Organometallic Synthesis of Colloidal α-/*β*-NiAl Nanoparticles and Selective Aluminum Oxidation in α-$Ni_{1-x}Al_x$ Nanoalloys

Mirza Cokoja,[†] Harish Parala,[†] Alexander Birkner,[‡] Osama Shekhah,[‡] Maurits W. E. van den Berg,[§] and Roland A. Fischer*[,†]

Lehrstuhl für Anorganische Chemie II—Organometallics and Materials, Lehrstuhl für Physikalische Chemie I, and Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany

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A novel soft chemical synthesis of $Ni_{1-x}Al_x$ nanoparticles ($0.09 \leq x \leq 0.50$) by cohydrogenolysis of [Ni(cod)$_2$] (**1**) with [(AlCp*)$_4$] (**2**) or with [(Me_3N)AlH_3] (**3**) in nonaqueous solution is presented (cod = 1,5-cyclooctadiene, Cp* = 1,2,3,4,5-cyclopentadienyl). The treatment of equimolar amounts of **1** and **2** in mesitylene solution under 3 bar of H_2 at 150 °C gave a brown-black colloidal solution of intermetallic *β*-NiAl particles, characterized by transmission electron microscopy/energy dispersive X-ray analysis (TEM/EDX) and powder X-ray diffraction (XRD). The solution was stable under 3 bar of H_2 at 150 °C for up to 8 h. The *β*-NiAl colloids were treated postsynthesis with ^{17}O-enriched 1-adamantanecarboxylic acid (ACA) as a surface capping group, giving nearly monodisperse α-NiAl colloids that were stable under argon at room temperature for weeks. The coordination of ACA at the α-NiAl surface was studied by ^{17}O NMR and IR spectroscopy. A series of α-$Ni_{1-x}Al_x$ samples with a variety of compositions (x = 0.50, 0.33, 0.25, 0.17, 0.09) were prepared analogously, and the samples were characterized by means of elemental analysis (ICP), XRD, and TEM/EDX. Air oxidation of α-$Ni_{1-x}Al_x$ nanoparticles leads to core−shell particles of the type $(Al_2O_3)_{\delta/2}$@$Ni_{1-x}Al_{x-\delta}$ ($0.09 \leq x \leq 0.50$; $x > \delta$). XRD, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) analyses showed that the Ni core is protected against oxidation down to an Al content of about 10 atom %.