Structural and Catalytic Investigation of Palladium-Gallium Intermetallic Compounds

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Introduction

Palladium in catalysis

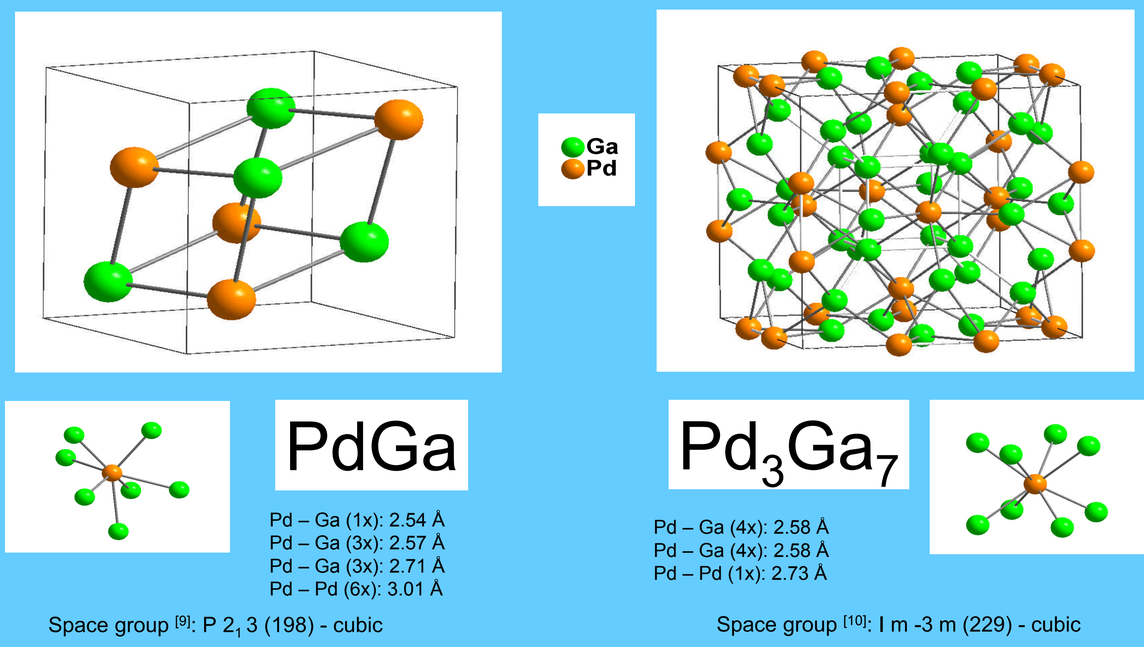
Acetylene hydrogenation to ethylene ($C_2H_2 + H_2 \rightarrow C_2H_4$) is a common method to remove traces of acetylene in the ethylene feed for the production of polyethylene [1]. Typical supported Pd catalysts show high activity but only limited selectivity and limited stability [1].

Increase of selectivity

Elimination of hydride formation [2,3].
Active site isolation [4,5].
Modification of electronic structure and thermodynamic properties [6,7,8].

Palladium intermetallic compounds

Pd-Ga intermetallic compounds are particular interesting as potential catalysts because of the isolation of Pd atoms in the structure.



Goal

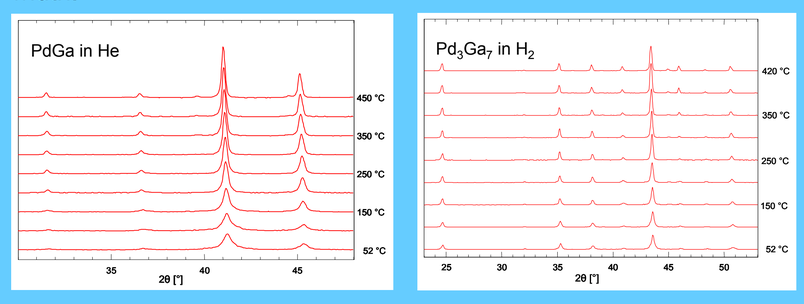
Determine thermal stability in different gas atmospheres with in situ XRD, in situ XAS measurements and thermal analysis, CO chemisorption and investigation of selectivity and reactivity for catalytic hydrogenation of acetylene.

Preparation

m Pd + n Ga $\rightarrow$ Pd_mGa_n by melting of approximate amounts of Pd and Ga (1:1 and 3:7) in a glassy carbon crucible under Ar atmosphere in a high frequency induction furnace. The samples were powdered in a ball mill.

In situ XRD

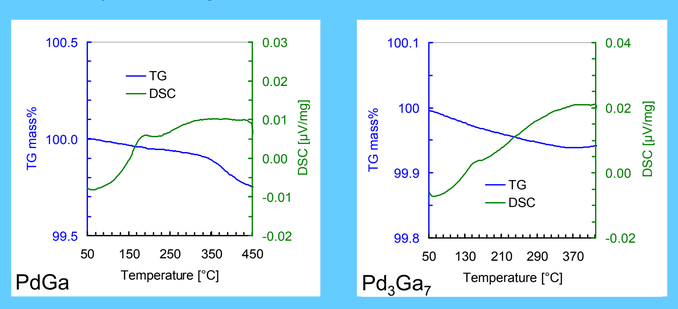
Determination of the structural stability in helium and hydrogen using in situ XRD. Only thermal lattice expansion and no phase transition was observable. Increasing particle size lead to decreasing line width.



In situ XRD measurements were conducted using a STOE diffractometer with Cu-Kα radiation in *Bragg-Brentano* geometry (secondary monochromator) equipped with a Bühler HDK chamber.

TG / DSC

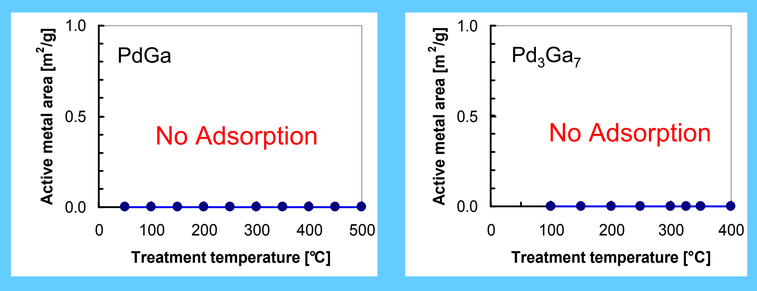
Thermal analysis of PdGa and Pd_3Ga_7 in hydrogen: The slight mass lost for both samples are due to the reduction of a surface oxide layer and the exothermic DSC peaks are induced by sintering effects.



Thermogravimetry and Differential Scanning Calorimetry were carried out in a Netzsch STA 449.

CO Chemisorption

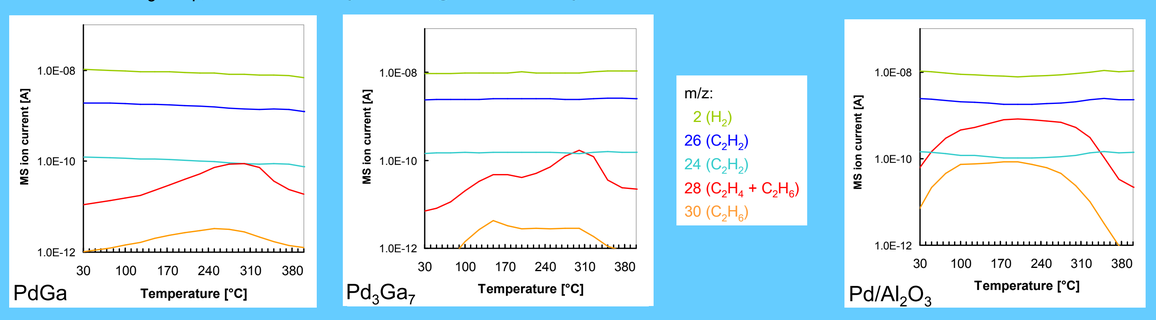
Investigation of the surface stability: hydrogen treatment at elevated temperature with following CO chemisorption to detect surface decomposition and Pd segregation.



CO chemisorption carried out in the Autosorb1C (Quantachrome Instruments). The pretreatment performed by 30 min of isothermal hydrogen treatment and a following evacuation. CO chemisorption measurements carried out at 298 K.

Catalysis: $C_2H_2 + H_2 \rightarrow C_2H_4$

Acetylene hydrogenation with PdGa, Pd_3Ga_7 and reference Pd/Al_2O_3 in 10% C_2H_2 and 20% H_2. Both, PdGa and Pd_3Ga_7, show activity and high selectivity



The data were obtained with the XAS set-up (see in situ EXAFS box) with a total gas flow of 20 ml/min. The amount of catalyst was PdGa (5 mg), Pd_3Ga_7 (6 mg) and reference Pd/Al_2O_3 (0.5 mg, 5 wt%).
The MS ion current for m/z= 28 (red) shows the formation of C_2H_4 and/or C_2H_6. The ion current for m/z= 30 (yellow) shows the formation of the by-product C_2H_6.

Results

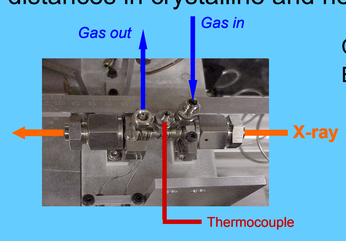
<u>Bulk characterisation of PdGa + Pd_3Ga_7</u>
High thermal stability under different atmospheres. Annealing of the ballmilling samples lead to sintering.

<u>Catalytic studies of PdGa + Pd_3Ga_7: Preliminary results</u>
The Pd-Ga alloys show activity for hydrogenation reactions.
The selectivity for the hydrogenation of acetylene to ethylene is higher compared to the commercial catalyst Pd on Al_2O_3.

<u>CO chemisorption</u>
No surface decomposition and Pd segregation detectable.

In situ EXAFS

In situ XAS in hydrogen and during acetylene hydrogenation is used for determination of the thermal stability and the detection of a possible hydrogen inclusion. In contrast to in situ XRD which provides structures and lattice parameters of crystalline phases EXAFS gives information about single atomic distances in crystalline and non-crystalline phases.

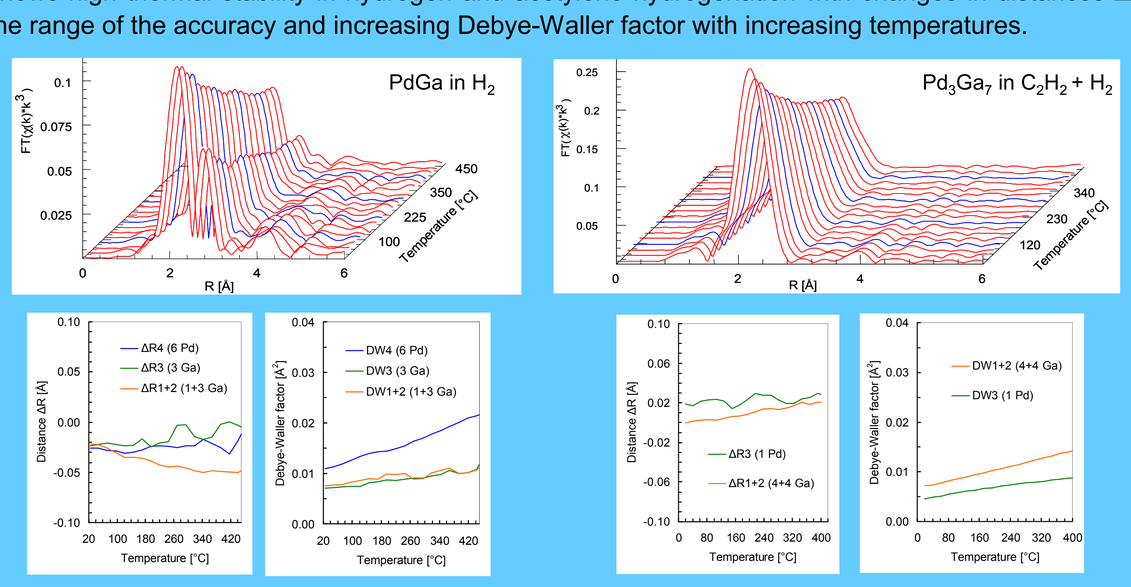


Cell for in situ XAS studies
EXAFS measured at HASYLAB X1 (Hamburg) at Pd K-edge (24.35 keV).

Cell parameters:	
Cell volume:	4 ml
Sample diameter:	5 mm pellet
Cell windows:	Al foil
Gas in:	Gas flow controller
Gas out:	Exhaust with MS detection

Reaction parameters:	
Sample mass:	9-11 mg
Diluent:	30 mg BN
Gas flow:	30-40 ml/min
Heating rate:	6 K/min

Radial distribution function of PdGa in hydrogen and Pd_3Ga_7 in acetylene hydrogenation. Diagrams below show selected refined distances and Debye-Waller factors. In situ EXAFS of PdGa and Pd_3Ga_7 shows high thermal stability in hydrogen and acetylene hydrogenation with changes in distances ΔR in the range of the accuracy and increasing Debye-Waller factor with increasing temperatures.



The theoretical EXAFS functions were calculated with FEFF 8 from crystallographic data and refined with WinXAS in R space.

Outlook

- Further preparation of high surface area samples.
- Quantitative catalytic studies.
- Surface investigation with XPS, IR and ISS.

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Literature

[1] G. Ertl, H. Knoezinger, J. Weitkamp: Handbook of heterogeneous catalysis, VCH, 1997
[2] W. Palczewska in Hydrogen Effects in Catalysis, Eds: Z. Paal, P.G. Denon, New York, (1988) 372-397
[3] G.C. Bond, P.B. Wells, *J. Cat.* 5 (1966) 65-74
[4] E.W. Shin, S.H. Moon et al. *Catal. Today* 44, (1998) 137-143
[5] S. Leviness, L. Guczi et al. *J Mol. Cat.* 25 (1984) 131-140
[6] D.C. Huang, W.F. Huang et al. *Catal. Lett.* 53 (1998) 155-159
[7] S. Verdier, D.Uzio et al. *J. Cat.* 218 (2003) 288-295
[8] P. Miegge, J.C. Bertolini et al. *J. Cat.* 149 (1994) 404-413
[9] E. Hellner, F. Laves, *Z. Naturforsch.* 2a (1947) 177-183
[10] H. Pfisterer, K. Schubert, *Z. Metallkunde* 41 (1950) 433-441