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Structural and Catalytic Investigation of Palladium-Gallium Intermetallic Compounds

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Introduction

Palladium constitutes an important catalyst for hydrogenation (e.g. the hydrogenation of acetylene to ethylene or 1,2-butadien to 1-buten) and for combustion reactions. Typical Pd-catalysts are supported on metal oxides and show high activity but only limited selectivity[1]. The limited selectivity of Pd catalysts may be caused by neighbouring active sites on the catalyst[2-6]. Binary intermetallic compounds prepared by the group of Prof. Y. Grin are stoichiometric compounds with ordered crystallographic structures. These materials are particularly interesting as potential catalysts because of the isolation of the Pd atoms in the structure. In both structures the Pd atoms are surrounded by a coordination sphere of Ga atoms (i.e. coordination number of 7 in PdGa and 8 in Pd_3Ga_7). This site isolation changes the geometry and the electronic structure of the active Pd atoms and may modify adsorption and desorption properties at the catalyst surface[9]. Therefore, this significant difference in the local structures of Pd metal clusters and the Pd-Ga intermetallic compounds permits to tailor the selectivity of palladium catalysts in hydrogenation reactions.

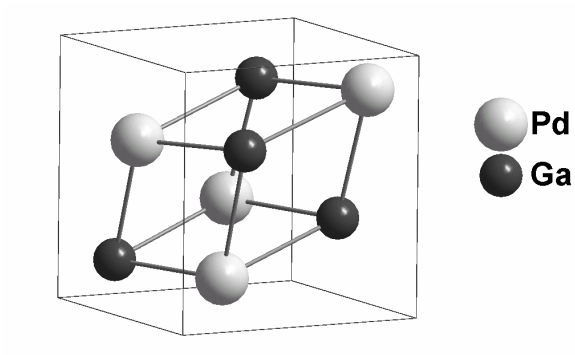


Figure 1: Unit cell of PdGa

Experimental

The thermal stability of PdGa and Pd_3Ga_7 in various atmospheres was investigated by in situ XAS (X-ray absorption spectroscopy) at both the Pd and the Ga K-edge, in situ XRD (X-ray diffraction), and thermal analysis (TG, DSC). The XAS experiments were carried out at beamline X1 and E4 at HASYLAB and Id24 at ESRF. Catalytic studies were carried out in a 4 ml cell reactor with MS detection and the surface area was determined by BET measurements and CO adsorption.

Results

BET measurements of the ground samples resulted in a surface area of 1-2 m^2/g for both compounds. The structural evolution of PdGa and Pd_3Ga_7 in helium, hydrogen, and oxygen in the temperature range from 293 to 773 K shows that the palladium-gallium ICs are stable under these conditions. Also no phase transition in this temperature range and no oxidation within the detection limit of XAS and XRD were observed. In 100% H_2 anomalous trends of the interatomic distances and XAS Debye-Waller factors were observed. These may correspond to the incorporation of hydrogen in the structure of the IC and to the onset of catalytic activity.

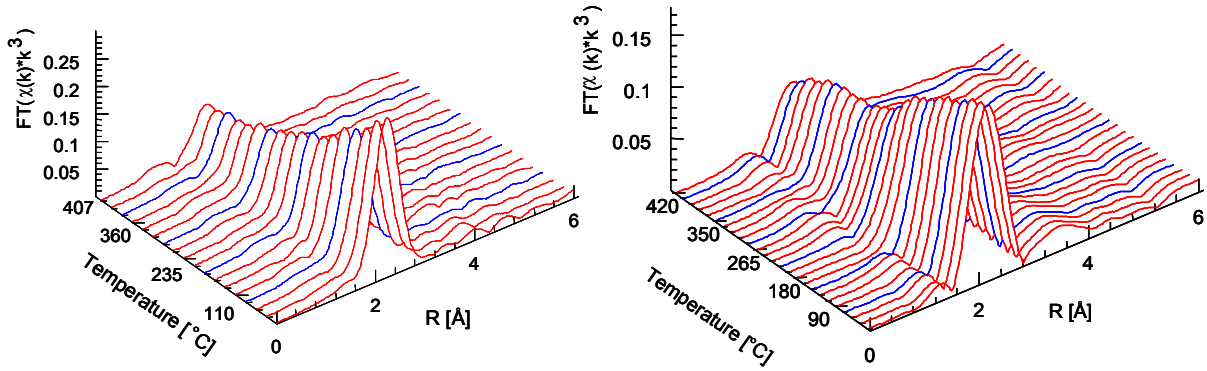
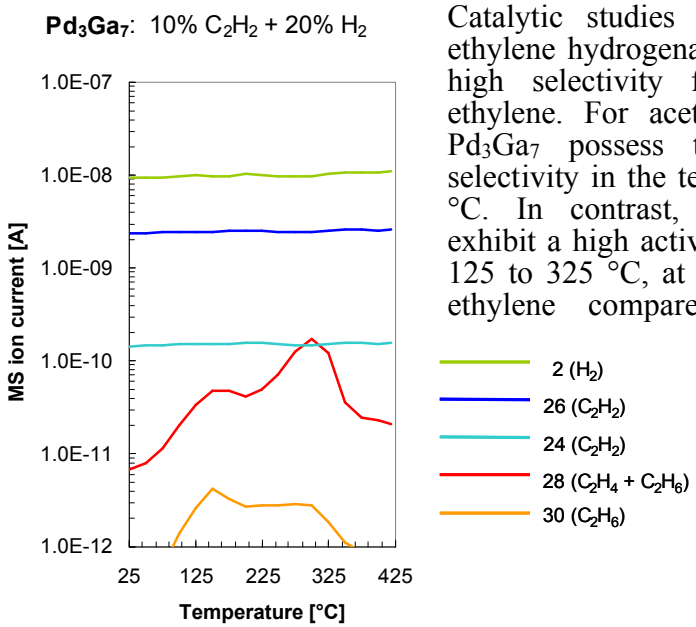


Figure 2: In situ EXAFS at Pd K-edge of Pd_3Ga_7 in 20% O_2 (left) and 100% H_2 (right).



Catalytic studies show activity for propene and ethylene hydrogenation, for CO oxidation as well as high selectivity for acetylene hydrogenation to ethylene. For acetylene hydrogenation, PdGa and Pd_3Ga_7 possess the maximum in activity and selectivity in the temperature range from 275 to 325 °C. In contrast, commercial Pd/Al_2O_3 catalysts exhibit a high activity in the temperature range from 125 to 325 °C, at a much lower selectivity towards ethylene compared to the PdGa intermetallic compounds. The low surface area of the PdGa was considerably increased by mechanical treatment (ball milling) which results in a solid with much higher activity while the structure, stability and selectivity of PdGa is retained.

Figure 3: Acetylene hydrogenation with Pd_3Ga_7. The MS ion current for m/z= 28 shows the formation of C_2H_4 and/or C_2H_6. The ion current m/z= 30 shows the formation of C_2H_6.

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