Nanometallurgy of Colloidal Aluminides: Soft Chemical Synthesis of $CuAl_2$ and α/β-CuAl Colloids by Co-Hydrogenolysis of $(AlCp^*)_4$ with $[CpCu(PMe_3)]$

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Received December 2, 2005. Revised Manuscript Received January 23, 2006

In this work, we present a novel soft chemical synthesis to aluminum nanoparticles based on the hydrogenolysis of the metastable organoaluminum (I) compound $(AlCp^*)_4$ (**1**) in mesitylene at 150 °C and 3 bar H_2. Aiming at the development of a general wet-chemical, nonaqueous route to M/E intermetallic nanophases (E = Al, Ga, In), we studied the co-hydrogenolysis of **1** with $[CpCu(PMe_3)]$ (**2**) as the model case aiming at Cu/Al alloyed nanoparticles. One equivalent of **1** combined with 2 equiv of **2** yields the nanocrystalline intermetallic θ-$CuAl_2$ phase ($Cu_{0.33}Al_{0.67}$), as revealed by elemental analysis, powder X-ray diffraction, transmission electron microscopy (TEM), and energy-dispersive X-ray analysis. The obtained $Cu_{0.33}Al_{0.67}$ material was also characterized by the ^{27}Al Knight Shift resonance. Alloy particles $Cu_{1-x}Al_x$ ($0.10 \leq x \leq 0.50$), typically 15 ± 5 nm (TEM) in size, are accessible as colloidal solutions by variation of the molar ratio of **1** and **2** and by the addition of poly(2,6-dimethyl-1,4-phenylene oxide) during hydrogenolysis. The ^{27}Al NMR Knight Shift resonance moves to high field starting form the value of 1639 ppm for pure nano-aluminum particles to 1486 ppm of $Cu_{0.33}Al_{0.67}$, reaching 1446 ppm for $Cu_{0.50}Al_{0.50}$, and was not detectable for Al contents below 50%. Upon oxidation (controlled exposure to the ambient), a selective oxidation of the Al component, presumably forming core−shell structured $Al_2O_3@Cu_{1-y}Al_y$ ($0.10 \leq y \leq 0.50$) particles, was studied by UV−vis spectroscopy, ^{27}Al magic-angle spinning NMR, and X-ray photoelectron spectroscopy. The Al content can be freely adjusted and lowered down to about 15 atom % ($Cu_{0.85}Al_{0.15}$) without oxidizing the Cu(0) core.