Shrinking of Hollow Cu_2O and NiO Nanoparticles at High Temperatures

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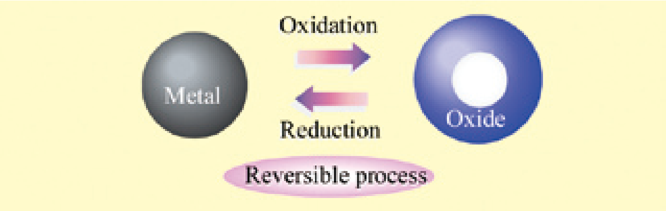
Hollow nanostructures have attracted much attention because their unique shape makes them applicable as delivery vehicles, fillers as well as for catalysis etc. Recently, the formation process of hollow metal-oxide nanoparticles via metal oxidation reactions has been studied for several metal nanoparticles. According to theoretical calculations, hollow nanospheres tend to shrink to solid nanospheres at high temperatures because the surface energy of a solid nanosphere is lower than that of any hollow nanosphere. But, no experimental study on the structural stability of hollow nanoparticles has been performed so far. In this work, shrinkage behavior of hollow Cu_2O and NiO nanoparticles, which were obtained via oxidation of Cu and Ni nanoparticles in air, was studied by transmission electron microscopy.

Hollow Cu_2O and NiO in annealing under 5×10^{-5} Pa were observed to have shrunk at 473 and 623 K, respectively, where the reduction reactions from oxides to metals started. As a result of shrinking associated with reduction, hollow oxides turned into solid metal nanoparticles after annealing at higher temperatures for a long time as shown in Fig. 1. These results indicate that the process, solid metal nanoparticles → hollow oxides, can be reversible by controlling the annealing condition. In addition, hollow oxides shrunk and collapsed through high-temperature oxidation. It was found that shrinking of hollow oxides during oxidation occurs at temperature where the diffusion coefficients of slower diffusing species reach around 10^{-22} m^2s^{-1}. Annealing at high temperatures both in a vacuum and in air leads to atomic movement that results in the annihilation of nano-holes inside hollow nanoparticles, and a consequent reduction in the extra inner-surface energy.



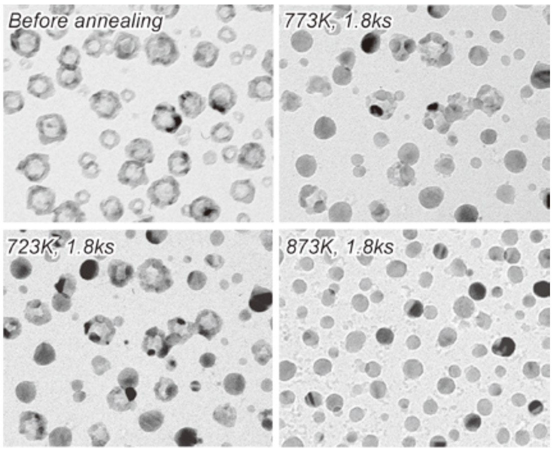


Fig. 1 TEM images showing that hollow NiO shrank into solid Ni nanoparticles in annealing at 5×10^{-5} Pa.

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Intramolecular Arylcyanation of Alkenes Catalyzed by Nickel/$AlMe_2Cl$

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Cleavage of carbon-carbon bonds by transition metals under homogeneous conditions has recently received much scientific and technological interest. The intramolecular arylcyanation of alkenes would be one of the most straightforward reactions in this category. A synergistic catalyst system derived from nickel and co-catalytic $AlMe_2Cl$ is efficient for the reaction by simultaneous activation of carbon-nitrogen triple bond by π-interaction with nickel(0) and σ-interaction with aluminum (Scheme 1). The reaction takes place in an exclusive exo-trig manner to give a wide range of nitriles having a benzylic quaternary carbon in good yields. The asymmetric version of the reaction provides novel access to quaternary stereocenters. It enables us to prepare a synthetic precursor of potent acetylcholinesterase inhibitors as well as an analgesic substance (Fig 1). Characterization of intermediates in the catalytic cycle has also been achieved. Moreover, the molecular structures of key intermediates concerning the cleavage of the carbon-carbon bond were unambiguously identified by X-ray crystallography. In both intermediates, the nitrogen atom of cyano group coordinates to Lewis acidic aluminum center. An important role of $AlMe_2Cl$ is the promotion of the coordination of the cyano group to nickel(0) and of the cleavage of the carbon-carbon bond by synergistic coordination.

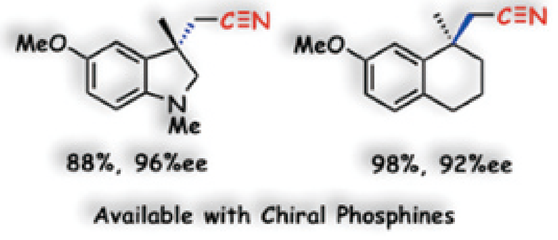
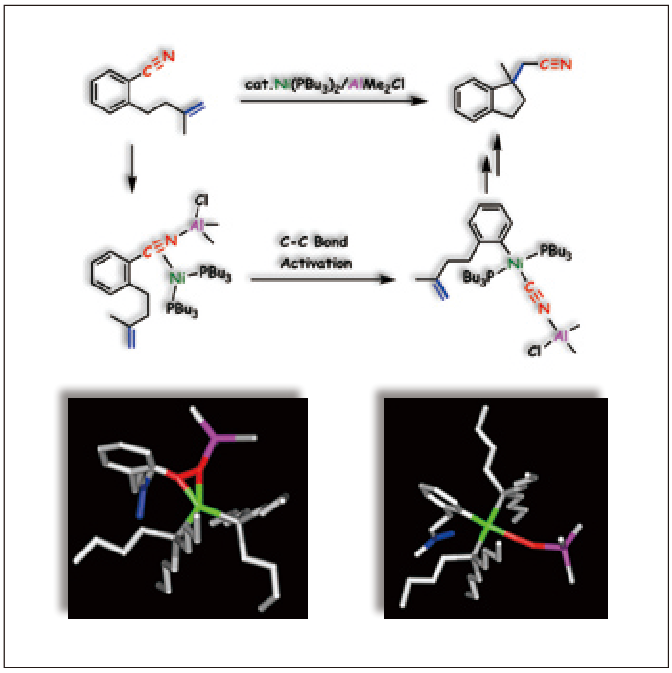


Fig. 1



Scheme 1