Structural and Catalytic Investigation of Binary Palladium-Gallium Intermetallic Compounds

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Introduction

Palladium in catalysis

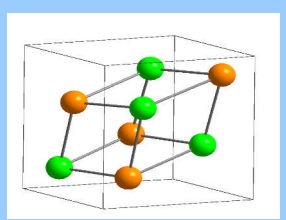
Acetylene hydrogenation to ethylene ($C_2H_2 + H_2 \rightarrow C_2H_4$) is a common method to remove traces of acetylene in the ethylene feed for the production of poly-ethylene[1]. Typical supported Pd catalysts show high activity but only limited selectivity and limited stability[1].

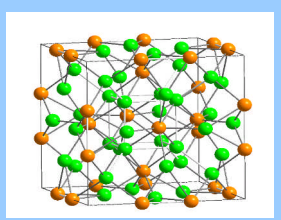
Increase of selectivity

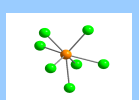
Elimination of hydride formation[2,3].
Active site isolation[4,5].
Modification of electronic structure and thermodynamic properties[6,7,8].

Palladium intermetallic compounds

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







PdGa

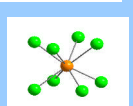
Pd – Ga (1x): 2.54 Å
Pd – Ga (3x): 2.57 Å
Pd – Ga (3x): 2.71 Å
Pd – Pd (6x): 3.01 Å

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

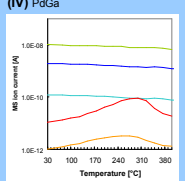


Goal

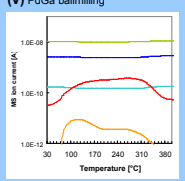
Determine thermal stability in different gas atmospheres with in situ XRD and in situ XAS measurements, CO chemisorption, and investigation of selectivity and reactivity for catalytic hydrogenation of acetylene.

Catalysis: $C_2H_2 + H_2 \rightarrow C_2H_4$

(IV) PdGa



(V) PdGa ballmilling



Acetylene hydrogenation with **(IV)** PdGa (5 mg), **(VI)** Pd_3Ga_7 (6 mg) and reference **(VII)** Pd/Al_2O_3 (0.5 mg, 5 wt%) in 10% C_2H_2 and 20% H_2.

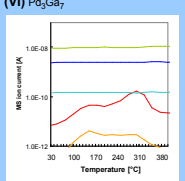
(V) PdGa after 1h of ballmilling. Activity increase with while selectivity preserved.

The data were obtained with the XAS set-up (see in situ EXAFS box). The total gas flow was 20 ml/min.

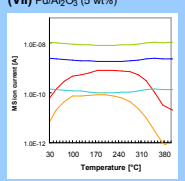
The MS ion current for m/z= 28 (red) shows the formation of C_2H_4 and/or C_2H_6. The ion current for m/z= 30 (yellow) shows the formation of C_2H_6.

m/z:
2 (H_2)
26 (C_2H_2)
24 (C_2H_2)
28 (C_2H_4 + C_2H_6)
30 (C_2H_6)

(VI) Pd_3Ga_7



(VII) Pd/Al_2O_3 (5 wt%)



Results

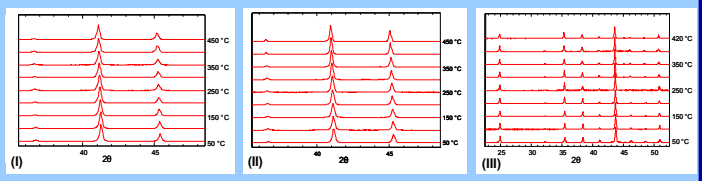
Bulk characterisation of PdGa + Pd_3Ga_7
High thermal stability under different atmospheres.

Catalytic studies of PdGa + Pd_3Ga_7: Preliminary results
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.

CO chemisorption
No surface decomposition and Pd segregation detectable.

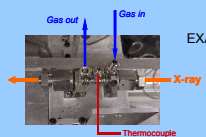
In situ XRD

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

In situ EXAFS



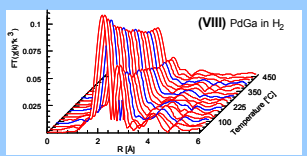
Cell for in situ XAS studies

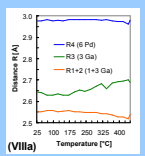
EXAFS measured at HASYLAB X1 (Hamburg) at Pd K-edge (24.35 keV).

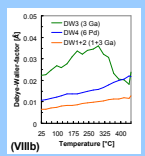
Cell parameters:	
Cell volume:	4 ml
Sample diameter:	5 mm pellet
Cell windows:	Al foil
Gas in:	Gas flow controller
Gas out:	Exhaust with MS detection

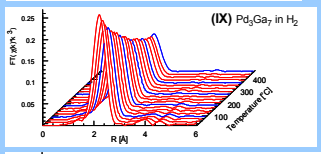
Reaction parameters:	
Sample mass:	9-11 mg
Diluent:	30 mg BN
Gas flow:	30-40 ml/min
Heating rate:	6 K/min

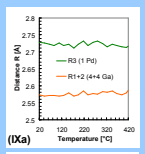
Determination of the thermal stability of **(VIII)** PdGa and **(IX)** Pd_3Ga_7 in 50% H_2. Diagrams **(VIIIa+b)** and **(IXa+b)** show selected refined distances and Debye-Waller factors. The theoretical EXAFS functions were calculated with FEFF 8 from crystallographic data and refined with WinXAS. PdGa shows an anomalous trend in DW3 **(VIIIb)** with a maximum at 300 °C. This may correspond to the maximum of catalytic activity **(IV+V)**. In situ EXAFS of Pd_3Ga_7 shows high thermal stability in hydrogen **(IXa+b)** and acetylene hydrogenation **(Xa+b)**.

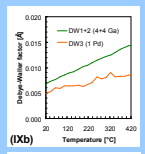


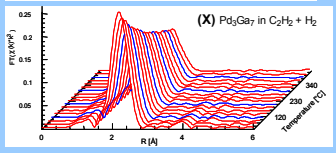


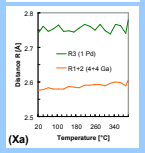


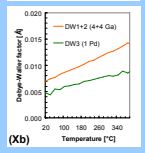








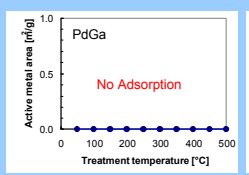


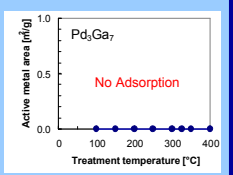


CO Chemisorption

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 car-ried out at 298 K.





Outlook

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

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