

In-situ characterization of supported of GaPd₂ catalyst for methanol synthesis

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A nanodispersed intermetallic GaPd₂/SiO₂ catalyst is prepared by simple impregnation of industrially relevant high surface area SiO₂ with Pd and Ga nitrates, followed by drying, calcination and reduction in hydrogen. The catalyst is tested for CO₂ hydrogenation to methanol at ambient pressure, revealing that the intrinsic activity of the GaPd₂/SiO₂ is higher than that of the conventional Cu/ZnO/Al₂O₃, while the production of the undesired CO is lower. A combination of complementary *in situ* and *ex situ* techniques are used to investigate the GaPd₂/SiO₂ catalyst. *In situ* X-ray Diffraction (XRD) show that the GaPd₂ intermetallic phase is formed upon activation of the catalyst via reduction and remains stable during CO₂ hydrogenation. Similar conclusions can be drawn from electron diffraction patterns and images acquired using Environmental TEM (ETEM), indicating that ETEM results are representative for the catalyst treated at ambient pressure. The chemical composition and the crystalline structure of the nanoparticles are identified by Scanning TEM Energy Dispersive X-Ray Spectroscopy (STEM-EDX), Selected Area Electron Diffraction (SAED) and atomically resolved TEM images, as shown in Figure 1.

The catalyst is further optimized in terms of metal content and reduction temperature in relation to the catalytic activity. The intrinsic activity is higher for the GaPd₂/SiO₂ catalyst with a metal loading of 13wt.% compared to catalysts with 23 and 7 wt.% metal loadings. The formation of the active phase revealed by *in situ* XRD of the calcined GaPd₂/SiO₂ catalyst with 23 wt% and 13 wt% metal loadings is compared. Figure 2 shows that the calcined catalyst with 23 wt% metal content reduces to metallic Pd already at room temperature and the GaPd₂ phase starts at 400°C. The calcined catalyst with 13 wt% metal content reduces to metallic Pd already at 140°C and the GaPd₂ phase starts at 300 °C. The reason for the different path can be attributed to the effect of the particle size and active sites which varies with catalyst metal loading.

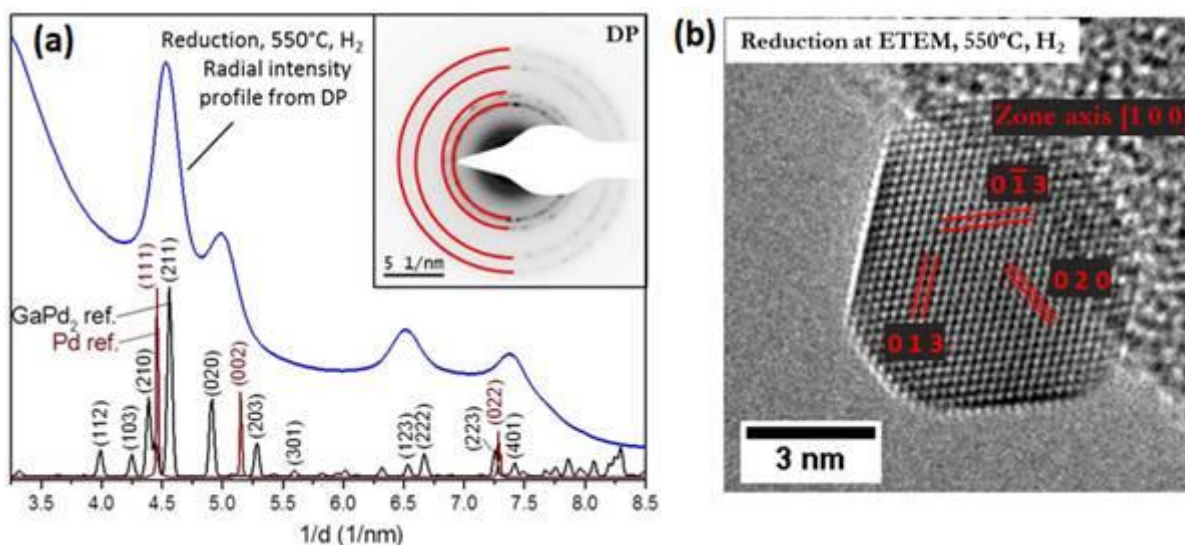


Figure 1. (a) Intensity profiles from diffraction patterns in the insets acquired in the ETEM under reduction conditions (550 °C, 4 mbar H₂). High-resolution TEM image of a GaPd₂ nanoparticle acquired in the ETEM under reduction conditions.

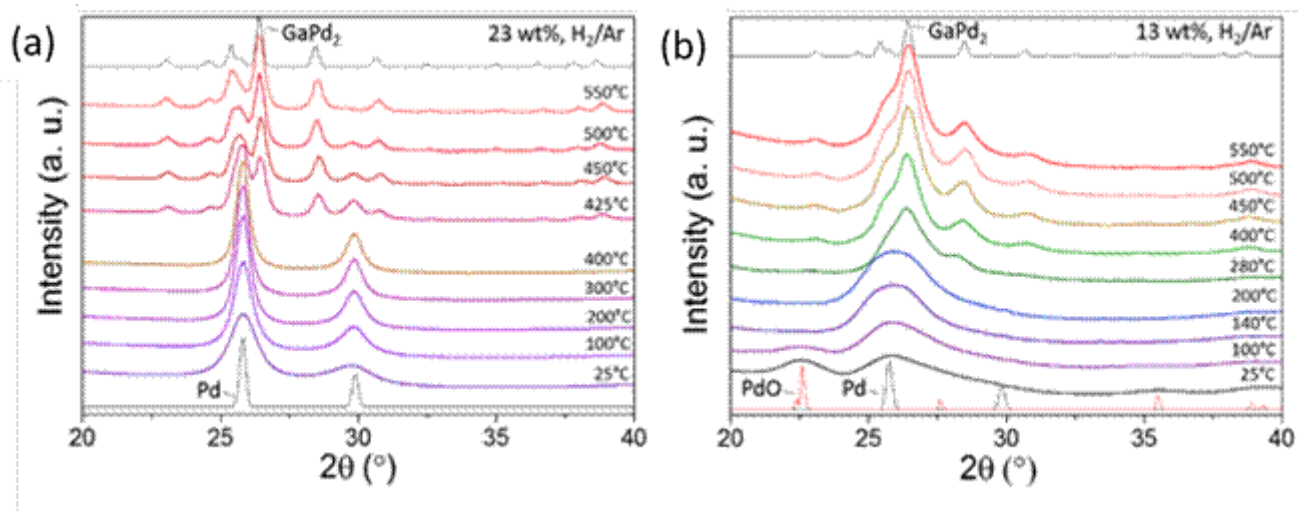


Figure 2. (a) *In-situ* XRD spectra during temperature programmed reduction in a mixture of 25% H_2/Ar acquired from the catalyst with (a) 23 wt% and (b) 13 wt% metal loading.