Structural and Catalytic Investigation of Active Site Isolation in Pd-Ga 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, 2]. Conventional supported Pd catalysts show high activity but only limited selectivity and limited stability.

Increase of selectivity

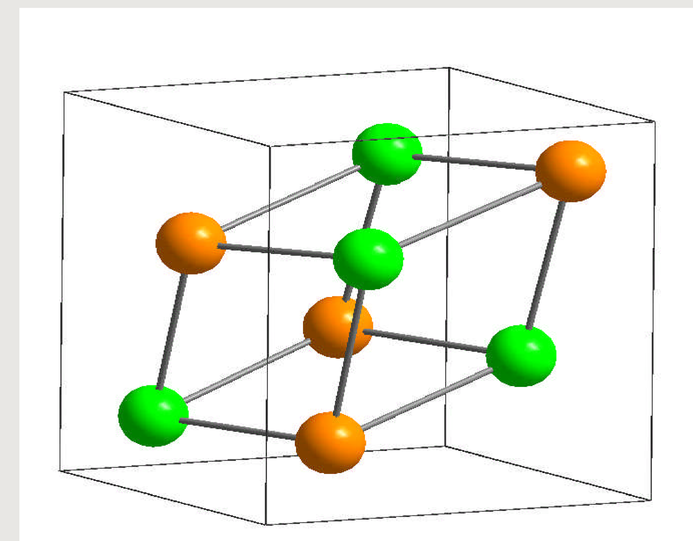
Active site isolation [3-5].
Elimination of hydride formation [6-8].

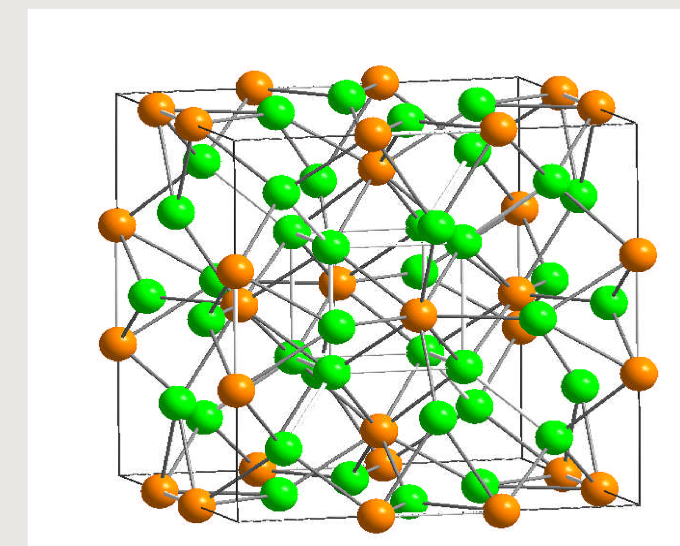
Palladium intermetallic compounds

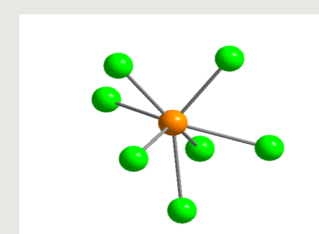
Pd-Ga intermetallic compounds are particular interesting as potential catalysts because of the isolation of Pd atoms in the structure.

Goal

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





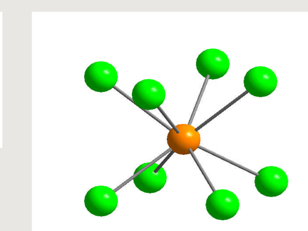


PdGa

Pd – Ga (1x): 2.54 Å
Pd – Ga (3x): 2.57 Å
Pd – Ga (3x): 2.71 Å
Pd – Pd (6x): 3.01 Å

Space group [9]: P 2_1 3 (198) - cubic

Pd_3Ga_7



Pd – Ga (4x): 2.58 Å
Pd – Ga (4x): 2.58 Å
Pd – Pd (1x): 2.73 Å

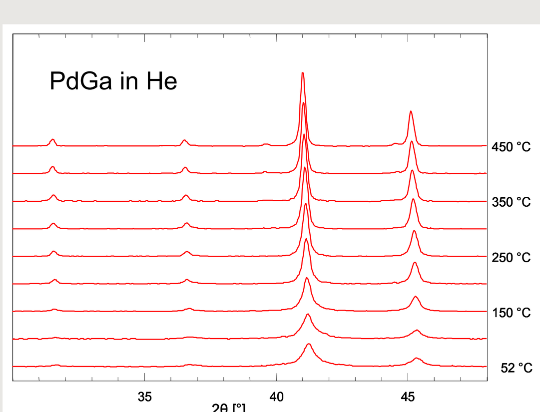
Space group [10]: I m -3 m (229) - cubic

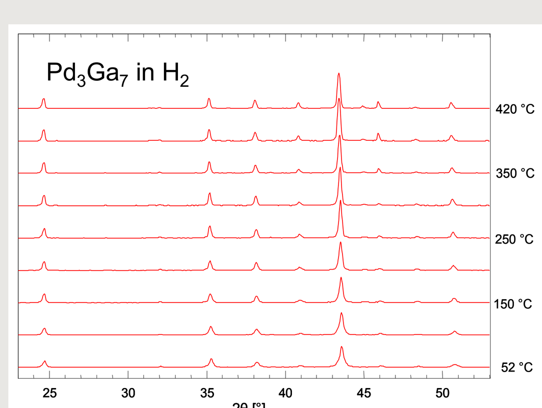
Preparation

m Pd + n Ga → Pd_mGa_n by melting of appropriate 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.

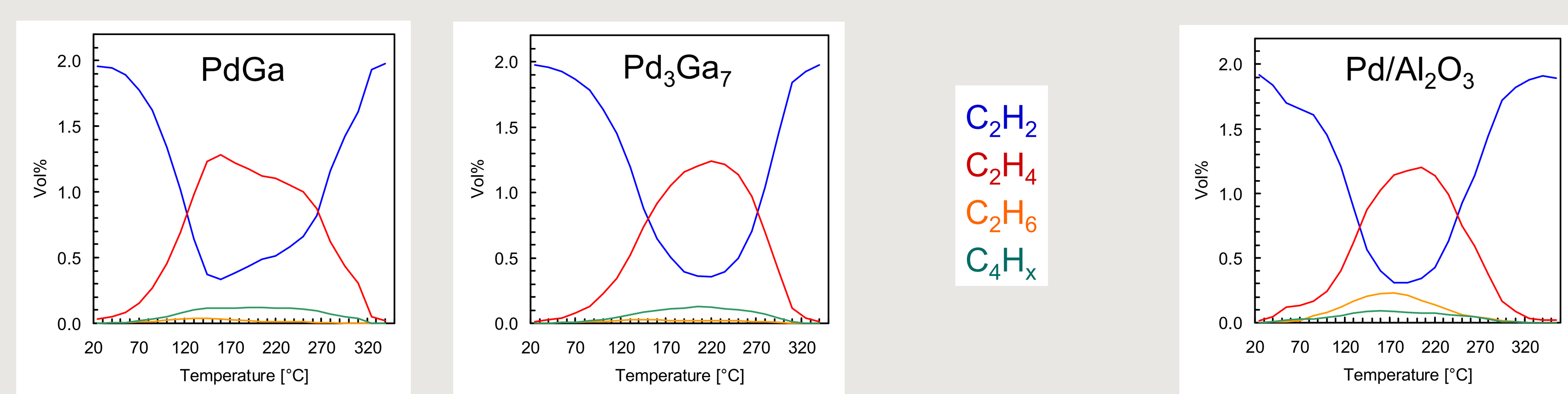




In situ XRD measurements were conducted using a STOE diffractometer with Cu-Kα radiation in *Bragg-Brentano* geometry (secondary monochromator) equipped with a Bühler HDK chamber.

Catalysis: $C_2H_2 + H_2 \rightarrow C_2H_4$

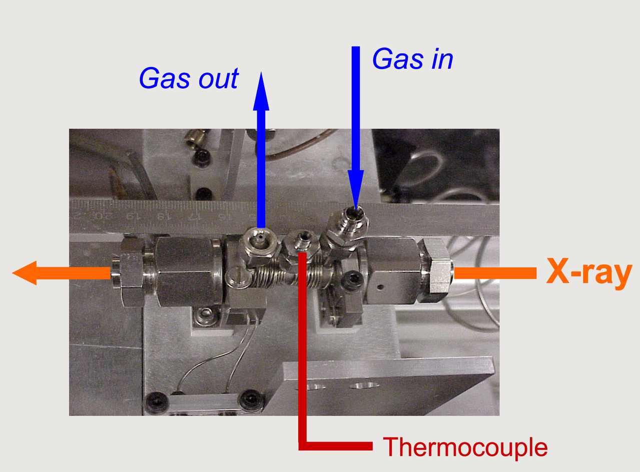
Acetylene hydrogenation with PdGa, Pd_3Ga_7 and reference Pd/Al_2O_3 in 2% C_2H_2 and 4% H_2. Both, PdGa and Pd_3Ga_7, show activity and high selectivity.



Catalysis studies were performed in a plug flow reactor (C_2H_2 / H_2 ratio 1:2, total flow 30 ml/min) with gas phase analysis using MicroGC Varian CP4900. The amount of catalyst was PdGa (50 mg), Pd_3Ga_7 (100 mg) and reference Pd/Al_2O_3 (0.5 mg, 5 wt%). The red curve shows the concentration of the product ethylene, yellow shows the total hydrogenated ethane and green the dimersation products.

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.



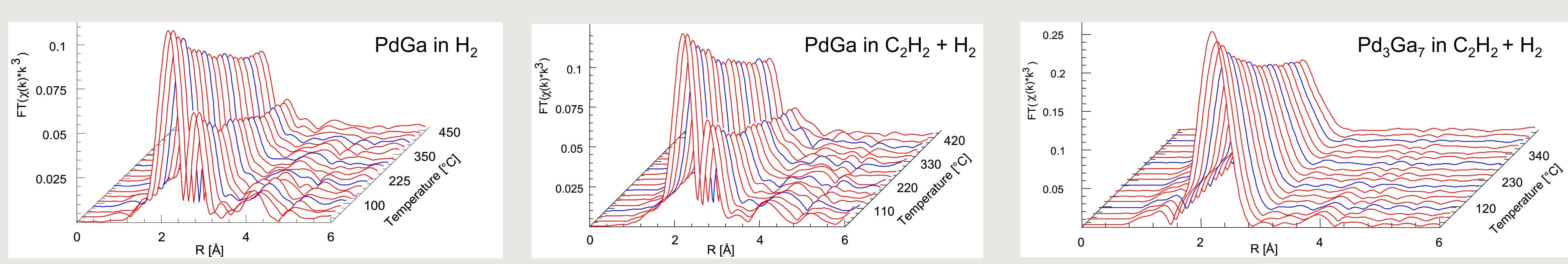
Cell for in situ XAS studies
EXAFS measured at HASYLAB X1 (Hamburg) at Pd K-edge (24.35 keV).

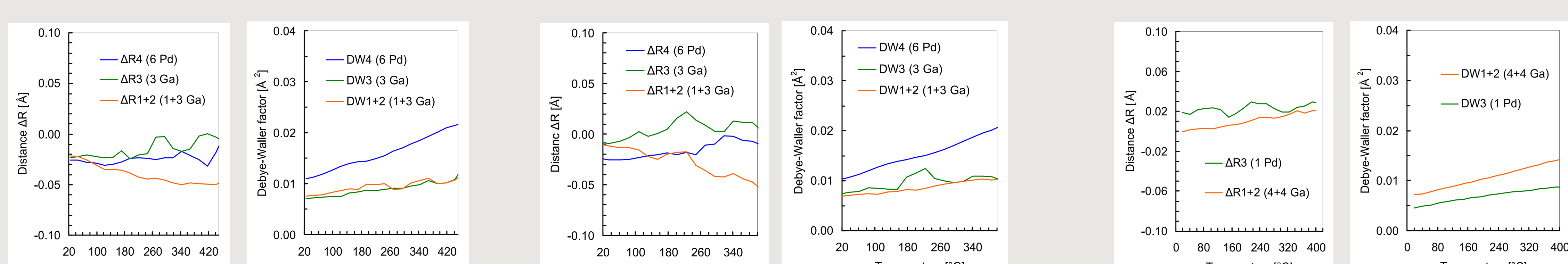
The theoretical EXAFS functions were calculated with FEFF 8 [11] from crystallographic data and refined with WinXAS [12] in R space.

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 PdGa 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.





Results

<u>Bulk characterisation of PdGa + Pd_3Ga_7:</u>
High thermal stability under different atmospheres and no hydride formation detectable.

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

Outlook

- Investigation of $PdSn_2$
- Preparation of high surface area samples (nano particles)
- Surface investigation with XPS, IR and ISS

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