

Synergistic Dehydrogenation of Dimethylamine-Borane by Oleylamine Stabilized Cu₃₉Pt₆₁ Nanoparticles

Sibel Duman, Hakan Demir

Bingol University, Department of Chemistry
12000, Bingol, TURKEY
sduman@bingol.edu.tr; hakandemir21@hotmail.com

Extended Abstract

Dimethylamine-borane (DMAB) complex (CH₃)₂NHBH₃ is considered to be the most promising candidate for hydrogen applications among all other practical hydrogen storage materials. It has 3.5 H₂%wt and is soluble in solutions (Jaska et al., 2001). More importantly, it is able to release hydrogen via a room-temperature dehydrogenation reaction in the presence of a suitable catalyst (Pun et al., 2007). The catalysts tested for DMAB dehydrogenation have mainly included nanoparticles (NPs) of noble metals Rh (Zahmakiran et al., 2009), Ir (Jaska et al., 2001) and Ru (Duman et al., 2013) which are all unsuitable for practical applications due to their limited resources and high price tags. However, in literature, there are no report concerning the use of non-noble Fe, Ni, Co, Cu and noble Pt catalysts in the DMAB dehydrogenation conditions. Therefore, synthesis of highly efficient bimetallic catalysts with much reduced usage of noble metals Rh, Ir, Ru, and Pt with non-noble metals is desired for dehydrogenation of DMAB.

Herein, we reported in situ generation, characterization, and catalytic activity of 4.8 ± 0.2 nm oleylamine (OAm)-stabilized CuPt NPs in the synergistic dehydrogenation of DMAB at room temperature. In this synthesis, OAm acted as the solvent, surfactant, and reductant. These NPs were reproducibly isolated from the reaction solution by filtration and characterized by TEM, XRD, HRTEM, ICP-OES, ¹¹B NMR, ATR-IR and UV-Visible spectroscopy. Among the 4.8 ± 0.2 nm OAm-stabilized CuPt NPs tested for the dehydrogenation of DMAB, the Cu₃₉Pt₆₁ NPs exhibited the highest catalytic activity and durability at room temperature. We also reported the results of a kinetic study on the hydrogen generation from the dehydrogenation of DMAB catalyzed by OAm-stabilized CuPt NPs depending on the catalyst concentration, substrate concentration, and temperature as well as the activation parameters of catalytic dehydrogenation of DMAB calculated from the kinetic data. Highly active OAm-stabilized Cu₃₉Pt₆₁ NPs providing a release of 1.0 equivalent H₂ per mole of DMAB with initial turnover frequency and activation energy were 121 h⁻¹ and 47 kJmol⁻¹, respectively. The kinetic studies on these Cu₃₉Pt₆₁ NPs reveal that the synergistic dehydrogenation of DMAB is first-order with respect to both catalyst concentration and substrate concentration. The poisoning experiments showed that the synergistic dehydrogenation of DMAB catalyzed by OAm-stabilized Cu₃₉Pt₆₁ NPs is heterogeneous catalysis. Testing the isolability and reusability of OAm-stabilized Cu₃₉Pt₆₁ NPs showed that the isolated and bottled sample of OAm-stabilized Cu₃₉Pt₆₁ NPs is readily dispersible in hexane and remains active in the synergistic dehydrogenation of DMAB. They retain 87% of their initial catalytic activity even at the fifth run with the complete conversion of Me₂NHBH₃ to [Me₂NBH₂]₂ plus 1.0 equivalent of H₂ per mol of DMAB at room temperature. On that account, OAm-stabilized Cu₃₉Pt₆₁ NPs are isolable and reusable heterogeneous catalysts in the synergistic dehydrogenation of DMAB. These results indicate that synthesis of OAm-stabilized CuPt NPs may represent a new approach to replace noble metals for the catalysis for future development of DMAB into a practical hydrogen storage material for renewable energy applications. Moreover, easily isolable, reusable, lower cost than alone Pt, most stability and the high catalytic activity of the in-situ generated OAm stabilized CuPt NPs make them a promising candidate to be employed as a

catalyst in developing highly efficient portable hydrogen generation systems using DMAB as solid hydrogen storage material.

Keywords: CuPt nanoparticles; synergistic dehydrogenation; dimethylamine borane; hydrogen storage.

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