

Structural and Catalytic Investigation of Active-Site Isolation in Pd-Ga Intermetallic Compounds



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Motivation and introduction

Structural investigation

Surface studies

Catalysis data



light alkanes
"naphtha"



steam cracker

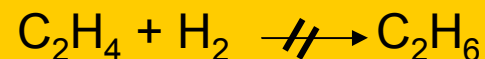
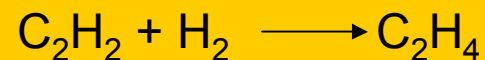
ethylene
+ propylene, acetylene,
butenes, ethane

1st purification

ethylene

+ traces of acetylene

selective hydrogenation
of acetylene in ethylene excess



ethylene
(≤ 3 ppm C_2H_2)


HDPE
polymerisation
"Ziegler-Natta"



polyethylene



Why active-site isolated intermetallic compounds?

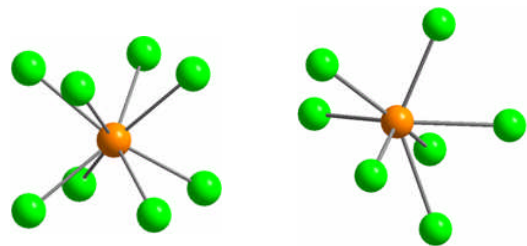
Pd metal

supported on metal oxides

✓ activity

✗ selectivity

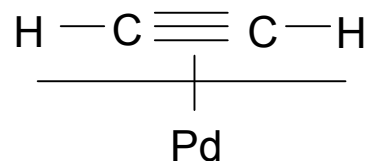
✗ long-time stability



Pd intermetallic compounds

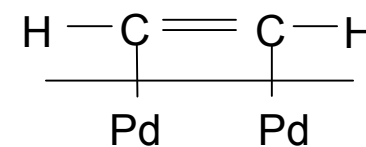
Not alloys!

1. Active-site isolation [1-3]



π -bonded

site isolated Pd atoms



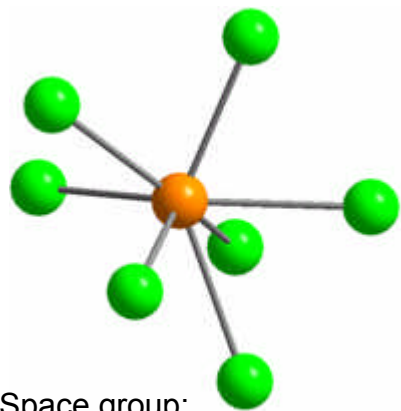
di- σ -bonded

neighbouring Pd atoms

2. Elimination of hydride formation [4-6]

1. E.W. Shin, S.H. Moon, et al. *Catal. Today* 44, 137 (1998)
2. S. Leviness, L. Gucci, et al *J. Mol. Catal.* 25, 131 (1984)
3. V. Ponec, *Adv. Catal.* 32, 149 (1983)
4. W. Palczewska in "Hydrogen Effects in Catalysis" (Z. Paal, P.G. Denon, Eds.) 372, Marcel Decker New York (1988)
5. G.C. Bond, and P.B. Wells *J. Catal* 5, 65 (1966)
6. A.M. Doyle, H.J. Freund, et al. *Angew. Chem. Int. Ed.* 42, 5240 (2003)

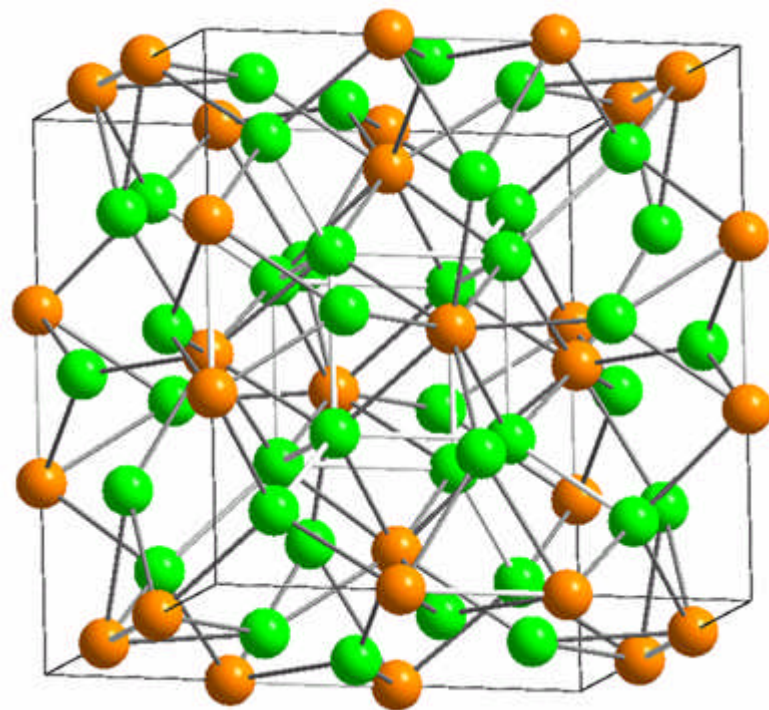
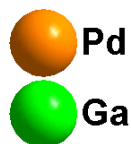
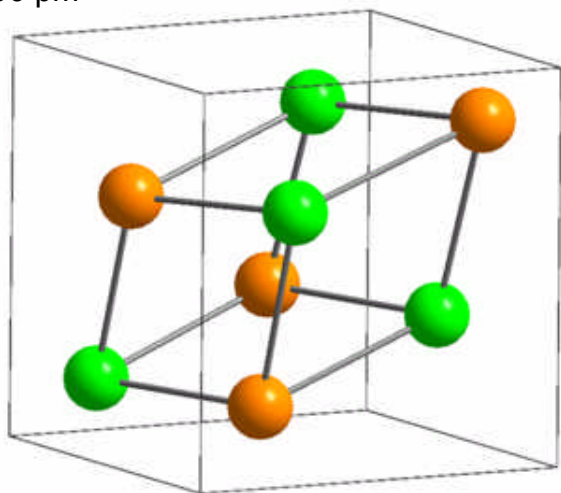
Pd-Ga intermetallic compounds: PdGa and Pd₃Ga₇



Pd – Ga (1x): 254 pm
Pd – Ga (3x): 257 pm
Pd – Ga (3x): 271 pm
Pd – Pd (6x): 301 pm

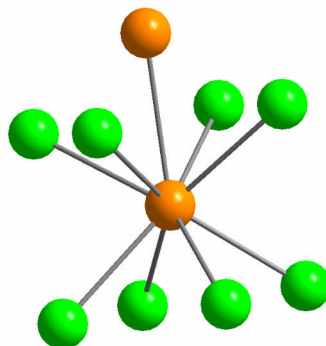
Space group:
cubic: $P 2_1 3$ (198)
 $a = 490$ pm

PdGa



Space group:
cubic: $I m \bar{3} m$ (229)
 $a = 877$ pm

Pd₃Ga₇



Pd – Ga (4x): 258 pm
Pd – Ga (4x): 258 pm
Pd – Pd (1x): 273 pm

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

H. Pfisterer, K. Schubert, *Z. Metallkunde* 41 (1950) 433-441



Pd-Ga intermetallic compounds

PdGa – Pd₃Ga₇

Pd intermetallic compounds

- Structurally defined catalysts with isolated Pd atoms
- Hydride formation?

Goal

Thermal stability in different atmospheres and hydride formation:

Surface investigation:

Catalytic studies:

Preparation

by mixing and melting appropriate amounts of the metals under Ar atmosphere. The samples were powdered in a ball mill

Methods

In situ XRD, in situ EXAFS, TG / DSC

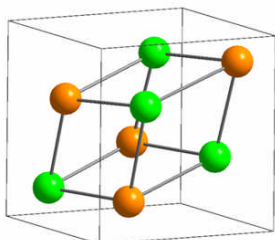
BET, CO chemisorption, XPS, ISS

GC, MS

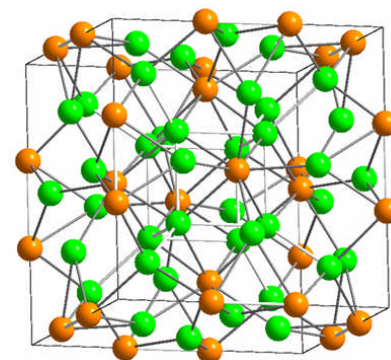


High structural stability of PdGa and Pd₃Ga₇

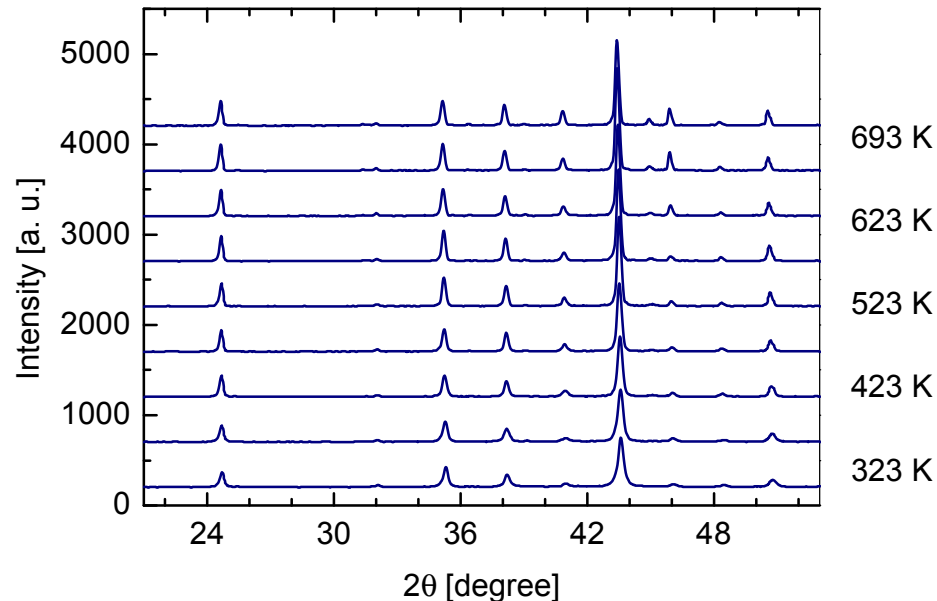
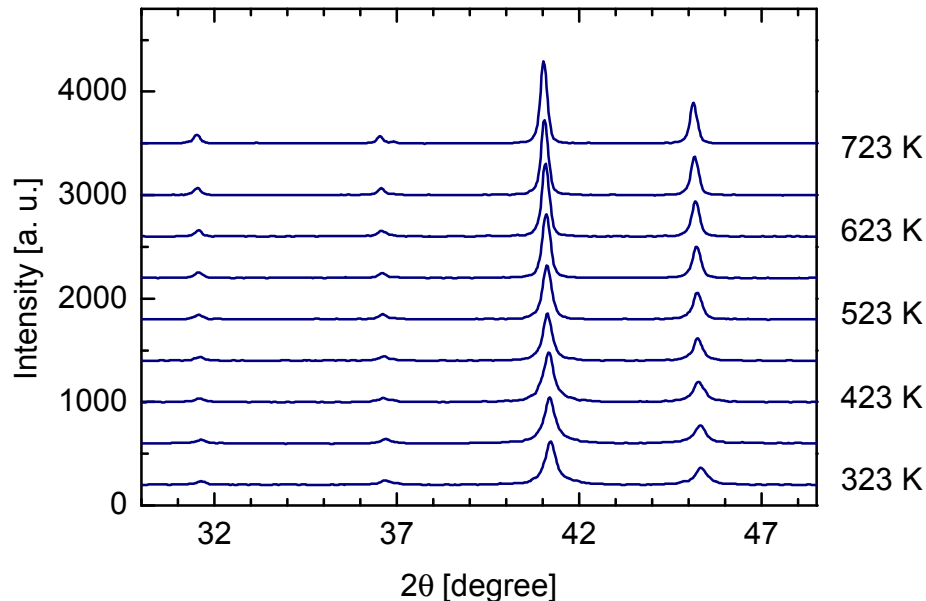
In situ XRD (long-range order) in 50% H₂ + 50% He



PdGa



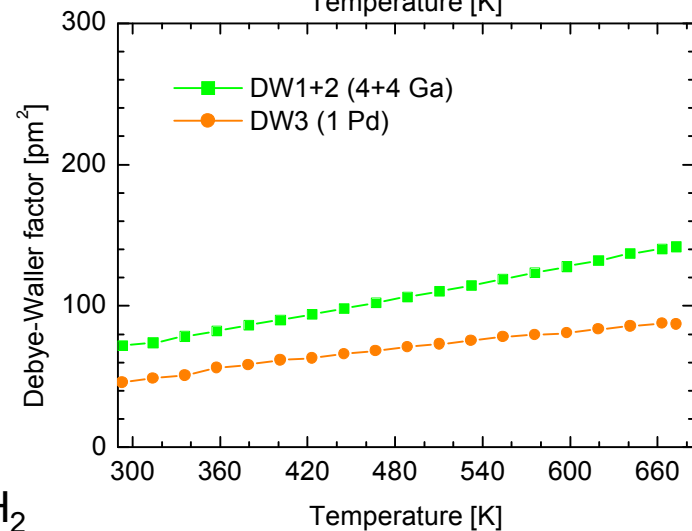
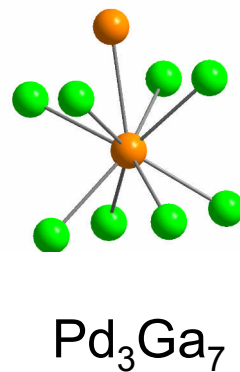
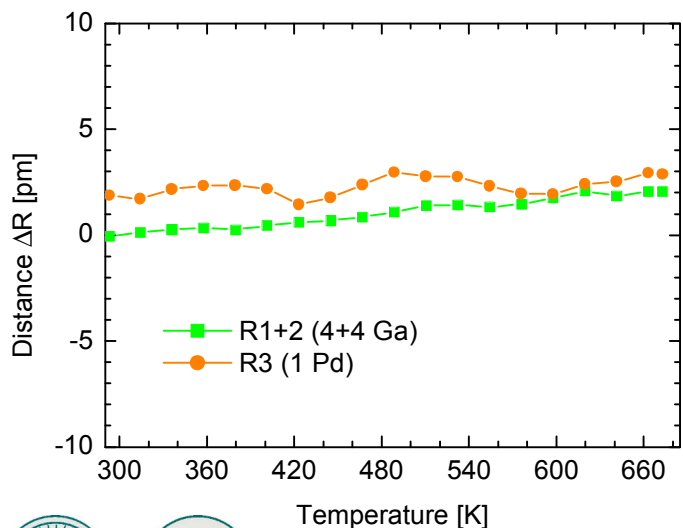
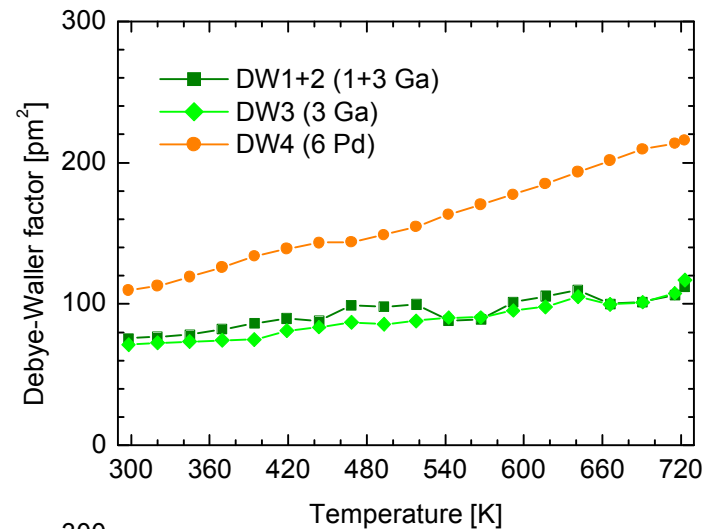
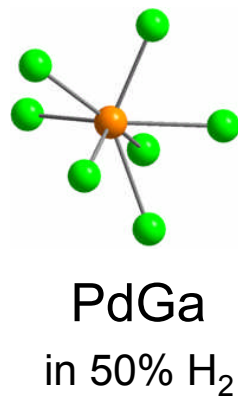
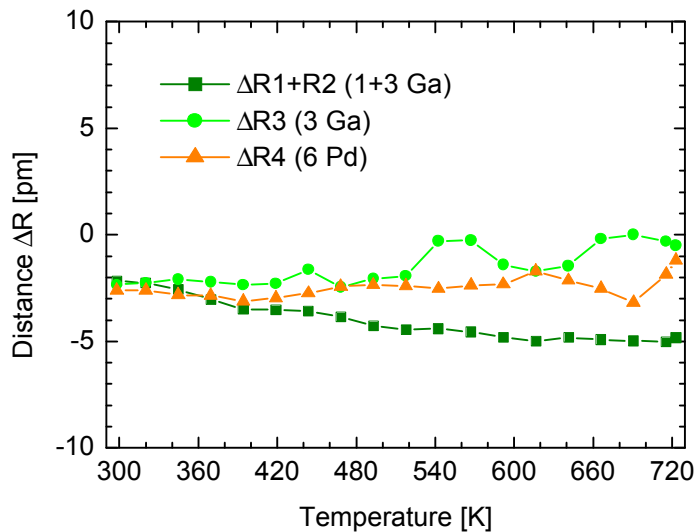
Pd₃Ga₇



→ no decomposition, phase transition or hydride formation

High structural stability of PdGa and Pd₃Ga₇

In situ EXAFS (local structure of Pd atoms) measured at Pd K edge (24.35 keV)



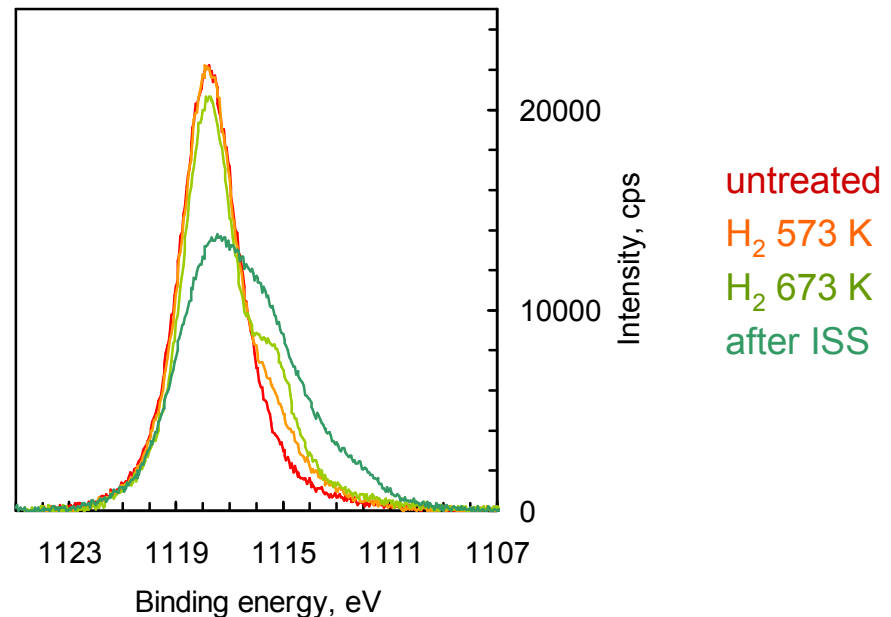
Surface characterisation of Pd-Ga intermetallic compounds

- BET:** surface area $\sim 1 \text{ m}^2/\text{g}$
- CO chemisorption:** no chemisorption of CO at RT detectable
- SEM / EDX:** inhomogeneous particle size distribution
Pd/Ga ratio homogeneous

XPS of PdGa Ga $2p^{3/2}$

predominantly Ga_2O_3
not removable with hydrogen
treatment

→ chemical etching





By-products:

total hydrogenation to C_2H_6

dimerisation to C_4H_x

1-butene, 1,3-butadiene, trans-butene, cis-butene, n-butane ...

Plug flow reactor:

2% C_2H_2 + 4% H_2 in He, total flow 30 ml/min

0.5% C_2H_2 + 5% H_2 + 50% C_2H_4 , total flow 30 ml/min

catalyst + 30 mg BN

Gas analysis:

MicroGC

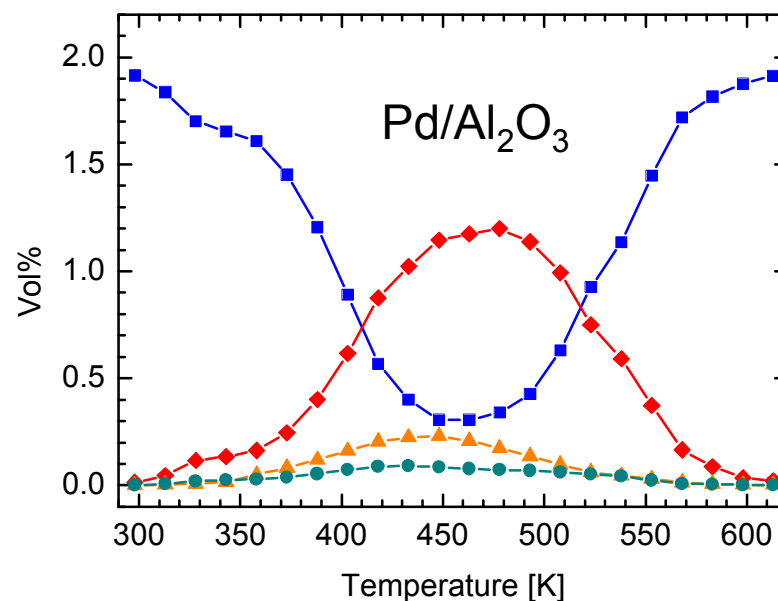
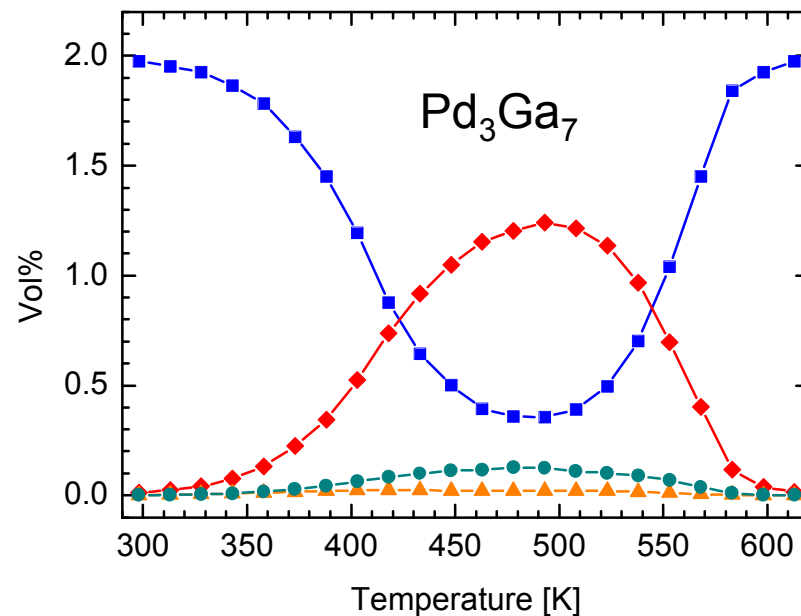
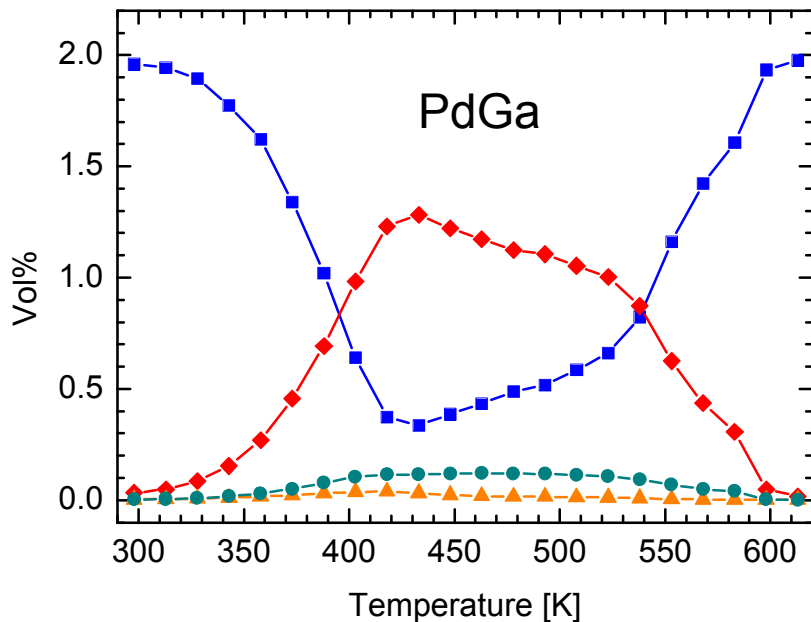
Varian CP 4900, 4-Channel GC

Reference:

$\text{Pd}/\text{Al}_2\text{O}_3$ 5 wt%, *commercial catalyst (Aldrich)*

BET: 114 m²/g, Pd metal surface: 5.3 m²/g





Acetylene hydrogenation

2% C₂H₂ + 4% H₂

PdGa: 50 mg

Pd₃Ga₇: 100 mg

Pd/Al₂O₃: 0.5 mg

C₂H₂

C₂H₄

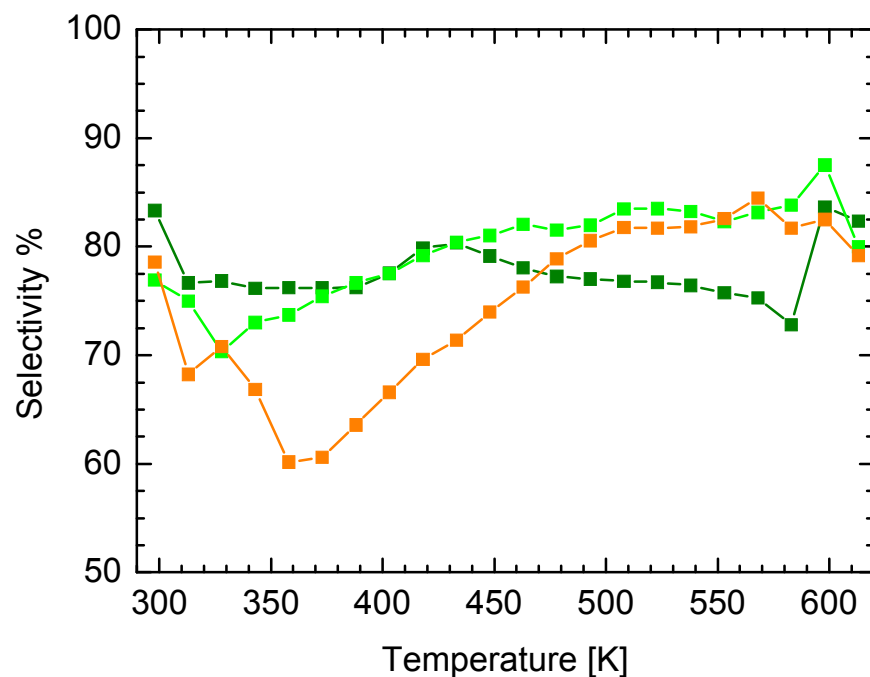
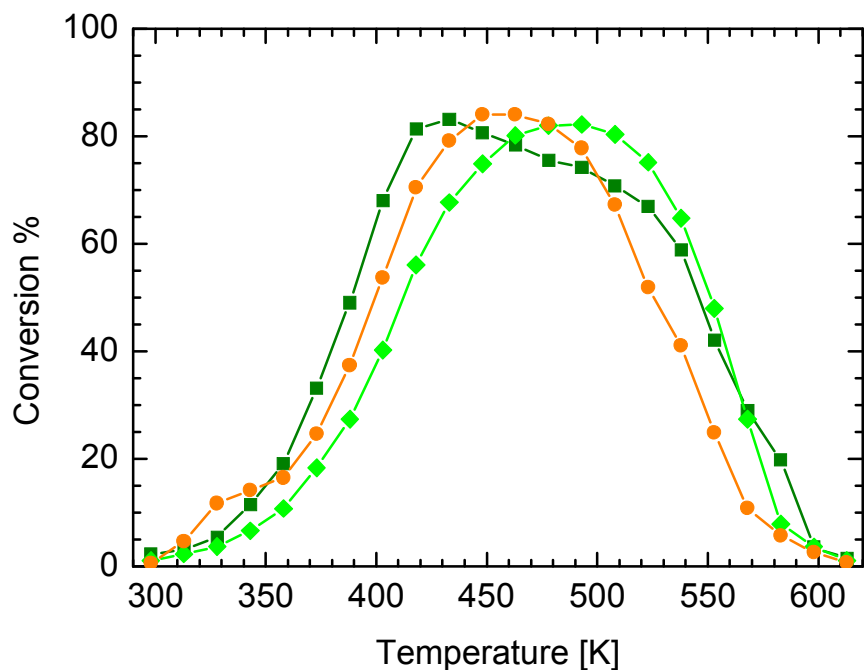
C₂H₆

C₄H_x

High selectivity of Pd intermetallic compounds

Conversion and selectivity in acetylene hydrogenation

PdGa – Pd₃Ga₇ – Pd/Al₂O₃



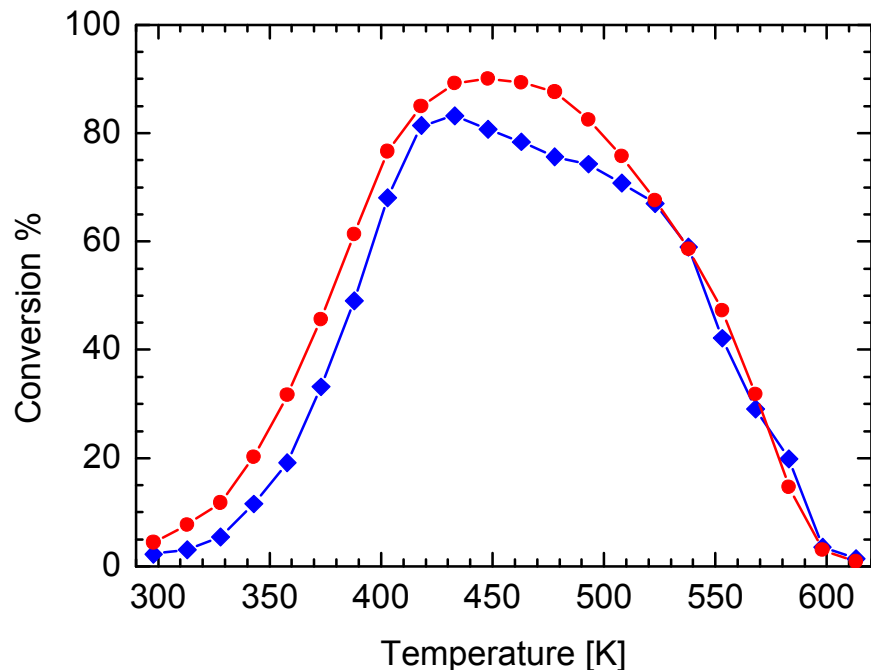
in 2% C₂H₂ + 4% H₂

PdGa: 50 mg, Pd₃Ga₇: 100 mg, Pd/Al₂O₃: 0.5 mg



Increased activity by chemical etching

Acetylene conversion of Pd-Ga intermetallic compounds untreated and after chemical etching in ammonia solution

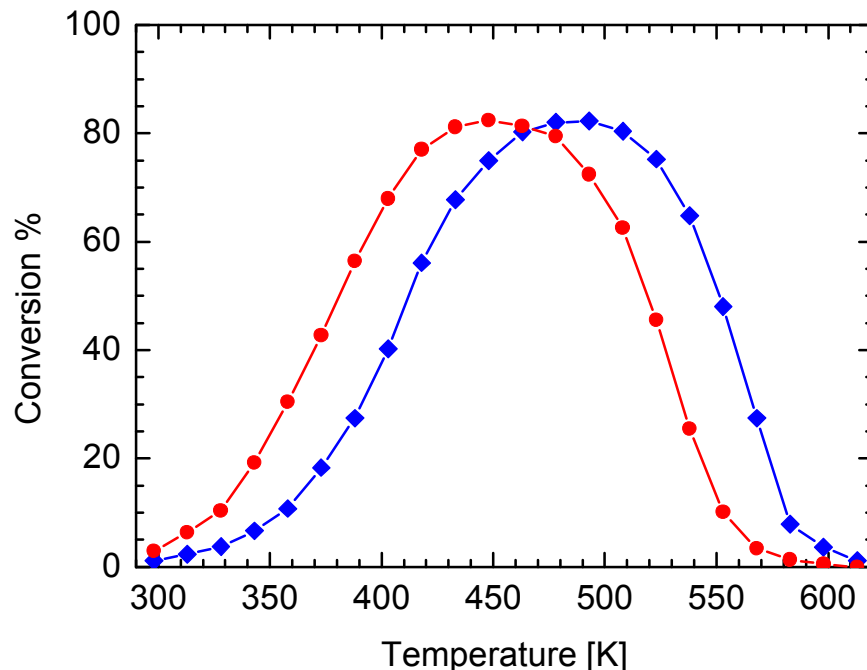


PdGa: 50 mg

PdGa: 5 mg

untreated

chemically etched

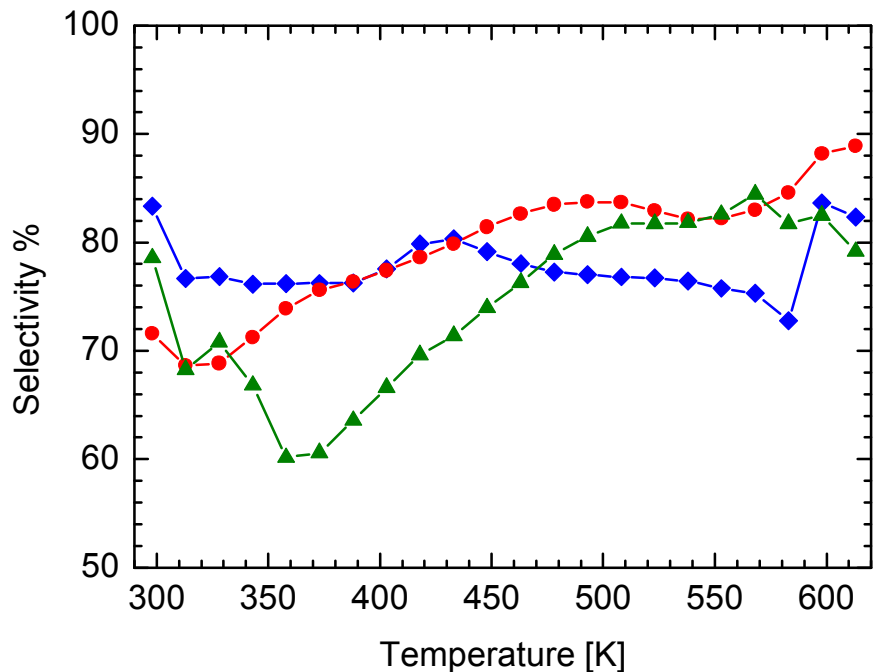


Pd₃Ga₇: 100 mg

Pd₃Ga₇: 15 mg

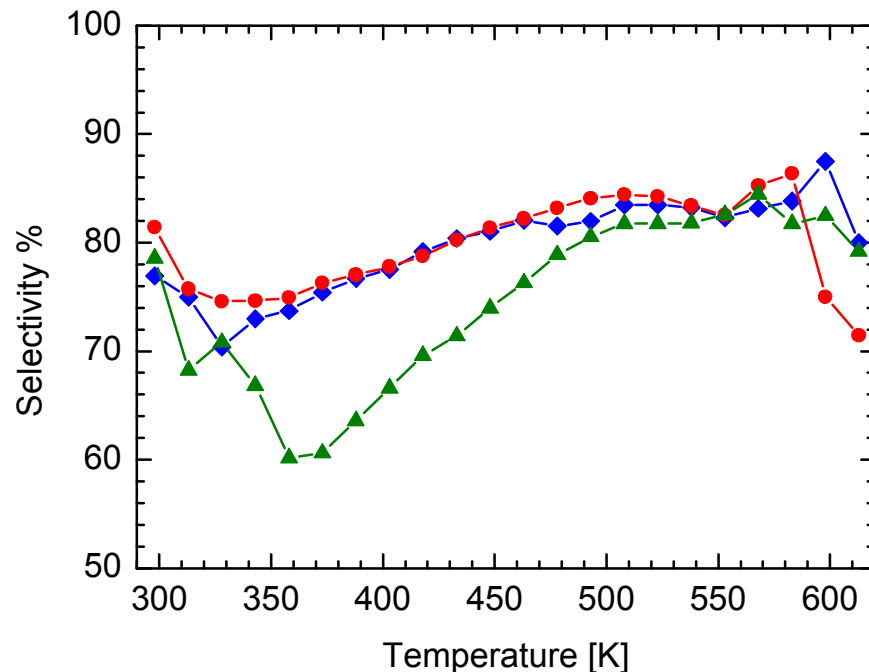
Increased activity by chemical etching

Selectivity of Pd-Ga intermetallic compounds untreated and after chemical etching in ammonia solution



PdGa: 50 mg
PdGa: 5 mg

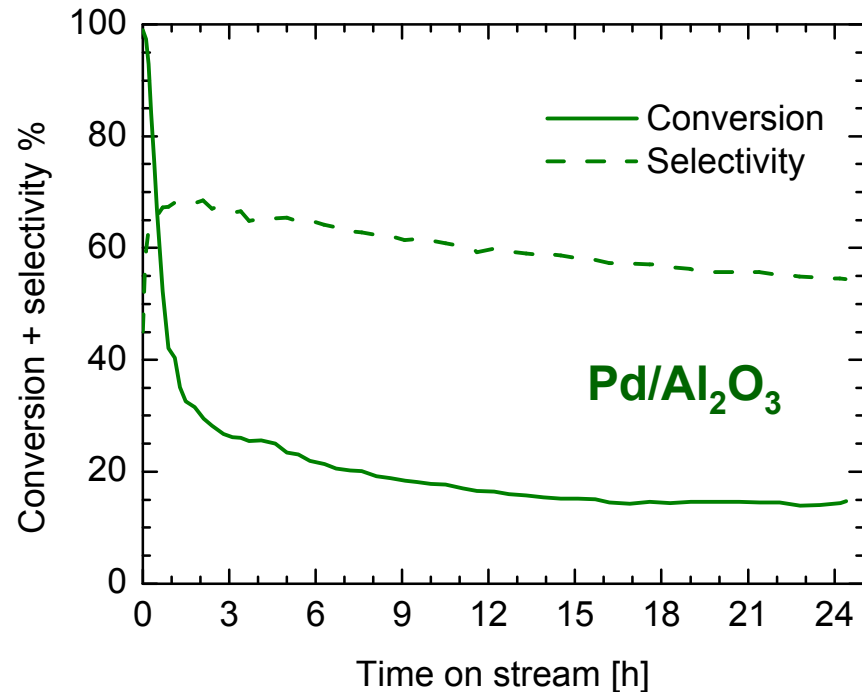
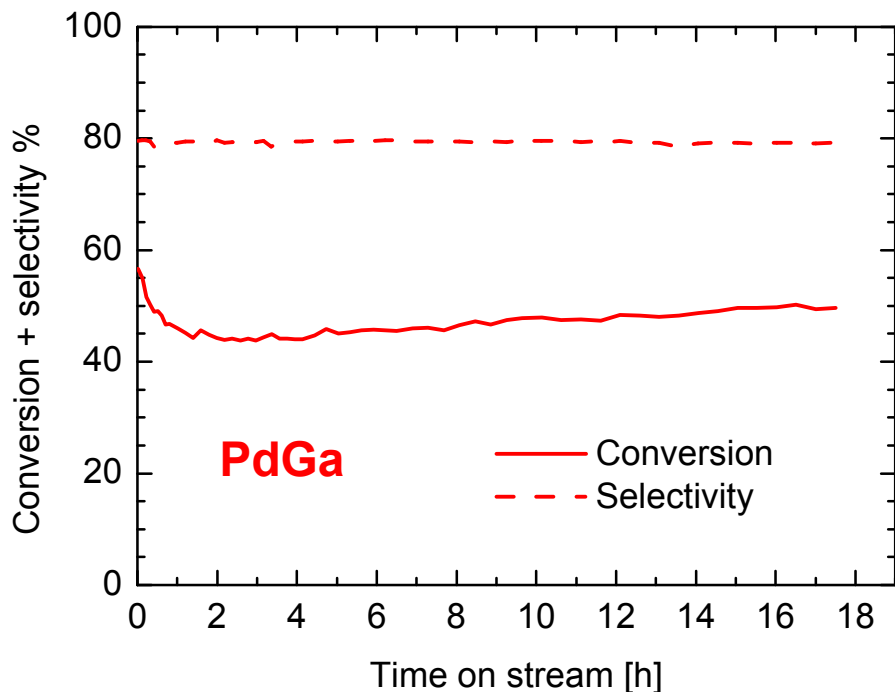
untreated
chemically etched
Pd/Al₂O₃: 0.5 mg



Pd₃Ga₇: 100 mg
Pd₃Ga₇: 15 mg

Long-term stability of Pd intermetallic compounds

Isothermal experiments at 398 K

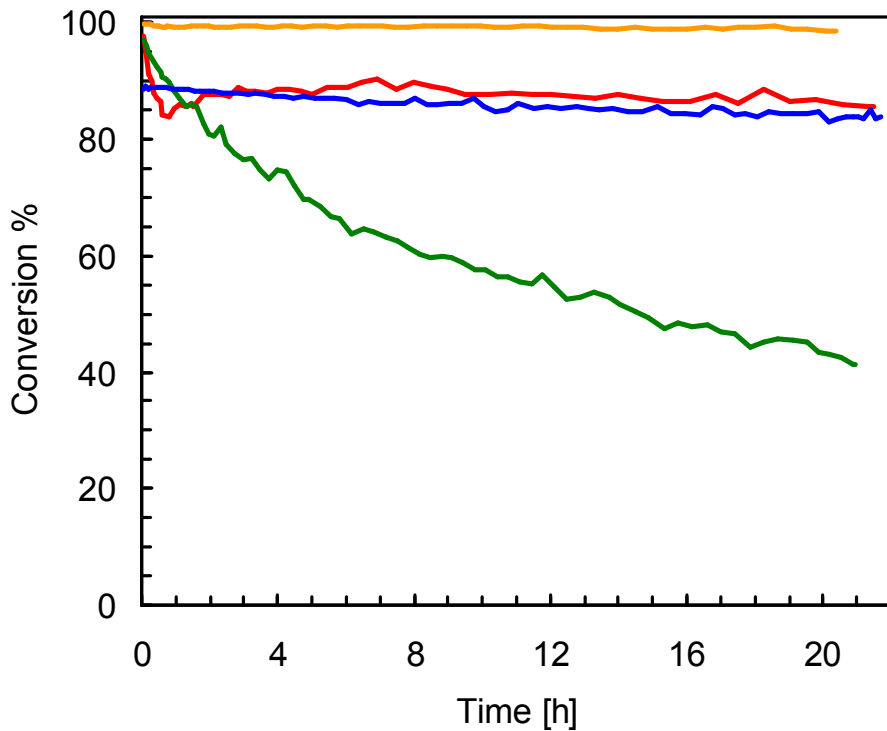


in 2% C₂H₂ + 4% H₂
PdGa: 50 mg, Pd/Al₂O₃: 0.5 mg

Long-term stability of Pd intermetallic compounds

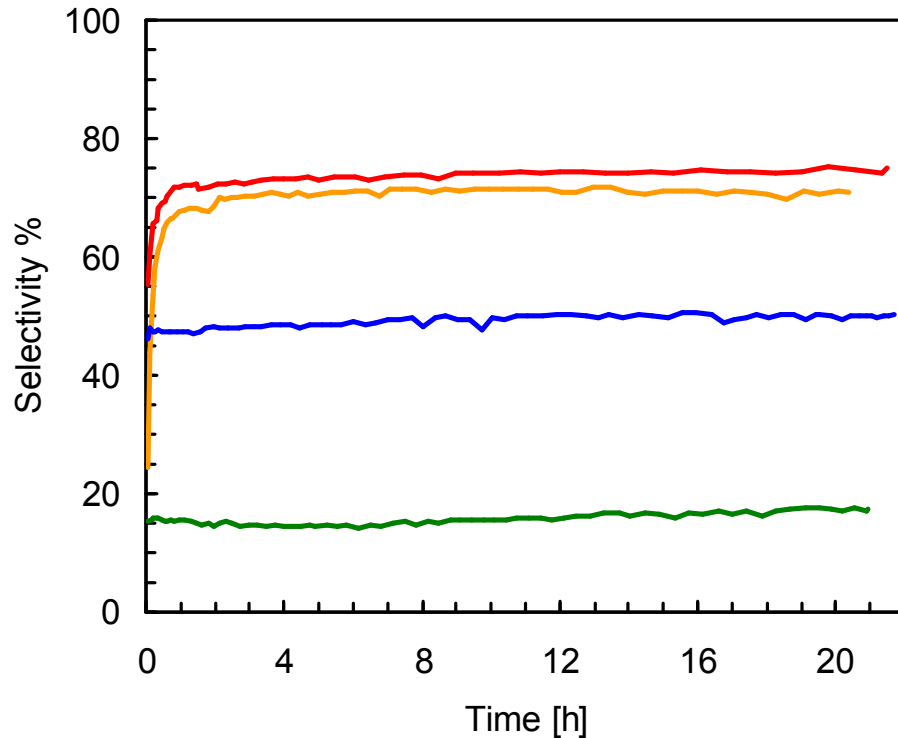
Isothermal experiments in ethylene excess at 473 K

0.5% C₂H₂ + 5% H₂ + 50% C₂H₄



PdGa: 40 mg

Pd/Al₂O₃: 0.15 mg



Pd₃Ga₇: 100 mg

Pd₂₀Ag₈₀: 200 mg

Conclusion

Active-site isolated Pd-Ga intermetallic compounds show

- o high structural stability and no hydride formation
 - o higher selectivity in acetylene hydrogenation compare to Pd and Pd based alloys
 - o catalytic long-term stability
- Isolation of active sites through selection of Pd-Ga intermetallic compounds leads to superior catalysts

Acknowledgement

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Ute Wild

Group Surfaces Analysis, Inorganic Chemistry, FHI

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