

Supported Crystalline Monodisperse Ga₂O₃ Nanoparticles with Tunable Size for the Catalytic Dehydrogenation of Propane

P. Castro-Fernández¹, A. Fedorov¹, P. M. Abdala¹, C. R. Müller^{1*}

¹ETH Zurich

Crystalline colloidal monodisperse Ga₂O₃ nanoparticles with tunable sizes ranging from 2.5 to 5.2 nm have been prepared from gallium acetylacetonate and oleylamine. Concentrated toluene solutions of these nanoparticles were impregnated onto various supports to give catalysts active for propane dehydrogenation (PDH) with selectivities and activities higher than those of a benchmark catalyst prepared from gallium nitrate. Importantly, this synthesis method allows characterizing Ga₂O₃ nanoparticles prior to their deposition on supports and it leads to active, well-defined supported Ga₂O₃ PDH catalysts amenable for a more direct evaluation of support and particle size effects on catalytic properties.

Conventional synthesis routes for gallium oxide-based catalysts typically use aqueous gallium nitrate solutions for impregnation of supports, followed by calcination.^[1] This approach usually gives ill-defined catalysts with a broad distribution of metal sites. Identification of the catalytically active sites in such systems is very challenging, if not impossible. Here, we report the synthesis of crystalline, ligand-capped Ga₂O₃ nanoparticles with controllable size that form a stable colloidal solution in an organic solvent (toluene). The synthetic methodology to such size-tunable nanoparticles has been developed previously for the preparation of solution-processable gallium oxide quantum dots for optoelectronic applications.^[2] We demonstrate that this method serves as a convenient entry to establish a structure-activity relationship for Ga-based catalysts that includes particle-support interactions, particle size effect and the nature of Ga sites.

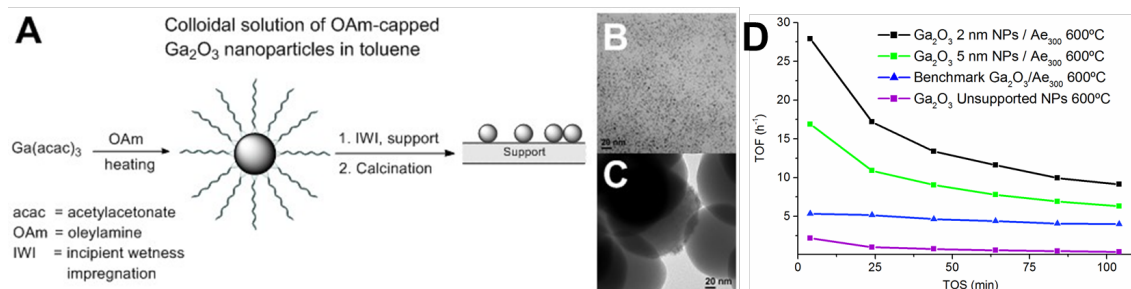


Figure 1. Synthesis of ligand-capped colloidal Ga₂O₃ nanoparticles and their impregnation onto supports (A). TEM images show Ga₂O₃ nanoparticles in a colloidal solution (B) and the same NPs after impregnation and calcination onto silica nanospheres (C). Catalytic performance for propane dehydrogenation at 550 °C (WHSV = 7.2 h⁻¹) (D).

By introducing synthetic protocols from quantum dots chemistry to catalysis, we have successfully produced stable colloidal solutions containing crystalline gallium oxide nanoparticles with controllable sizes. Depositing these nanoparticles onto various supports gives catalysts that are active for propane dehydrogenation. Our results show that colloidal routes allow to prepare catalysts with higher activity and selectivity per total gallium when compared to the benchmark systems obtained through a *conventional* route, i.e. the impregnation of aqueous solutions of Ga(NO₃)₃ on the support. The colloidal approach uses pre-formed, well-defined gallia NPs and therefore allows for a more direct and systematic evaluation of the catalyst performance, an important step towards the development of structure-activity relationships in gallia systems.

[1] Isao Takahara, Masahiro Saito, Megumu Inaba, Kazuhisa Murata, *Catalysis Letters* **2004**, 96, 29–32. [2] Ting Wang, Shokouh S. Farvid, Mutalifu Abulikemu, Pavle V Radovanovic, *Journal of the American Chemical Society* **2010**, 132, 9250–9252.