OLEYLAMINE STABILIZED PALLADIUM(0) NANOCLUSTERS AS HIGHLY ACTIVE HETEROGENEOUS CATALYST FOR THE DEHYDROGENATION OF AMMONIA BORANE

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ABSTRACT

Palladium(0) nanoclusters having an average particle size of 3.2 nm were generated in situ from the reduction of palladium(II) acetylacetonate in the presence of oleylamine (OAm) during the dehydrogenation of ammonia-borane (AB) in THF under inert gas atmosphere at room temperature. OAm stabilized palladium(0) nanoclusters were stable enough to be isolated as solid materials and characterized by TEM, HRTEM, XRD, UV-Vis and FT-IR techniques. They were found to be highly active catalyst in the hydrogen generation from the dehydrogenation of AB; totally two equivalents of hydrogen gas per AB were generated even at low catalyst concentration and room temperature. The first and second equivalent of H2 generation from AB were completed in ~20 and 100 min, respectively, from the dehydrogenation of AB in the presence palladium(0) nanoclusters corresponding to an initial turnover frequency of 240 h⁻¹ (the best among the heterogeneous palladium catalyst and in the top five among all the catalyst systems tested for the dehydrogenation of AB). ¹¹B-NMR study of the reaction shows that hydrogen evolution likely takes place in one or both of two parallel routes; (i) through the formation of cyclopolyborazane followed by its polymerization to polyborazylene and (ii) through the formation of long-chain B-N linear polymers. Carbon disulfide poisoning experiments indicate that the dehydrogenation of AB catalyzed by OAm stabilized palladium(0) nanoclusters is heterogeneous catalysis. Moreover, the work reported here includes a wealthy collection of kinetic data to determine the rate law and apparent activation energy for the catalytic dehydrogenation of AB.