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Rational catalyst design by using the concept of active-site isolation for the selective hydrogenation of acetylene: the Pd-Ga 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 industrially used to remove traces of acetylene in the ethylene feed for the production of polyethylene.

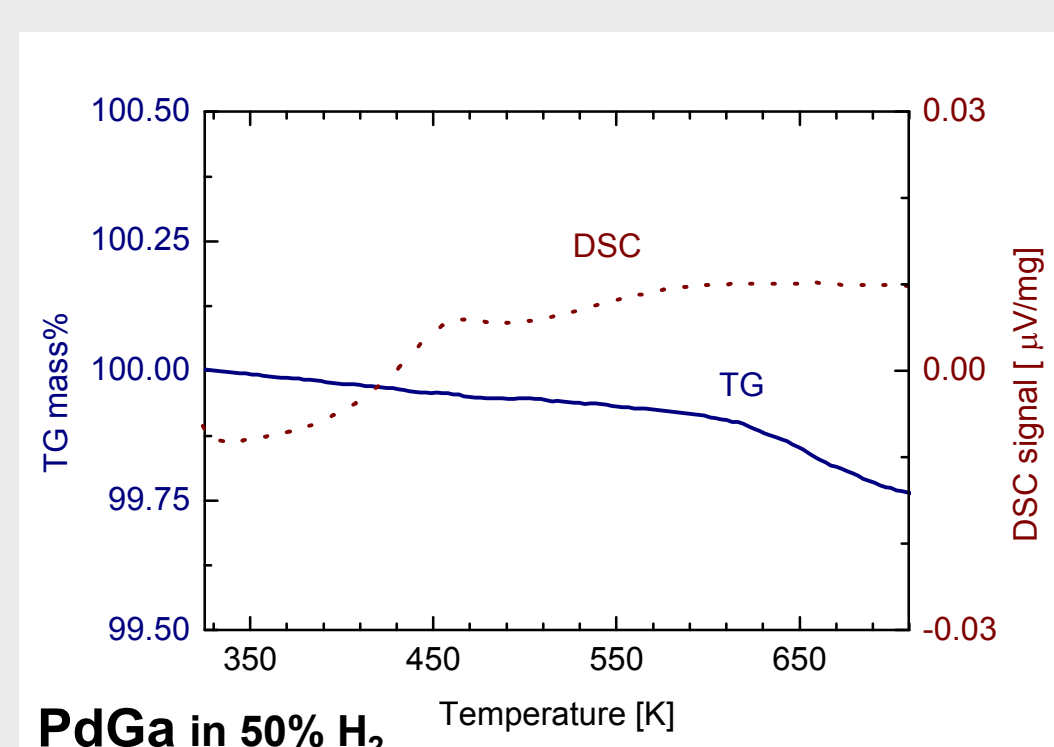
Conventional supported Pd catalysts show high activity but only limited selectivity and stability [1].

Active site isolation

The hydrogenation of acetylene and ethylene is influenced by the arrangement of the active sites on the surface [2-4]. Unsaturated hydrocarbons can form different kinds of adsorbed species on a Pd surface. Only the weakly π -bonded acetylene is hydrogenated in high selectivity to ethylene. In contrast, the di- σ -bonded species will partly be hydrogenated to ethane or decompose to carbon deposits.

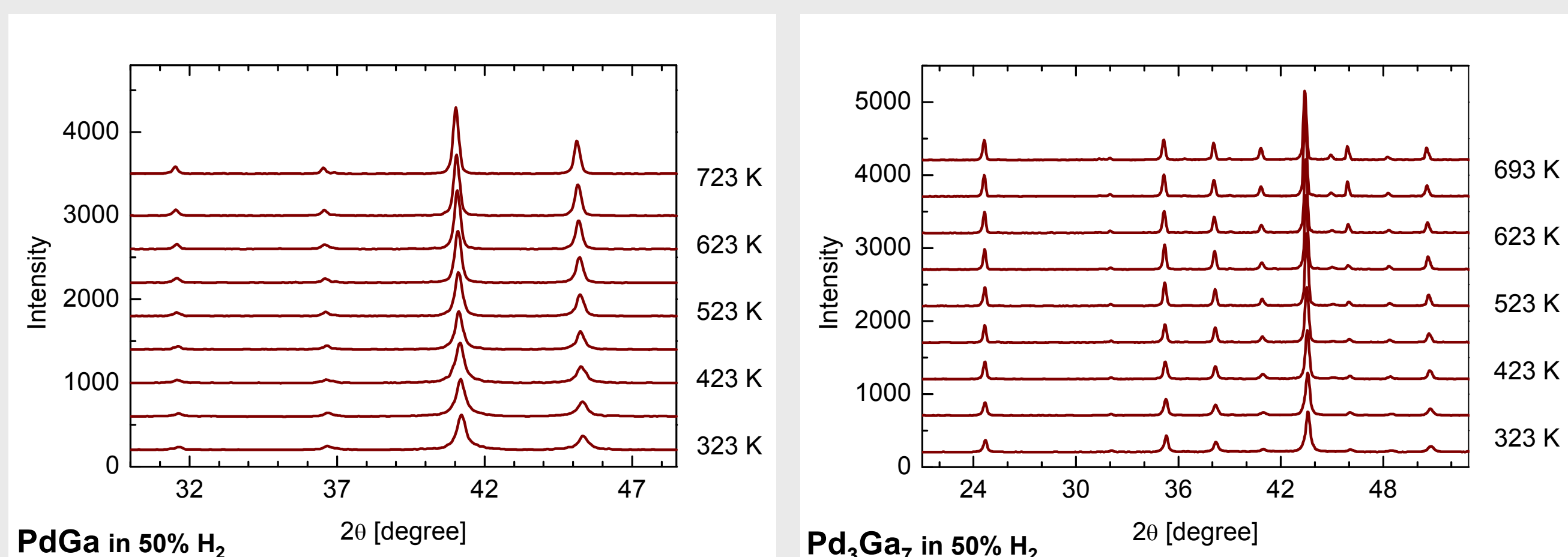
Structural stability

Thermal analysis (TG/DSC), in situ XRD (crystalline long-range order) and in situ XAS measurements (coordination of Pd atoms) were performed to investigate the structural stability of PdGa and Pd₃Ga₇ during thermal treatment in helium, hydrogen and oxygen. Both Pd-Ga intermetallic compounds showed high stability and no hydride formation was detected.



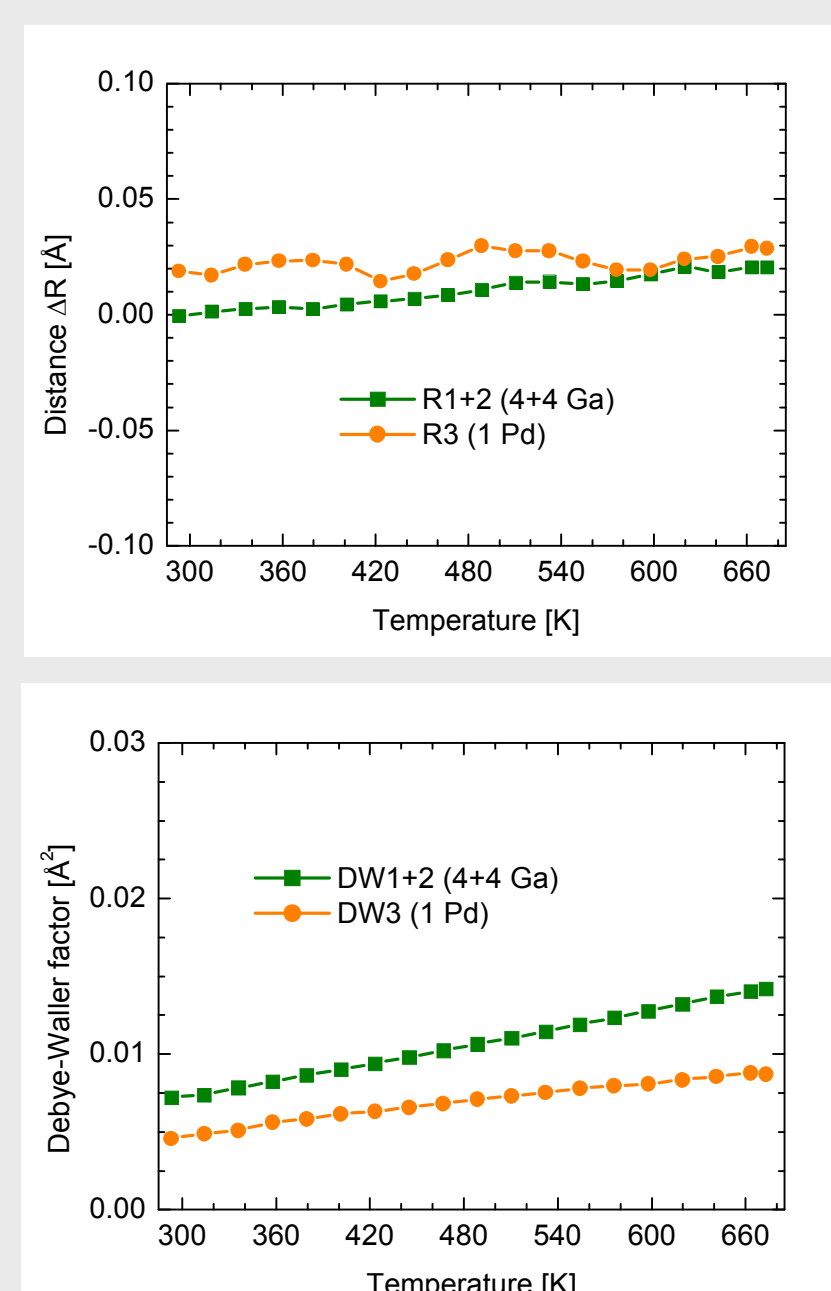
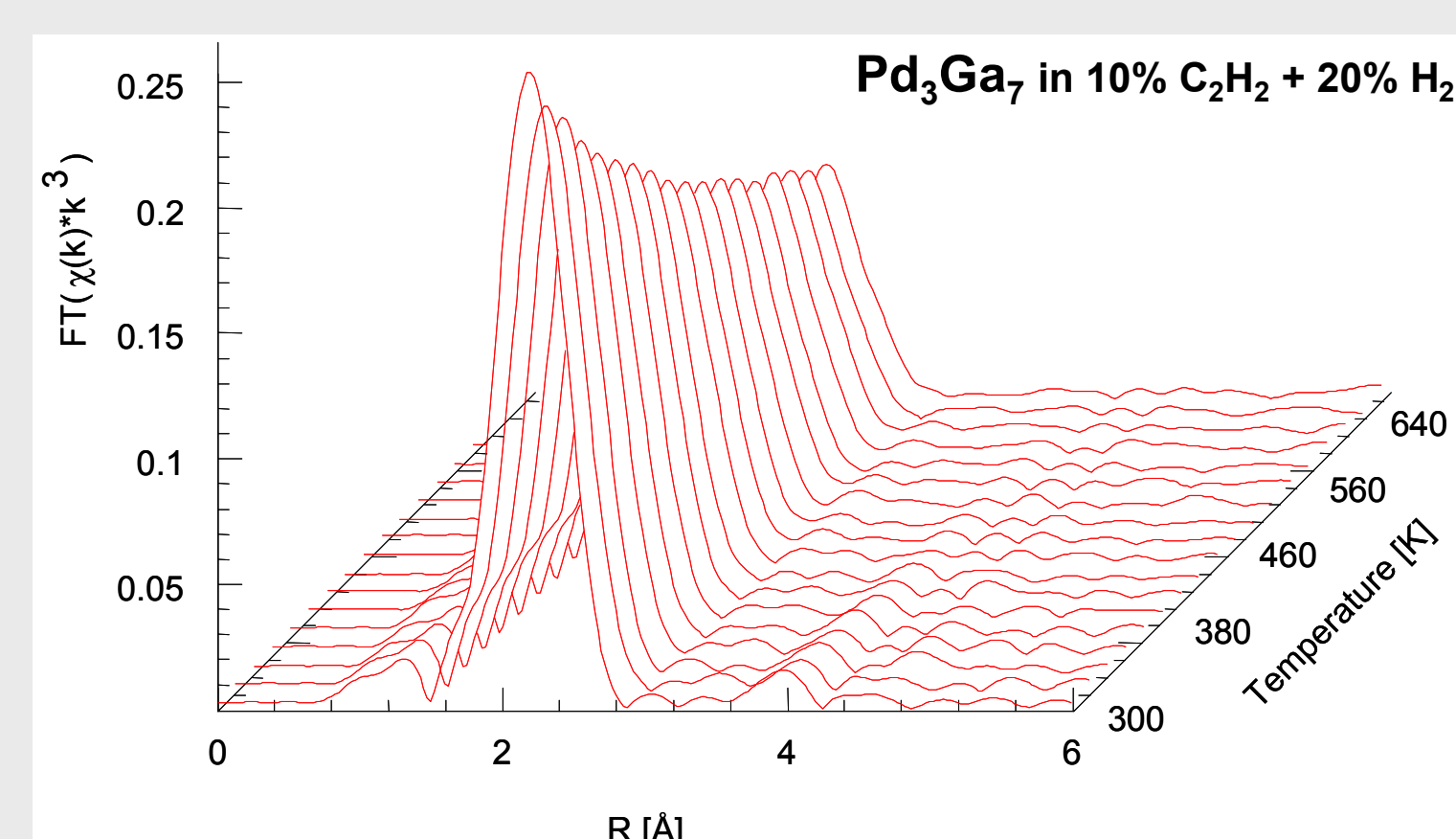
TG and DSC of PdGa in 50% H₂ + 50% He shows high structural stability. A mass loss above 600 K is due to surface oxide reduction.

In situ XRD of PdGa and Pd₃Ga₇ in 50% H₂ + 50% He showed no decomposition, phase transition or hydride formation during thermal treatment from 323 K to 723 K and 693 K, respectively.



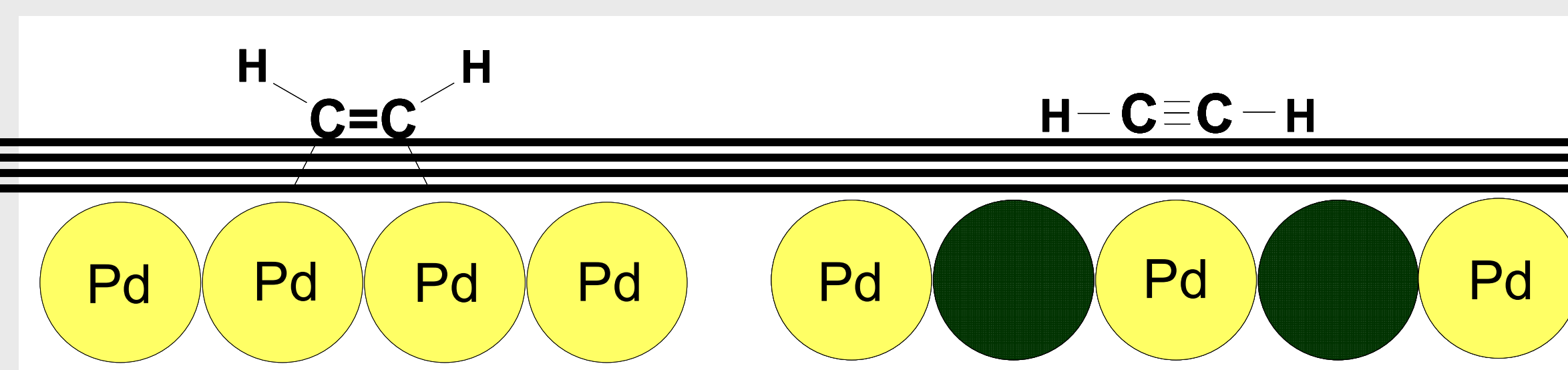
The Fourier transformed radial distribution function of Pd₃Ga₇ in 10% C₂H₂ + 20% H₂: The Pd K-edge XAS exhibited a slightly decreasing amplitude due to thermal disorder caused by the increasing temperature.

EXAFS refinement of selected Pd-Ga and Pd-Pd interatomic distances resulted in a nearly constant trend and the expected linear increase of the corresponding Debye-Waller factors during thermal treatment.



Palladium intermetallic compounds

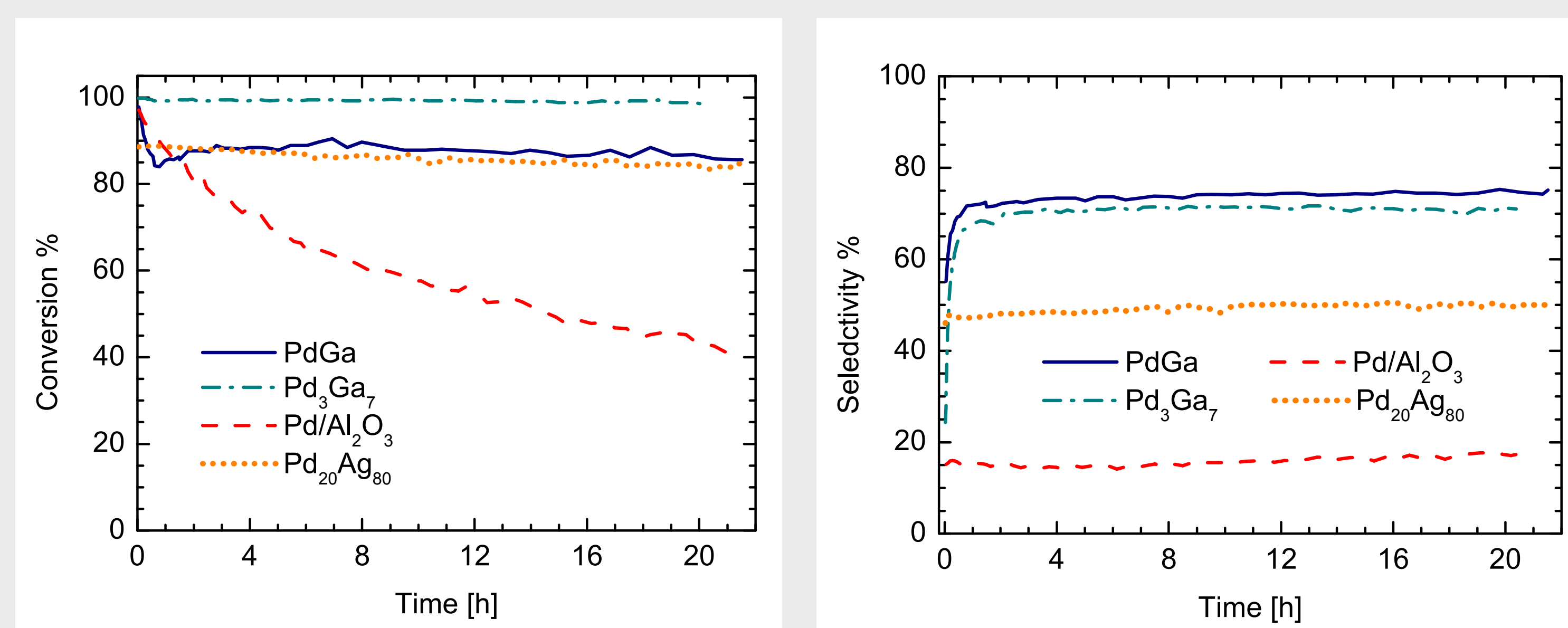
The Pd-Ga intermetallic compounds PdGa [5] and Pd₃Ga₇ [6] are particularly interesting as potential catalysts because of the reduced Pd-Pd coordination and increased average interatomic Pd-Pd distances. Hence, the acetylene molecules preferentially adsorb in the π -bonded mode and are hydrogenated in high selectivity to ethylene.



In contrast to Pd-Ga intermetallic compounds, Pd based alloys necessitates a high dilution of the Pd by a second metal to obtain isolated Pd sites due to the random atomic distribution. Furthermore, segregation may lead to the formation of Pd clusters on the catalyst surface.

Catalysis C₂H₂ + H₂ → C₂H₄

Both Pd-Ga intermetallic compounds show high selectivity during acetylene hydrogenation. The selectivity was considerably higher compared to the references Pd/Al₂O₃ and a silver-rich Pd alloy. In addition, PdGa and Pd₃Ga₇ exhibited a remarkable catalytic long-term stability due to their isolation of Pd atoms which suppresses oligomerisation and carbon deposits.



Conversion and selectivity of acetylene hydrogenation in excess of ethylene of PdGa (40 mg), Pd₃Ga₇ (100 mg), Pd/Al₂O₃ (0.15 mg) and Pd₂₀Ag₈₀ (200 mg) in 0.5% C₂H₂ + 5% H₂ + 50% C₂H₄ at 473 K.

Summary

Pd-Ga intermetallic compounds PdGa and Pd₃Ga₇ show high structural stability in reactive and inert gas atmospheres.

PdGa and Pd₃Ga₇ show activity, catalytic long-term stability and higher selectivity in acetylene hydrogenation compared to commercial Pd/Al₂O₃ and a silver-rich Pd based alloy.

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

Literature:

[1] A.N.R. Bos, K.R. Westerterp, Chem. Eng. Proc. 32 1 (1993) 1-7

[2] E. G. Derouane, J. Mol. Catal. 1984, 25, 51-58

[3] L. Guzzi, J. Mol. Catal. 1984, 25, 13-29

[4] V. Ponec, Adv. Catal. 1983, 32, 149-214

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

[6] K. Khalaff, K. Schubert, J. Less-Common Met. 1974, 37, 129-140