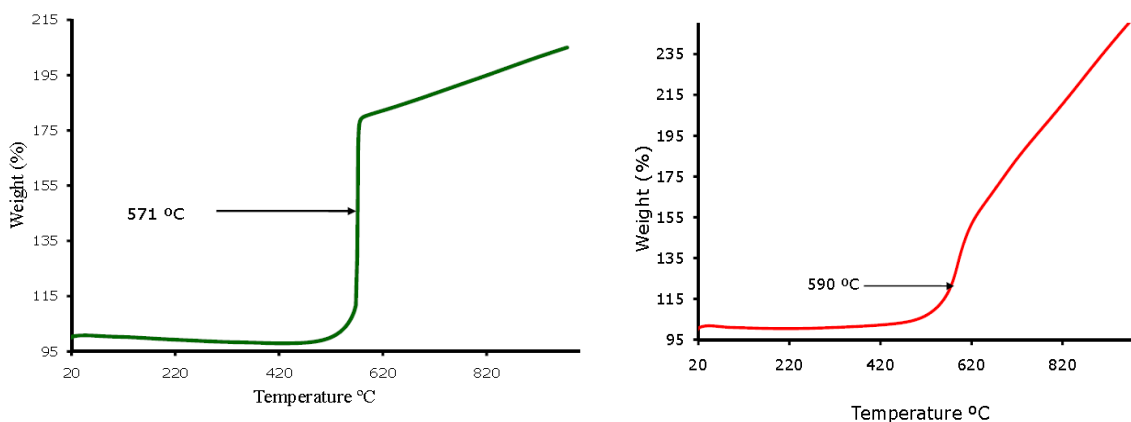


Figure 1. TGA studies under pure oxygen of the unfunctionalized boron nanoparticles (left) and the fluorine terminated boron nanoparticles (right).

High energy nanomaterials such as nanothermites⁵⁻⁷ and Al nanoparticles⁷ have been a topic of increasing research for applications as propellants and explosives.^{8,9} It is well known that a strong correlation often exists between the energy density of a nanomaterial and its sensitivity; a related issue is that nanoparticles are strongly driven to agglomerate and densify,

owing to their relatively high surface free energies.¹⁰ One approach to addressing these problems is to passivate the nanomaterials by functionalizing their surfaces.¹¹ In 2005, Higa and co-workers claimed that treatment of aluminum particles with solutions of transition metal acetylacetonate (acac) complexes resulted in the deposition of a uniform coat of the zerovalent transition metal that stabilized the nanoparticle toward oxidation.¹²

We find that treatment of aluminum nanoparticles with transition metal acac complexes yields aluminum particles decorated with discrete transition metal nanocrystals (Figure 2) and does not result in a core-shell structure. Powder X-ray diffraction and scanning transmission electron microscopy (STEM) analysis of the particles reveals the nanocrystals vary in size depending on the transition metal. For platinum a narrow size distribution of small nanocrystals (1-3 nm) decorate the surface of the aluminum particles whereas for gold a broad size distribution of nanocrystals (2-70 nm) decorate the surface.

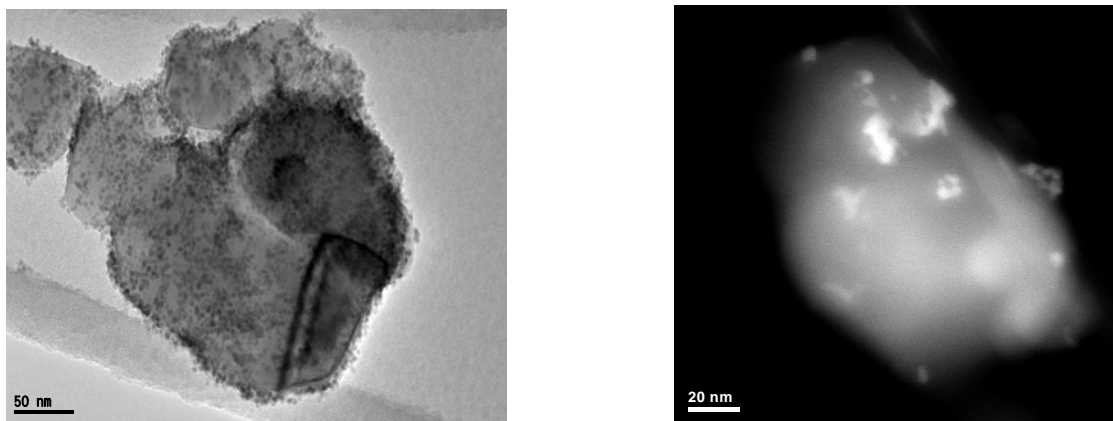


Figure 2. Representative TEM and (S)-TEM micrographs of nickel (left) and palladium (right) nanocrystals decorating the surface of aluminum nanoparticles.

Copper alkene complexes play a number of important roles in chemistry and biology. For example, they have been used as chemical vapor deposition (CVD) precursors¹³ and as atomic layer deposition (ALD) precursors¹⁴ for copper metal. In order to explore the preparation of new types of copper alkene complexes for CVD and ALD applications, we have investigated the structures and metal-alkene binding studies of copper(I) triflate of three chelating tri-alkenes: the cis,cis,trans (cct), cis,trans,trans (ctt), and trans,trans,trans (ttt) isomers of 1,5,9-cyclododecatriene (cdt). The X-ray crystal structures show that, in all three compounds, the triflate ligand and all three C=C double bonds of the triene are bound to the copper center, which adopts a distorted tetrahedral coordination geometry. Competitive binding studies in toluene show that free energy of the copper ctt complex is lowest, and that the free energies of the ttt and cct isomers are higher by 0.3 and 3.7 ± 0.1 kcal mol⁻¹, respectively. For the ttt and cct isomers, binding to the metal is attended by conformational changes that increase the conformational energy of the ring; this increase is a penalty that destabilizes the resulting copper complexes relative to that of the ctt isomer.

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