Electron-microscopic characterization of pure oxide methanol steam reforming catalysts

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Based on the already well-known catalytic methanol steam reforming selectivity of Pd-Ga and Pd-In bimetallic particles supported on the respective oxide supports [1], a detailed structural investigation of different pure oxide model supports (Ga_2O_3, In_2O_3 and SnO_2) by high-resolution transmission electron microscopy, selected area diffraction and electron-energy loss spectroscopy is combined with catalytic studies in the methanol steam reforming reaction to reveal the contribution of the supporting oxide to the activity and selectivity of bimetallic particles.
In order to facilitate structural studies and the subsequent establishment of structure-activity correlations, a thin film model routine has been followed. This concept involves the deposition of the respective oxides by thermal evaporation onto vacuum-cleaved NaCl(001) single crystal planes. Depending on the deposition parameters (substrate temperature, oxygen background pressure, deposition rate) and the structural match of the oxide with the NaCl(001) substrate, epitaxially grown oxide nanoparticles with different shapes and composition could be prepared and their catalytic activity and selectivity examined.
As low substrate temperatures (300 K) in all three cases favor the formation of amorphous films, differences in structure and shape were only detected at higher substrate temperatures. At 600K, Ga_2O_3 films reconstruct into regular, but still amorphous, sphere-like aggregates (Figure 1). Their size is controlled by a re-evaporation/re-oxidation equilibrium of sub-stoichiometric Ga-oxide species present during the evaporation process [2]. In contrast, deposition of In_2O_3 at 600 K under otherwise identical experimental conditions leads to epitaxially grown, well-shaped In_2O_3 nano-pyramides, as judged by SAED and weak-beam dark-field imaging (Figure 2) [3]. Oxidative and reductive film stability, a prerequisite for catalyst stability and regeneration, has also been tested in the temperature range 300 K to 673 K. Film structure and morphology proved to be stable in 1 bar O_2 and 1 bar H_2 at temperatures $T < 673$ K for both Ga_2O_3 and In_2O_3. In contrast to Ga_2O_3, decomposition of In_2O_3 films has been observed in H_2 at temperatures $T \geq 673$ K. This has been addressed to a generally easier reducibility of In_2O_3 compared to Ga_2O_3. The deposition of tin oxide at substrate temperatures $T \geq 473$ K yields epitaxial SnO particles (Figure 3), which can either be transformed to SnO_2 by oxidation at 673 K in 1 bar O_2 or to β-Sn by reduction in 1 bar H_2 at $T \geq 473$ K. In contrast to Ga_2O_3 and In_2O_3, this offers a convenient pathway to trigger the formation of different single tin compounds which can in turn be structurally and catalytically characterized.

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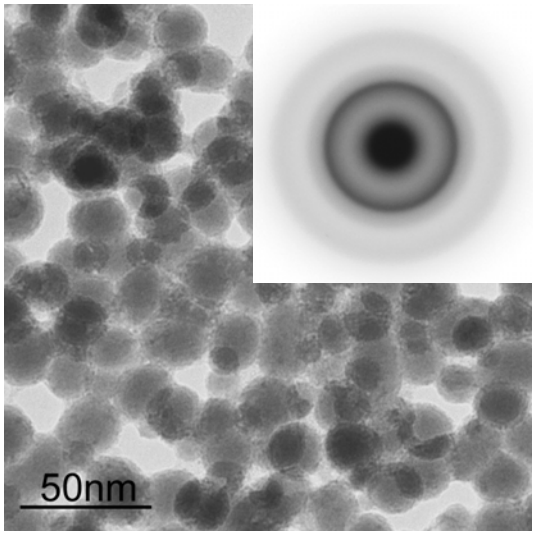

Figure 1

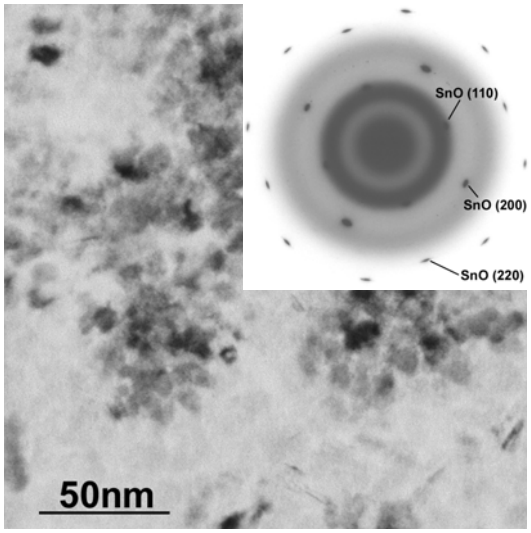

Figure 3

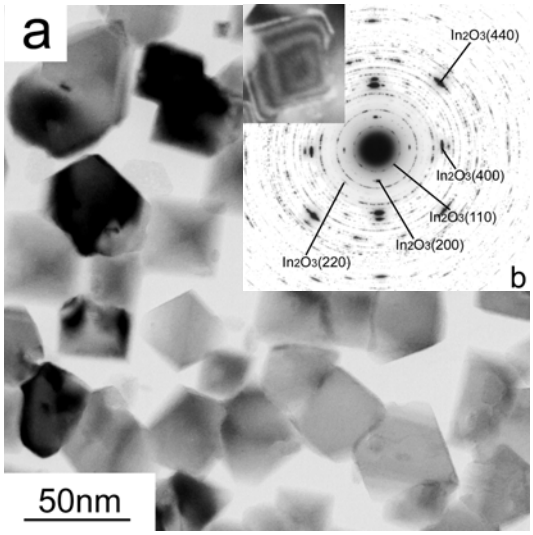

Figure 2