

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 for hydrogenation and oxidation reactions.

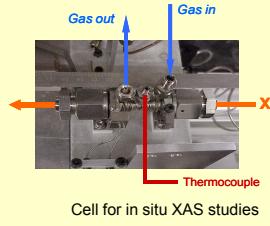
Motivation

- The limited selectivity of Pd catalyst is due to neighbouring active sites of the catalyst surface^[2].
- Active site isolation may increase selectivity. The structure of the selected Pd-Ga alloys provide isolated Pd atoms.

Goal

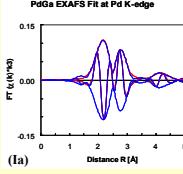
- Determine the thermal stability in different gas atmospheres with in situ XRD and XAS measurements.
- Investigate selectivity and reactivity for catalytic hydrogenation of acetylene

In situ EXAFS



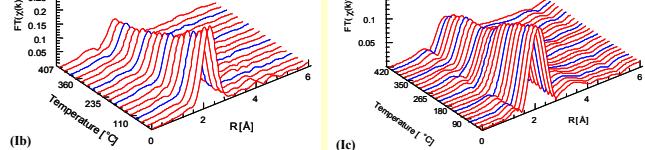
EXAFS measured at HASYLAB X1 (Hamburg) and ESRF ID24 (Grenoble) at Pd K-edge (24.35 keV).

| 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 |



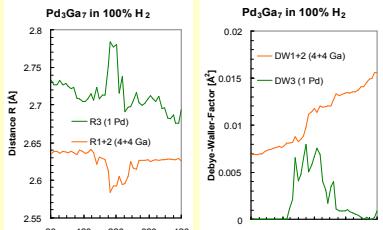
| Shell | CN | R [Å] | D R [Å] | s ² [Å ²] |
|-------|----|-------|---------|----------------------------------|
| Pd-Ga | 1 | 2.53 | -0.01 | 0.0065 |
| Pd-Ga | 3 | 2.56 | -0.01 | 0.0065 |
| Pd-Pd | 3 | 2.67 | -0.04 | 0.0336 |
| Pd-Pd | 6 | 2.98 | -0.03 | 0.0085 |
| Pd-Ga | 3 | 3.99 | -0.02 | 0.0157 |
| Pd-Pd | 6 | 4.38 | -0.02 | 0.0117 |

Characterisation of the sample at RT with XAS at the Pd K-edge. The theoretical EXAFS functions were calculated with FEFF 8 from crystallographic data. The refinements (Ia) were performed with WinXAS. The result of the refinement agrees to the crystallographic data.



Determination of the thermal stability of Pd₃Ga₇ in (IIb) in 5% H₂ and (Ie) in 100% H₂.

Diagrams (Id) and (Ie) show the refined distances and the Debye-Waller factors of Pd₃Ga₇ in 100% H₂. In the temperature range from 160 to 270 °C a change R1+2 and R3 and a strong increase of both Debye-Waller-factors are observed.



Summary

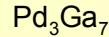
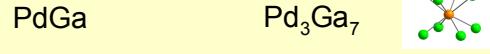
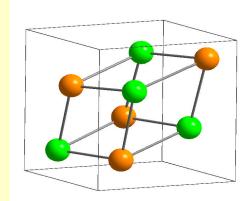
Bulk characterisation of PdGa + Pd₃Ga₇

- High thermal stability under different atmospheres.
- In 100% H₂ anomalous trends of the interatomic distances and Debye-Waller factors are observed. That may correspond to the incorporation of hydrogen and to the onset of catalytic activity (Fig. IIb).

Catalytic studies of PdGa + Pd₃Ga₇: Preliminary results

- The Pd-Ga alloys show activity for hydrogenation reactions.
- Increased activity can be obtained by mechanical treatment (ball milling) and with conservation of the structure.
- The selectivity of the hydrogenation to ethylene in respect to ethane is higher compared to the commercial catalyst Pd on Al₂O₃.

Structure

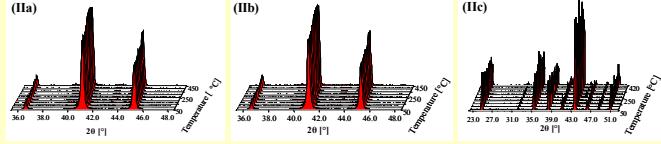


Space group^[3]: P 2₁3 (198) - cubic

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

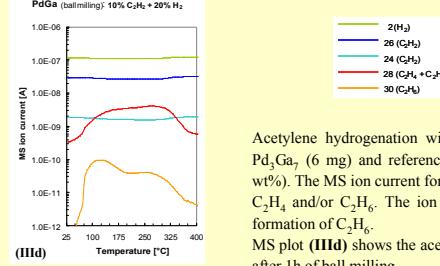
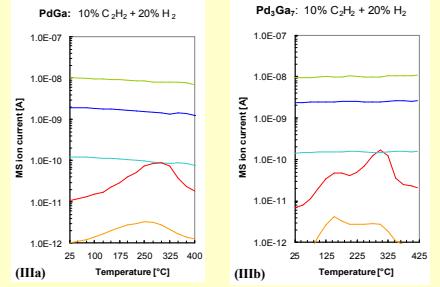
In situ XRD

In situ XRD measurements were conducted using a STOE diffractometer with Cu-K α radiation in Bragg-Brentano geometry (secondary monochromator).



In situ XRD of PdGa in (IIa) 10% H₂, (IIb) 20% O₂ and (IIc) Pd₃Ga₇ in 10% H₂

Catalysis



Acetylene hydrogenation with (IIIa) PdGa (5 mg), (IIIb) Pd₃Ga₇ (6 mg) and reference (IIIc) Pd/Al₂O₃ (0.5 mg, 5% w/w). The MS ion current for m/z= 28 shows the formation of C₂H₄ and/or C₃H₆. The ion current for m/z= 30 shows the formation of C₂H₆.

MS plot (IIIId) shows the acetylene hydrogenation with PdGa after 1h of ball milling.

Outlook

- Surface determination with CO chemisorption.

- Preparation of high surface area samples by mechanical treatment (ball milling).

- Quantitative catalytic studies.

Acknowledgement

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Literature

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[3] E. Hellner, F. Laves, Z. Naturforsch. 2a (1947) 177-183

[4] H. Pfleiderer, K. Schubert, Z. Metallkunde 41 (1950) 433-441