Structural and Catalytic Investigation of Binary Palladium-Gallium Intermetallic Compounds

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Introduction

Palladium is well known as an important catalyst for hydrogenation and for combustion reactions[1]. Typical Pd catalysts are supported on metal oxides and show high activity but limited selectivity and stability under hydrogenation and oxidation reaction conditions.

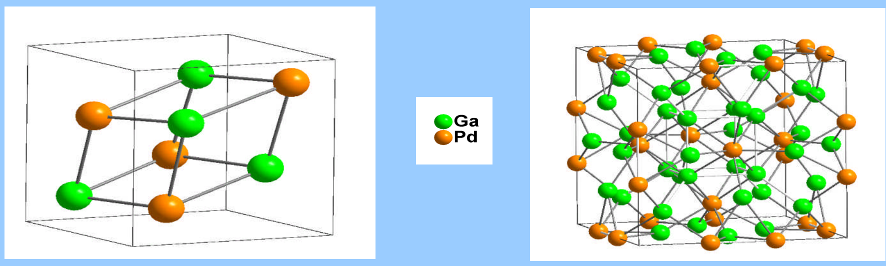
Motivation

The limited selectivity of Pd catalyst is due to neighbouring active sites on the catalyst surface[2]. Active site isolation may increase selectivity. The structures of the Pd-Ga compounds studied contain isolated Pd atoms.

Goal

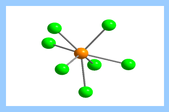
Determination of thermal stability in different gas atmospheres with in situ XRD and XAS measurements. Investigation of selectivity and reactivity for catalytic hydrogenation of acetylene.

Structures



PdGa

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

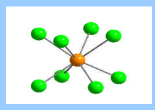


Pd – Ga (1x): 2.54 Å
Pd – Ga (3x): 2.57 Å
Pd – Ga (3x): 2.71 Å
Pd – Pd (6x): 3.01 Å

Pd_3Ga_7

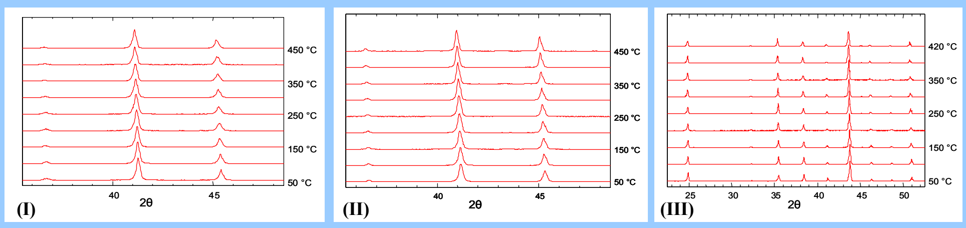
Space group[4]: I m -3 m (229) - cubic

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



In situ XRD

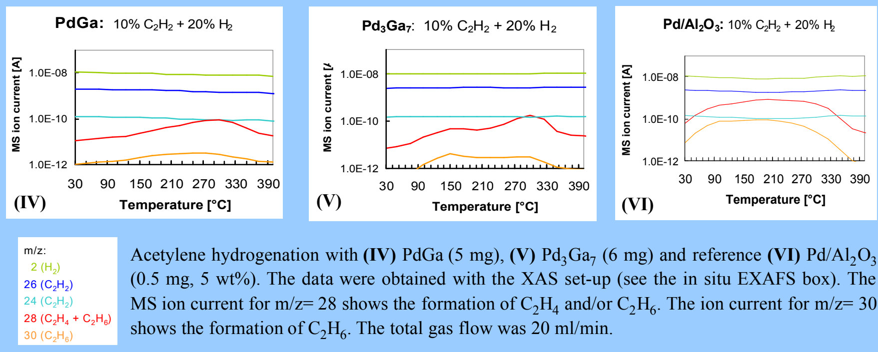
In situ XRD measurements were conducted using a STOE diffractometer with Cu-Kα radiation in *Bragg-Brentano* geometry (secondary monochromator) equipped with a Bühler HDK chamber.



In situ XRD of PdGa in **(I)** 10% H_2, **(II)** 20% O_2 and **(III)** Pd_3Ga_7 in 10% H_2

Catalysis

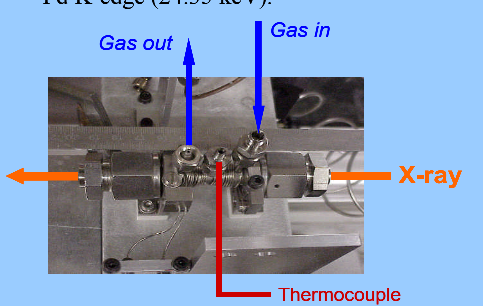
$C_2H_2 + H_2 \rightarrow C_2H_4$



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

In situ EXAFS

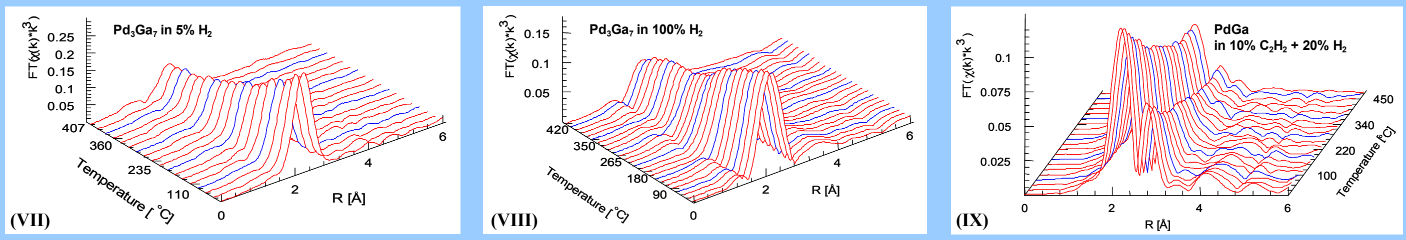
EXAFS measured at HASYLAB X1 (Hamburg) and ESRF ID24 (Grenoble) at Pd K-edge (24.35 keV).

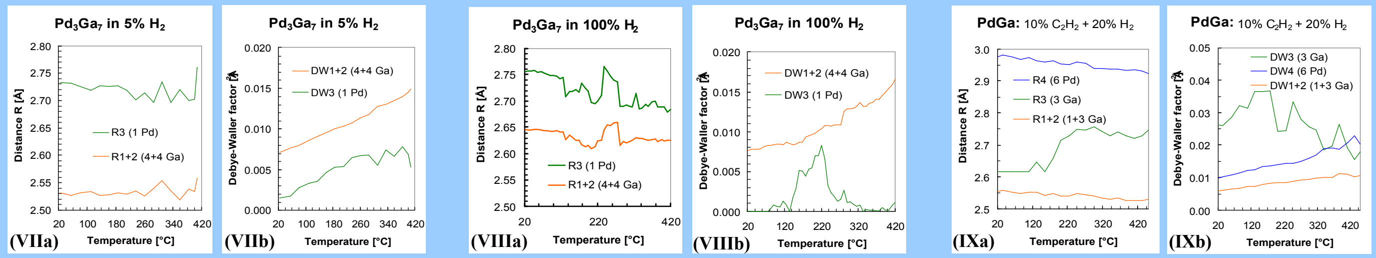


Cell for in situ XAS studies

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

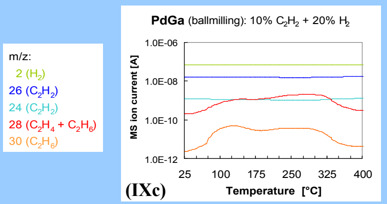
Reaction parameters:	
Sample mass:	9-11 mg
Diluent:	30 mg BN
Gas flow:	30-40 ml/min
Heating rate:	6 K/min





Determination of the thermal stability of Pd_3Ga_7 in 5% H_2 **(VII)** and **(VIII)** 100% H_2. Diagrams **(VIIa)** and **(VIIb)** show selected refined distances and Debye-Waller factors of Pd_3Ga_7 in 5% and 100% H_2 **(VIIIa+b)**. In the temperature range from 180 to 250 °C changes in R1+2 and R3 and a strong increase of the Debye-Waller factor (DW3) are observed. That may be correlated to the onset of catalytic activity shown in **(V)**.

Acetylene hydrogenation over PdGa after ballmilling: Increase of activity with maintenace of the structure. Diagram **(IX)** shows time resolved FT and the first shells with the refined distances **(IXa)** and Debye-Waller factors **(IXb)**. There is maybe a correlation to the catalytic data shown in **(IXc)**.



Summary

<u>Bulk characterisation of PdGa + Pd_3Ga_7</u>

- High thermal stability under different atmospheres.
- In 100% H_2 anomalous trends of the interatomic distances and Debye-Waller factors for Pd_3Ga_7 are observed. That may correspond to the incorporation of hydrogen and to the onset of catalytic activity **(V)**.
- During acetylene hydrogenation PdGa show a strong increase of distance R3 **(IXa)** that may correspond to the local minimum in the catalytic activity **(IXc)**.

<u>Catalytic studies of PdGa + Pd_3Ga_7: Preliminary results</u>

- The Pd-Ga alloys show activity for hydrogenation reactions.
- Increased activity can be obtained by mechanical treatment (ball milling) while the structure and stability of the material is preserved.
- The selectivity for the hydrogenation of acetylene to ethylene is higher compared to the commercial catalyst Pd on Al_2O_3.

Outlook

- Further preparation of high surface area samples by mechanical treatment.
- Quantitative catalytic studies.

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