Structural and Catalytic Investigation of Active Site Isolated Pd-Ga and Pd-Sn Intermetallic Compounds

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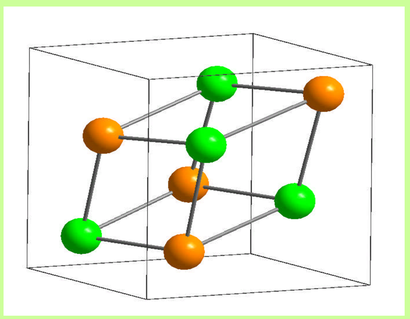
Introduction and motivation

Palladium in catalysis

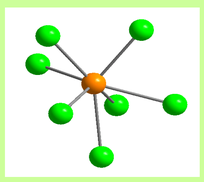
Acetylene hydrogenation to ethylene ($C_2H_2 + H_2 \rightarrow C_2H_4$) is a common method to remove traces of acetylene in the ethylene feed for the production of polyethylene. Conventional supported Pd catalysts show high activity but only limited selectivity and limited stability [1-3].

Active site isolation

The hydrogenation of acetylene and ethylene is influenzed by the arrangement of the active sites at the surface [4-6]. Unsaturated hydrocarbons could form different kinds of adsorbed species on the surface. Only the weakly π-bonded acetylene lead to a hydrogenation to ethylene with high selectivity. In contrast, the di-σ-bonded species will partly be hydrogenated to ethane [7].

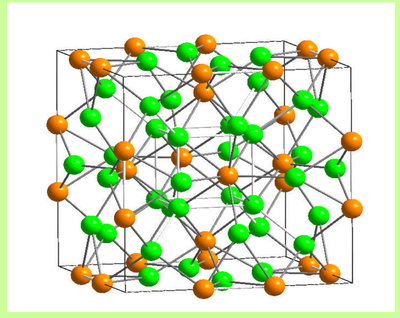


Space group [8]: P 2_1 3 (198) - cubic

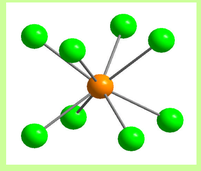


Pd – Ga (1x): 2.54 Å
Pd – Ga (3x): 2.57 Å
Pd – Ga (3x): 2.71 Å
Pd – Pd (6x): 3.01 Å

PdGa

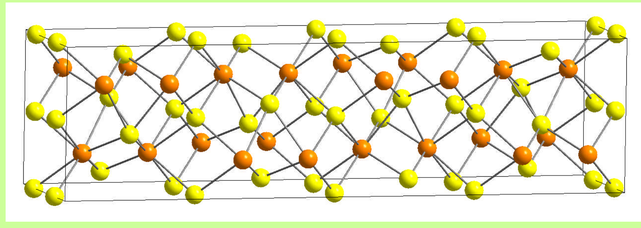


Space group [9]: I m -3 m (229) - cubic

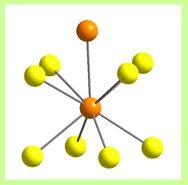


Pd – Ga (4x): 2.58 Å
Pd – Ga (4x): 2.58 Å
Pd – Pd (1x): 2.73 Å

Pd_3Ga_7



Space group [10]: I 41/a c d (14201) - tetragonal



Pd – Sn (2x): 2.80 Å
Pd – Sn (2x): 2.82 Å
Pd – Sn (4x): 2.83 Å
Pd – Pd (1x): 2.84 Å

$PdSn_2$

Palladium intermetallic compounds

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

Preparation

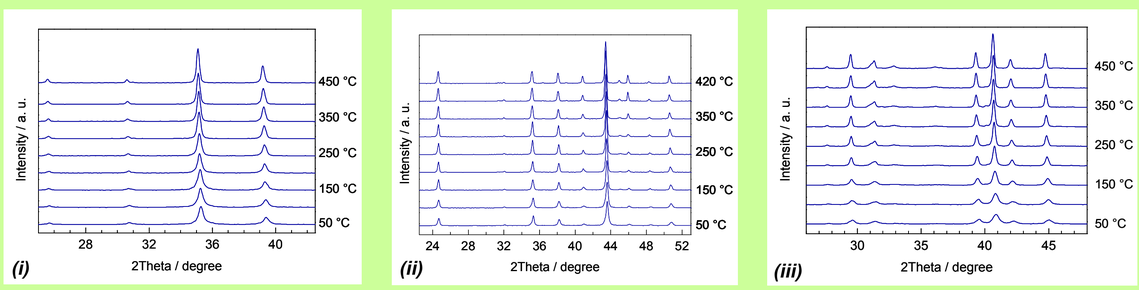
Pd intermetallic compounds were prepared by melting of appropriate amounts of Pd, Ga and Sn in a glassy carbon crucible under Ar atmosphere in a high frequency induction furnace. The samples were powdered in a ball mill.

Goal

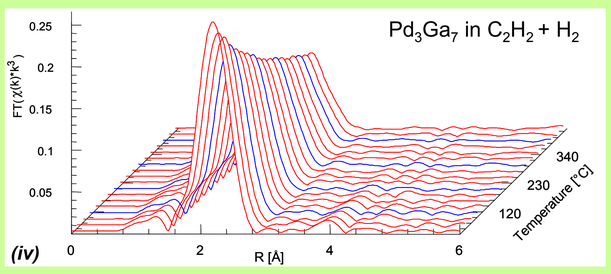
Determine thermal stability in different gas atmospheres with in situ XRD, in situ XAS measurements and thermal analysis, investigation of selectivity and reactivity for catalytic hydrogenation of acetylene.

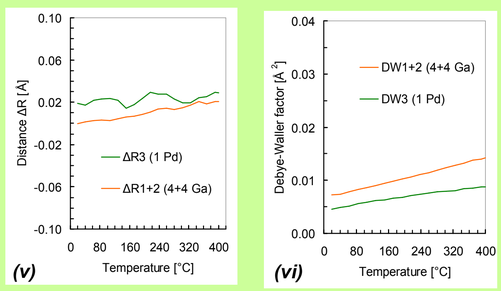
Structural stability

Determination of the structural stability of PdGa, Pd_3Ga_7 and $PdSn_2$ (***i-iii***) in 50% hydrogen using ***in situ XRD***. Only thermal lattice expansion and no phase transition and no hydride formation was observable. Increasing particle size leads to decreasing line width.



In situ EXAFS during acetylene hydrogenation (10% C_2H_2 + 20% H_2) is used for determinating of the thermal stability and detecting possible hydrogen inclusion. In contrast to in situ XRD which provides lattice parameters of crystalline phases EXAFS gives information about local structures in crystalline and non-crystalline phases.

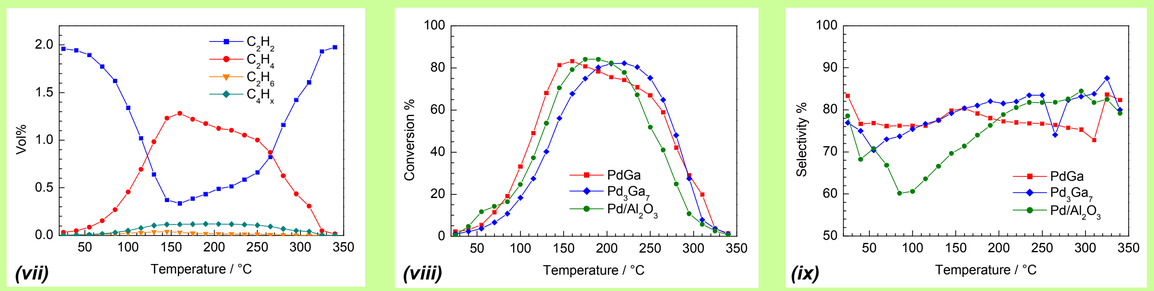




In situ XAS measured at HASYLAB at Pd K-edge. (iV) shows the radial distribution function of Pd_3Ga_7 in acetylene hydrogenation. Diagrams on the right side show selected refined distances and Debye-Waller factors of Pd_3Ga_7. In situ EXAFS of Pd-Ga and Pd-Sn intermetallic compounds show high thermal stability up to 350 °C in hydrogen and acetylene hydrogenation with changes in distances ΔR in the range of the accuracy and increasing Debye-Waller factor with increasing temperatures.

Catalysis $C_2H_2 + H_2 \rightarrow C_2H_4$

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



(vii) shows the acetylene hydrogenation with PdGa. The catalyst shows high activity in the temperature range from 100 to 280 °C. The by-products are C_4-hydrocarbons and ethane. Acetylene conversion of PdGa (m= 50 mg), Pd_3Ga_7 (m= 100 mg) and Pd/Al_2O_3 (0.5 mg) is plotted in diagram ***(viii)***. The different activity/mass ratio are due to the low surface area of the Pd intermetallic compounds (BET ~1 m^2, Pd/Al_2O_3: 114 m^2). Pd-Ga intermetallic compounds show significantly higher selectivity compared to the commercial Pd supported catalyst ***(ix)***. Catalytic studies of $PdSn_2$ are made more difficult because of tin segregation, surface oxidation and deactivation.

Surface investigation

XPS investigation of PdGa and Pd_3Ga_7 shows Ga_2O_3 at the surface which could not be significantly reduced by hydrogen treatment at elevated temperature.

Ga $2p^{3/2}$ peak of PdGa ***(x)*** as prepared, treated at 300 °C and 400 °C and after ISS. Only after sputtering with He ions an additional peak indicates the presence of (inter-)metallic Ga (BE= 1116 eV) in the near surface region.

Results and discussion

Pd-Ga and Pd-Sn intermetallic compounds show ***high structural stability*** in reactive and inert gas atmospheres.

PdGa and Pd_3Ga_7 show ***activity*** and ***higher selectivity*** in acetylene hydrogenation compare to commercial Pd/Al_2O_3.

Preparation of $PdSn_2$ have to be improved to obtain an oxide-free catalyst.

Intermetallic compounds possess a ***high potential*** to investigate the validity of structural concepts like active site isolation in heterogeneous catalysis and may be promising candidates for further ***industrial application***.

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