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

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Motivation and introduction

Acetylene hydrogenation – active site isolation

– Pd intermetallic compounds

Structural investigation

In situ XRD – In situ EXAFS

Surface studies

BET – CO chemisorption – SEM – XPS

Catalysis data

Activity – selectivity – stability

light alkanes

"naphtha"

steam cracker

ethylene

+ traces of acetylene

selective hydrogenation

of acetylene in ethylene

$C_2H_2 + H_2 \longrightarrow C_2H_4$

$C_2H_4 + H_2 \not\longrightarrow C_2H_6$

ethylene

(≤ 3 ppm acetylene)

polymerisation

"Ziegler-Natta"

HDPE

polyethylene

Why active-site isolated intermetallic compounds?

Pd metal

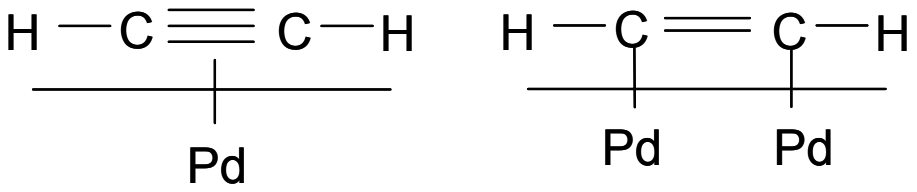
supported on metal oxides

✓ activity

✘ selectivity

✘ long-time stability

1. Active-site isolation [1-4]

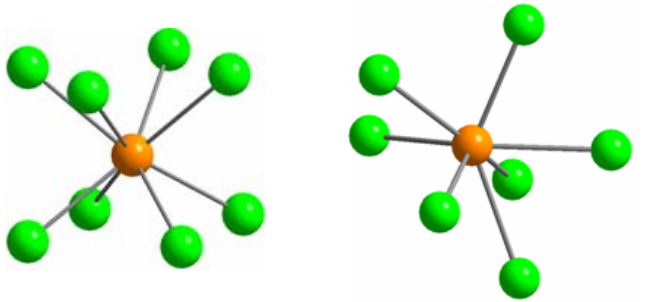


π-bonded

site isolated Pd atoms

di-σ-bonded

neighbouring Pd atoms



Pd intermetallic compounds

Not alloys!

2. Elimination of hydride formation [5-7]

1. Derouane, E. G. *J. Mol. Cat.* 1984, *25*, 51
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5. Palczewska, W. *Hydrogen Effects in Catalysis*; Marcel Decker: New York, 1988; pp 372
6. Bond, G. C.; Wells, P. B. *J. Catal.* 1966, *5*, 65
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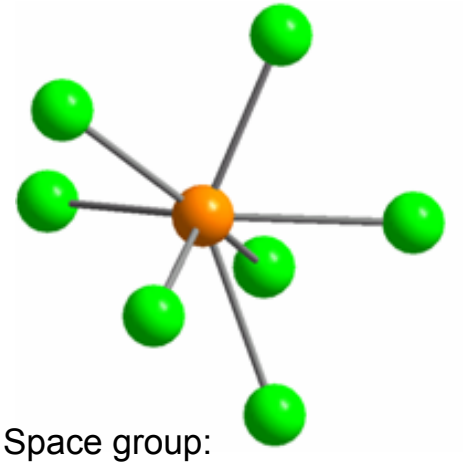
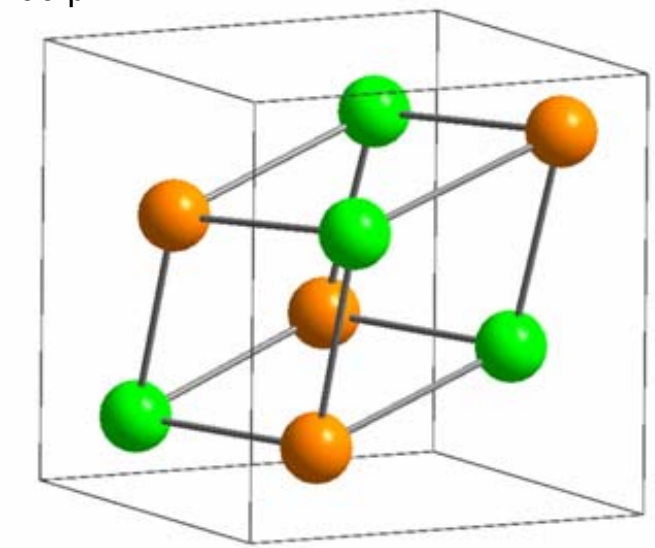
Pd-Ga intermetallic compounds: PdGa and Pd_3Ga_7



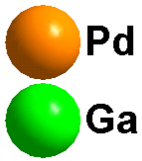
Pd – Ga (1x): 254 pm
Pd – Ga (3x): 257 pm
Pd – Ga (3x): 271 pm
Pd – Pd (6x): 301 pm

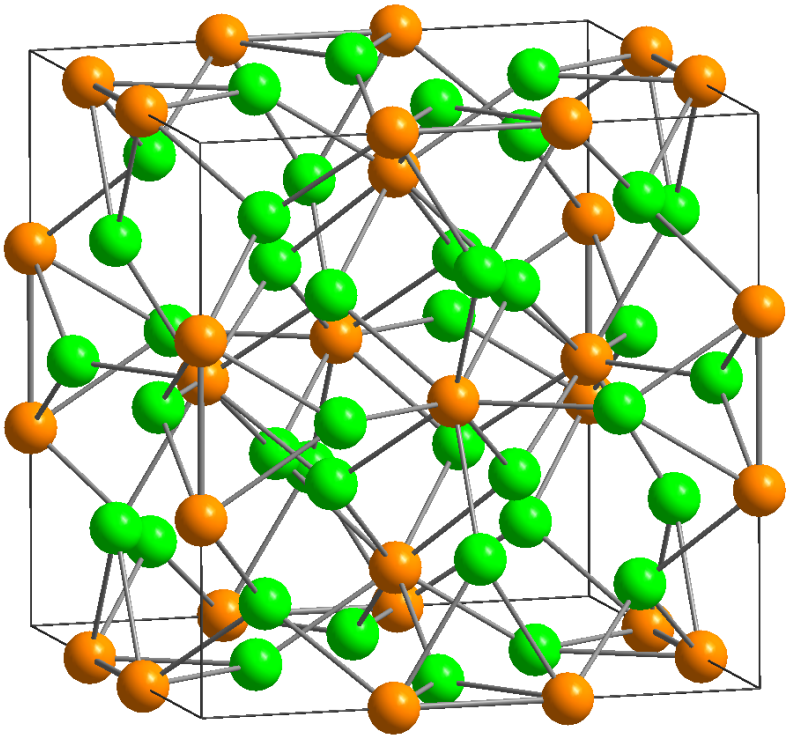
PdGa

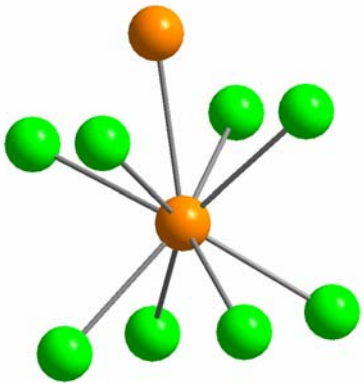
Space group:
cubic: P 2_1 3 (198)
a = 490 pm



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







Pd_3Ga_7

Space group:
cubic: I m -3 m (229)
a = 877 pm

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

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

Pd-Ga intermetallic compounds

$PdGa$ – Pd_3Ga_7

Pd intermetallic compounds

- Structurally defined catalysts with isolated Pd atoms
- Catalysis?

Preparation

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

Goal

Thermal stability in different atmospheres and hydride formation:

Surface investigation:

Catalytic studies:

Methods

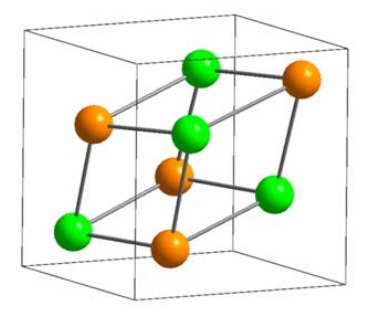
In situ XRD, in situ EXAFS, TG / DSC

BET, CO chemisorption, XPS, ISS

GC, MS

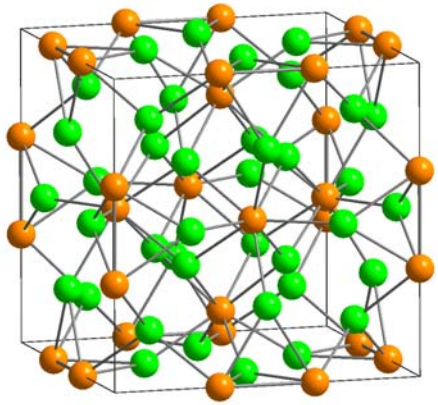
High structural stability of PdGa and Pd_3Ga_7

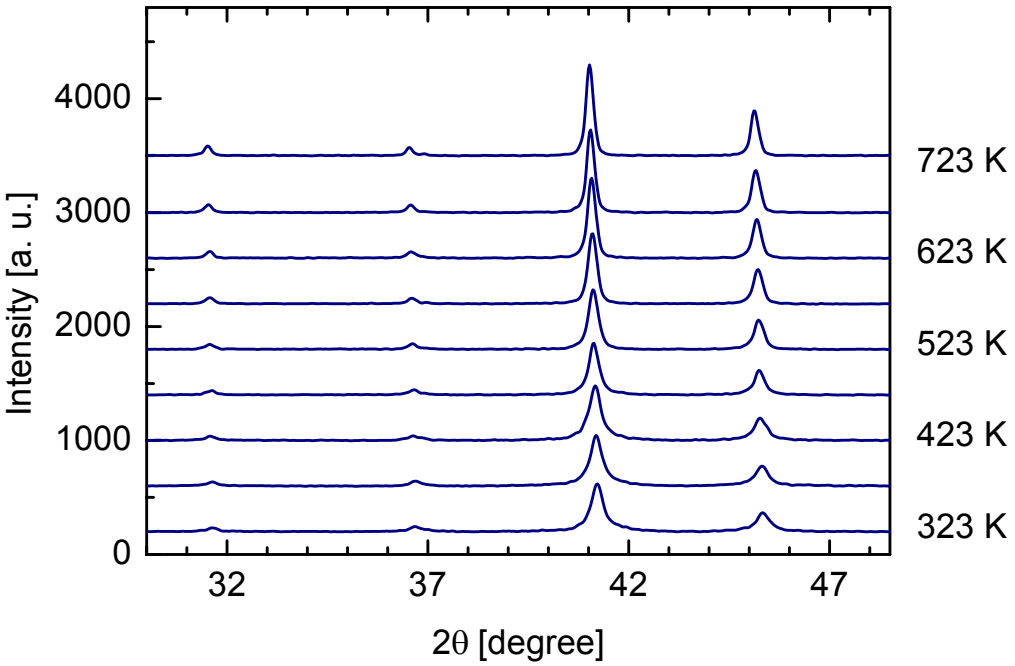
In situ XRD (long-range order) in 50% H_2 + 50% He

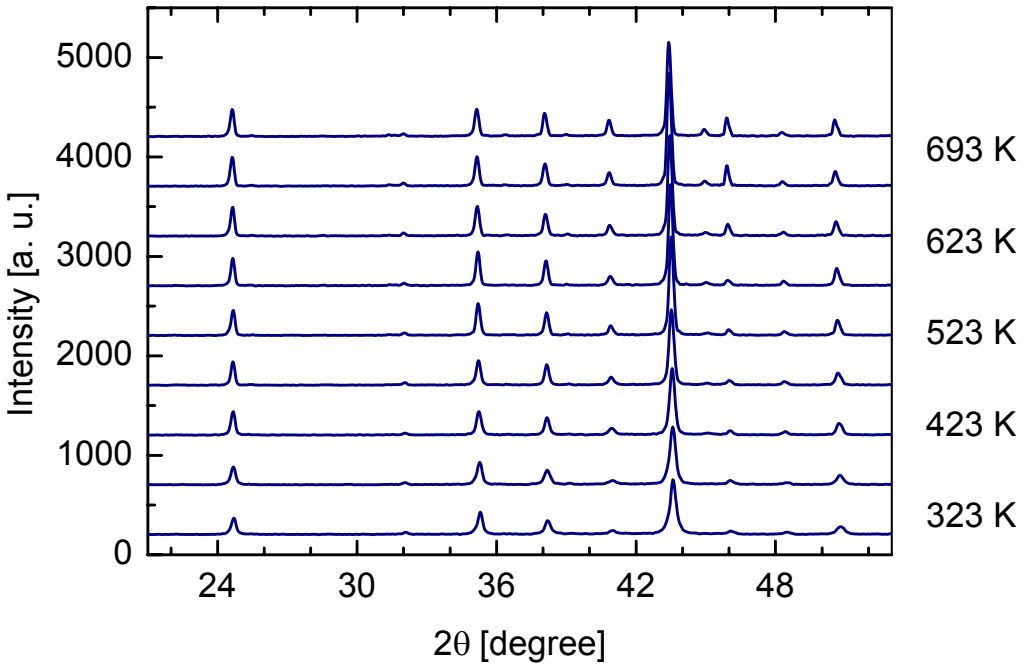


PdGa

Pd_3Ga_7





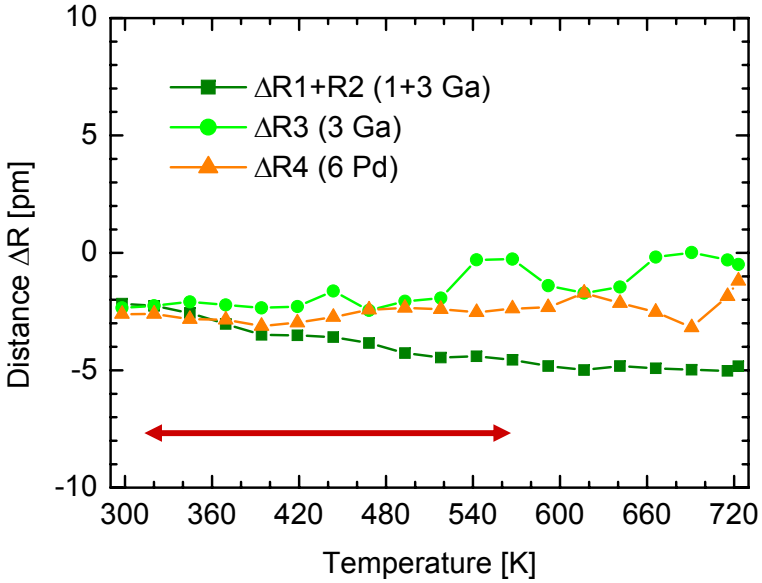


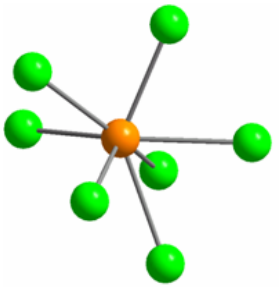
Cu Kα

→ no decomposition, phase transition or hydride formation

High structural stability of PdGa and Pd_3Ga_7

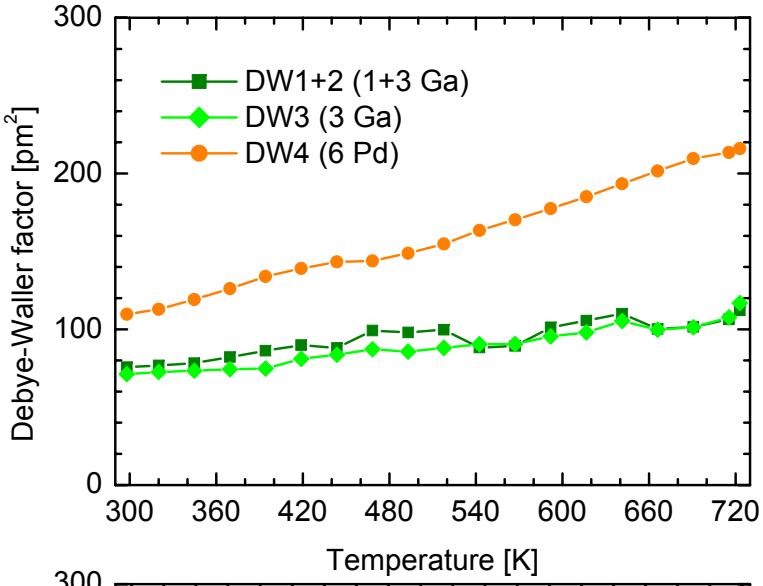
In situ EXAFS (local structure of Pd atoms) measured at Pd K edge (24.35 keV)

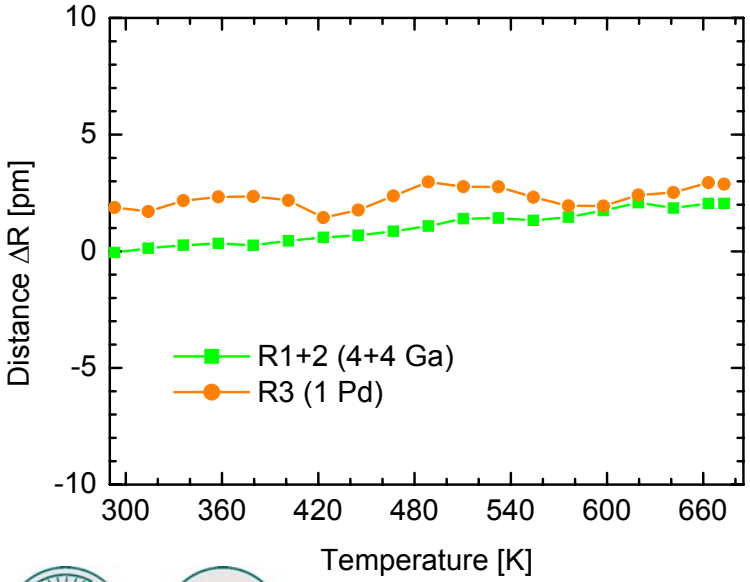


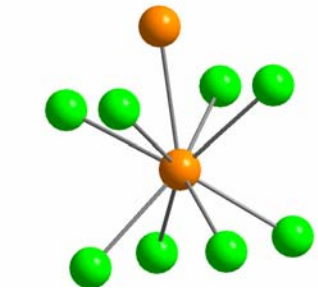


PdGa

in 50% H_2

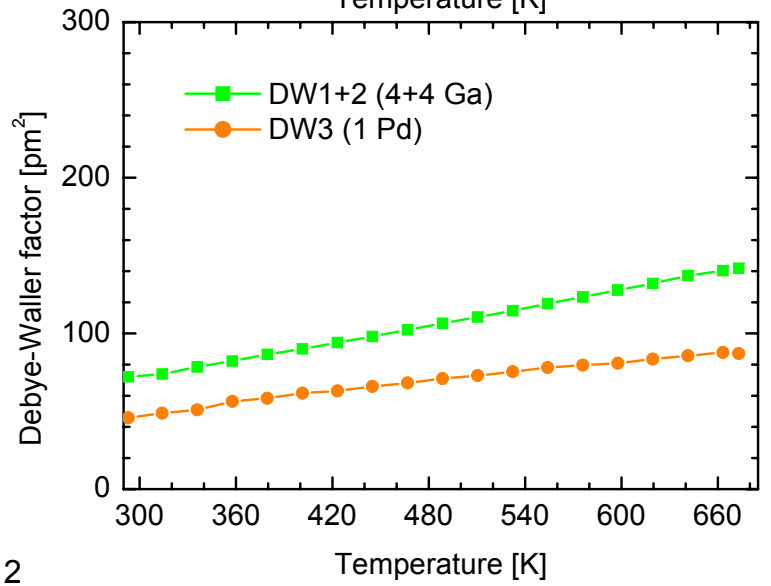






Pd_3Ga_7

in 10% C_2H_2 + 20% H_2



Surface characterisation of Pd-Ga intermetallic compounds

BET: surface area ~ 1 m^2/g

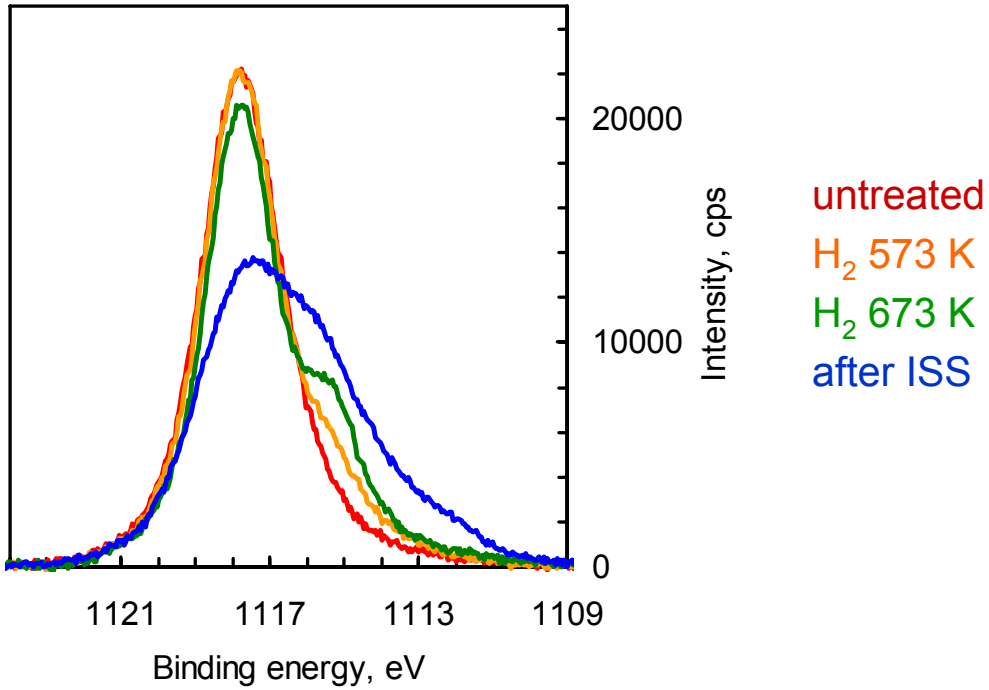
CO chemisorption: no chemisorption of CO at RT detectable

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



Acetylene hydrogenation: $C_2H_2 + H_2 \rightarrow C_2H_4$

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:

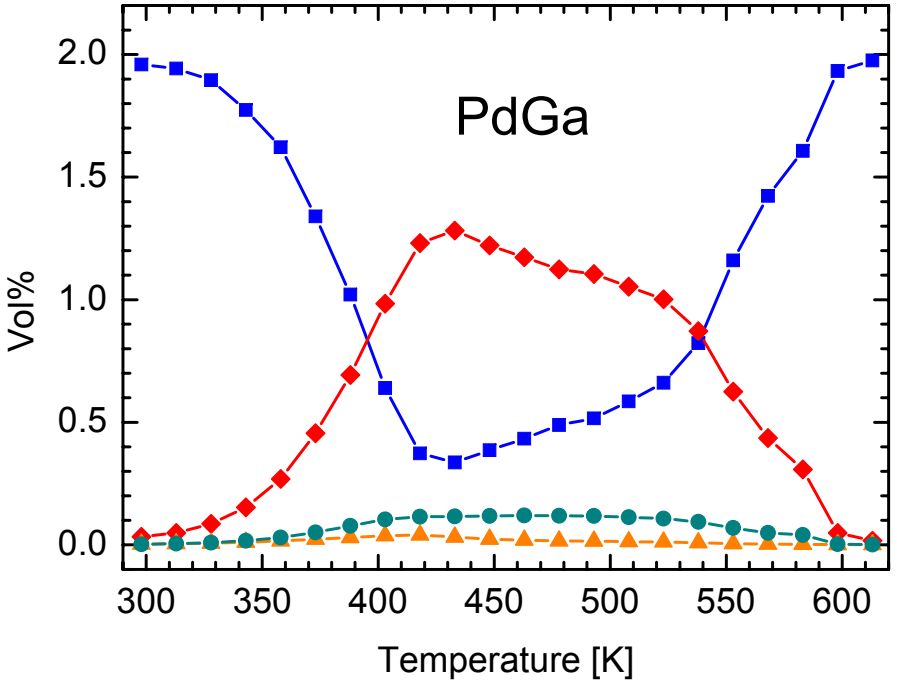
MicroGC

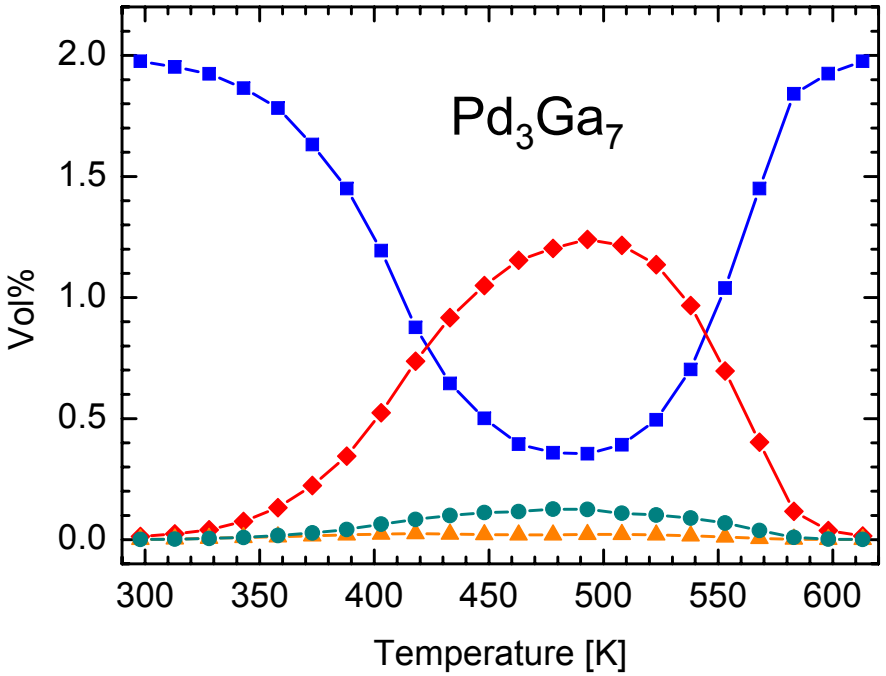
Varian CP 4900, 4-Channel GC

Reference:

Pd/Al_2O_3 5 wt%, *commercial catalyst (Aldrich)*

BET: 114 m^2/g, Pd metal surface: 5.3 m^2/g





Acetylene hydrogenation

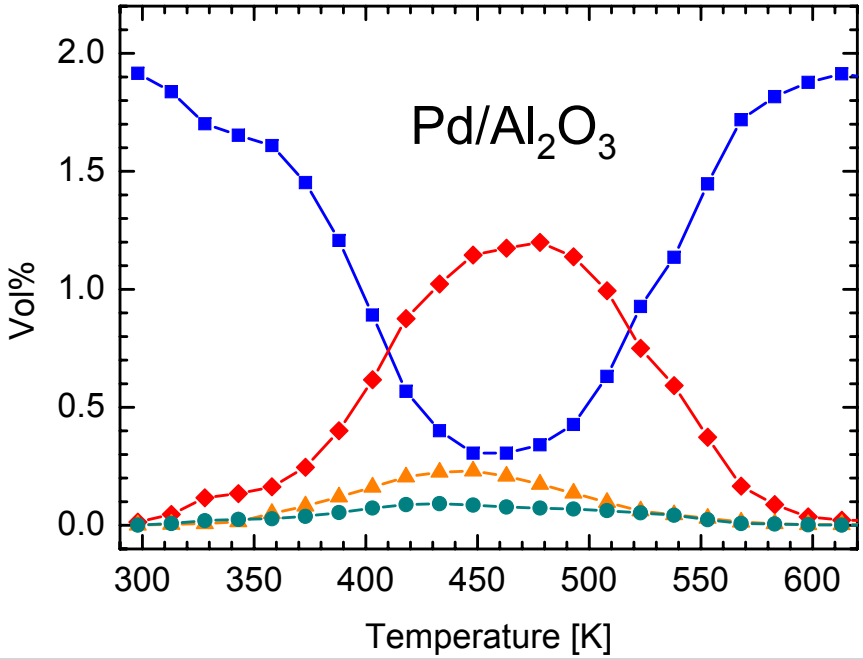
2% C_2H_2 + 4% H_2

PdGa: 50 mg

Pd_3Ga_7: 100 mg

Pd/Al_2O_3: 0.5 mg

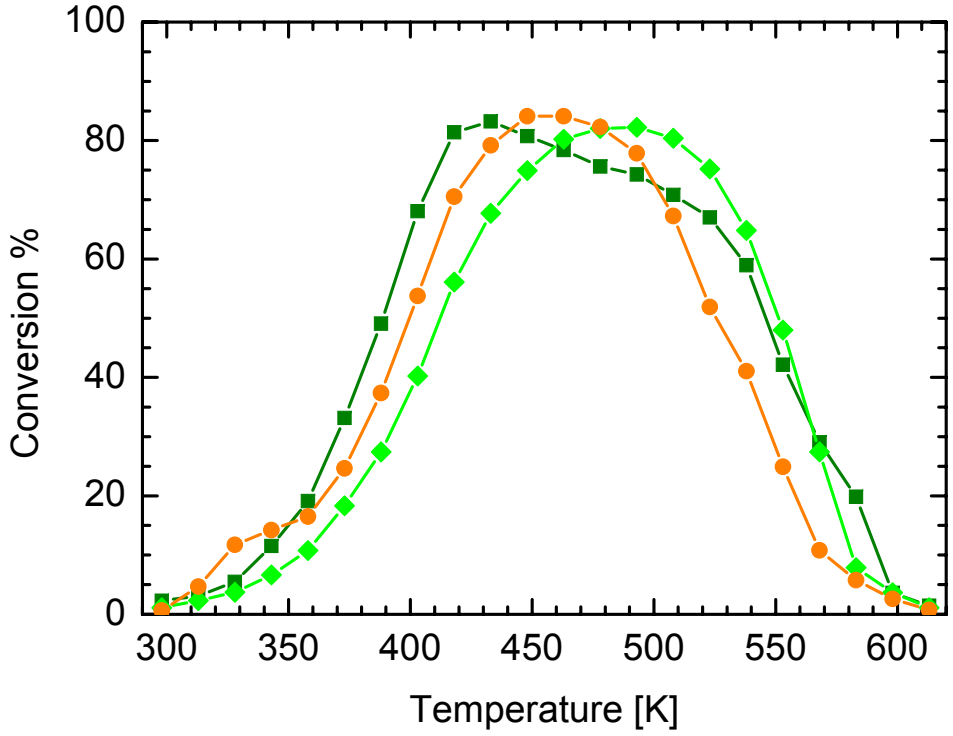
C_2H_2
C_2H_4
C_2H_6
C_4H_x

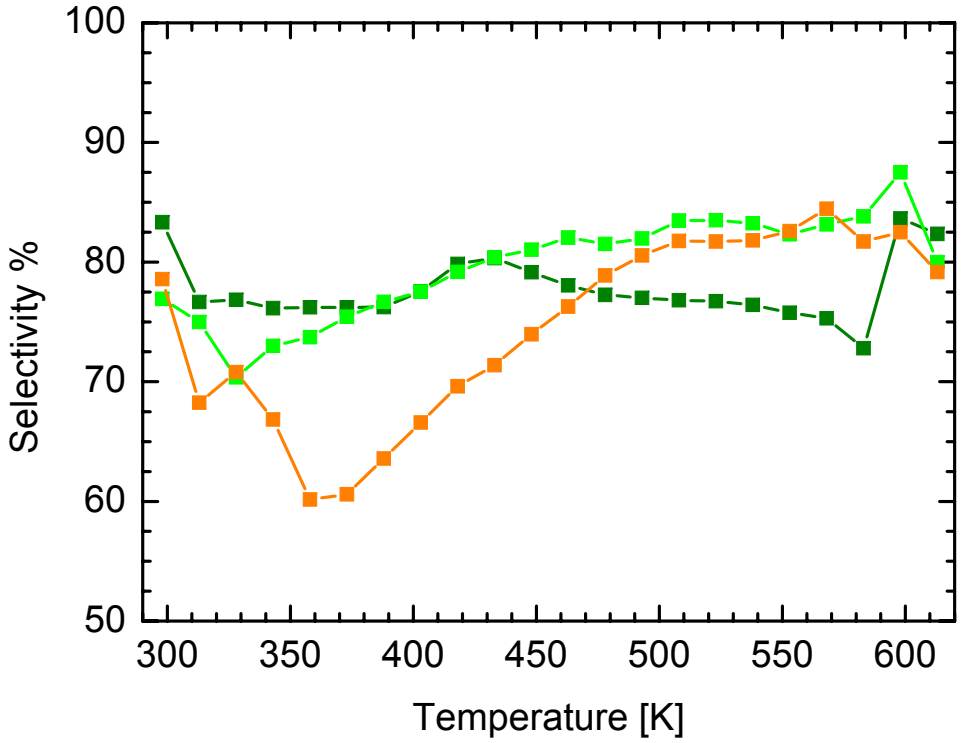


High selectivity of Pd intermetallic compounds

Conversion and selectivity in acetylene hydrogenation

PdGa – Pd_3Ga_7 – Pd/Al_2O_3



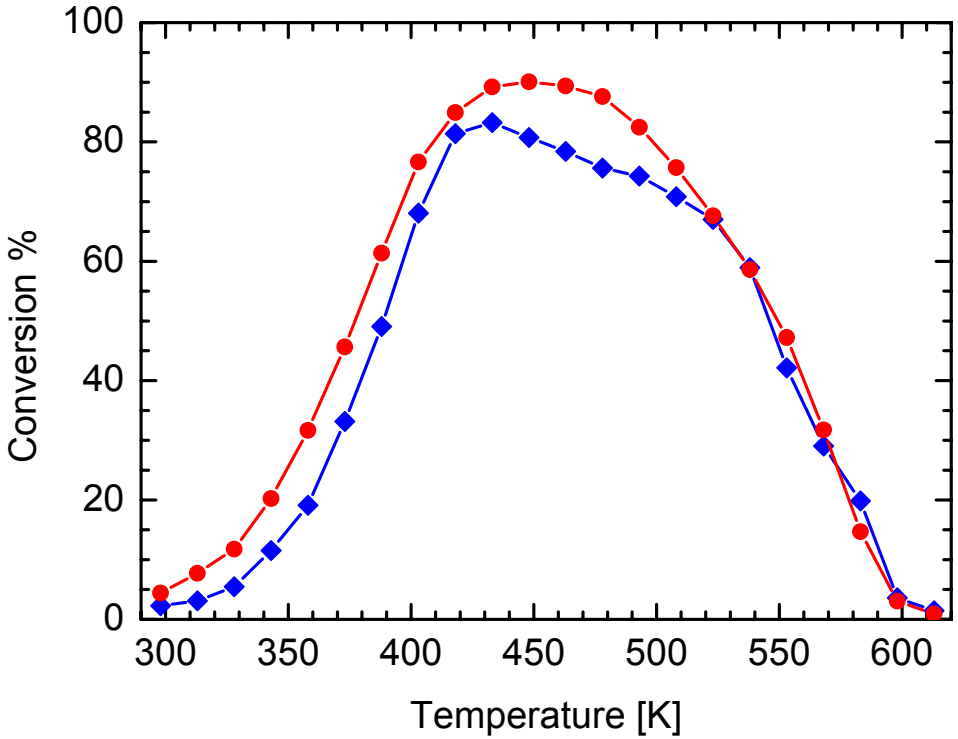


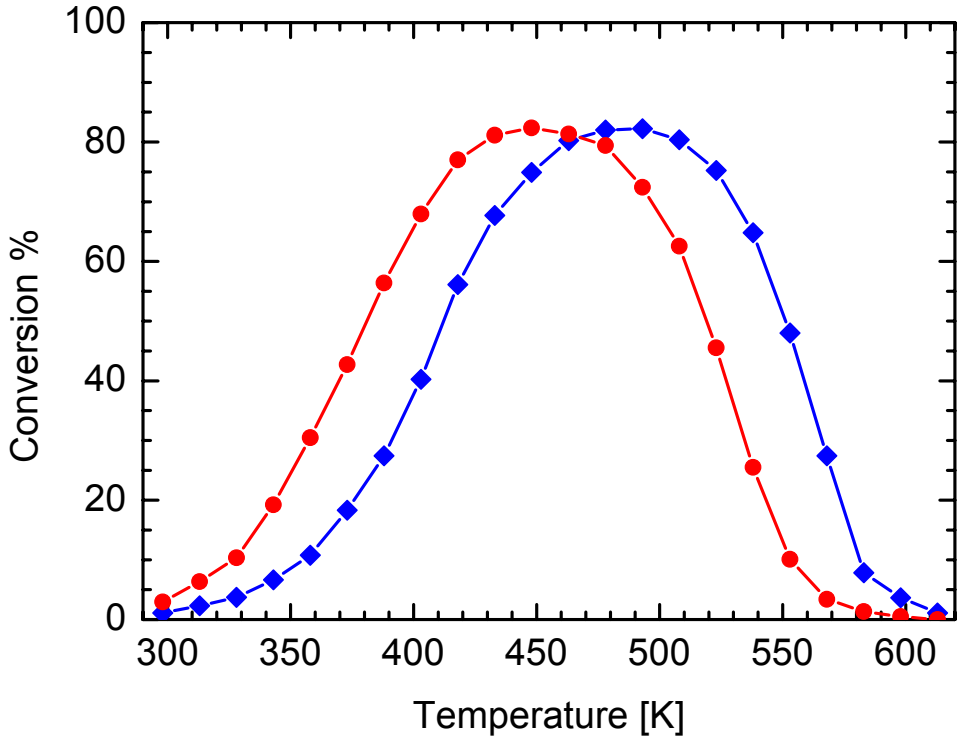
in 2% C_2H_2 + 4% H_2

PdGa: 50 mg, Pd_3Ga_7: 100 mg, Pd/Al_2O_3: 0.5 mg

Increased activity by chemical etching

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



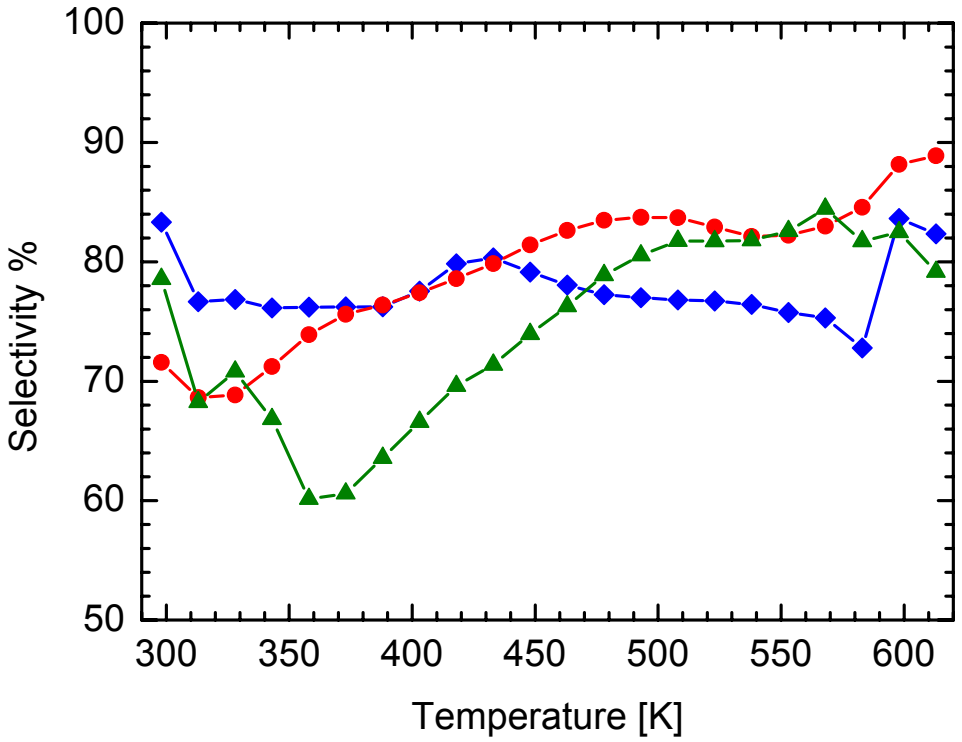


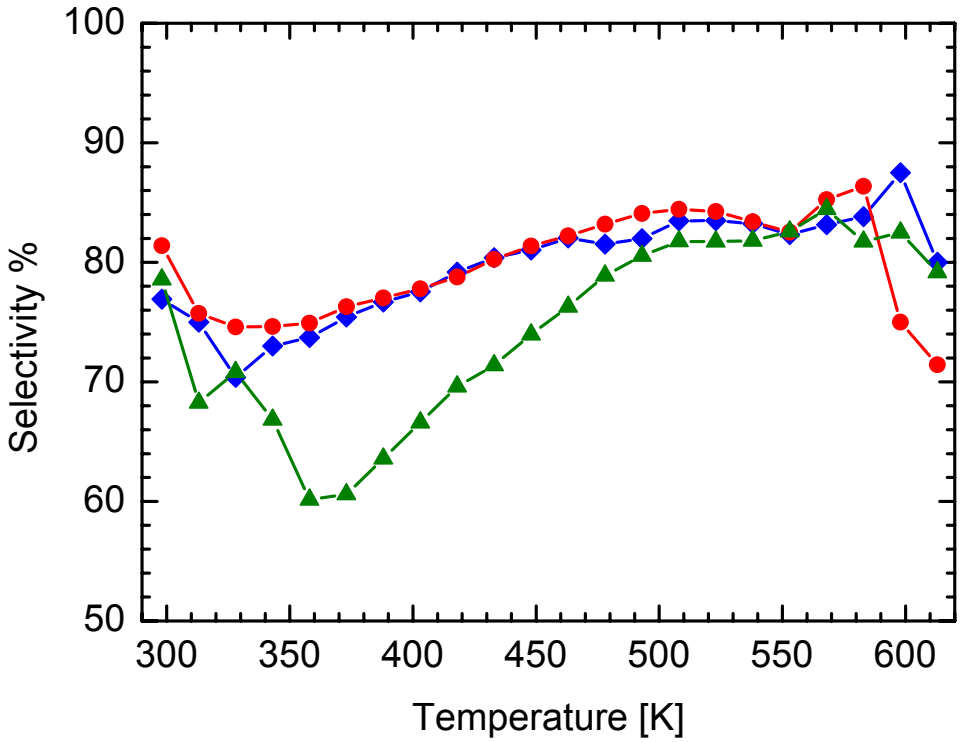
PdGa: 50 mg **untreated** **Pd_3Ga_7: 100 mg**

PdGa: 5 mg **chemically etched** **Pd_3Ga_7: 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/Al_2O_3: 0.5 mg

Pd_3Ga_7: 100 mg

Pd_3Ga_7: 15 mg

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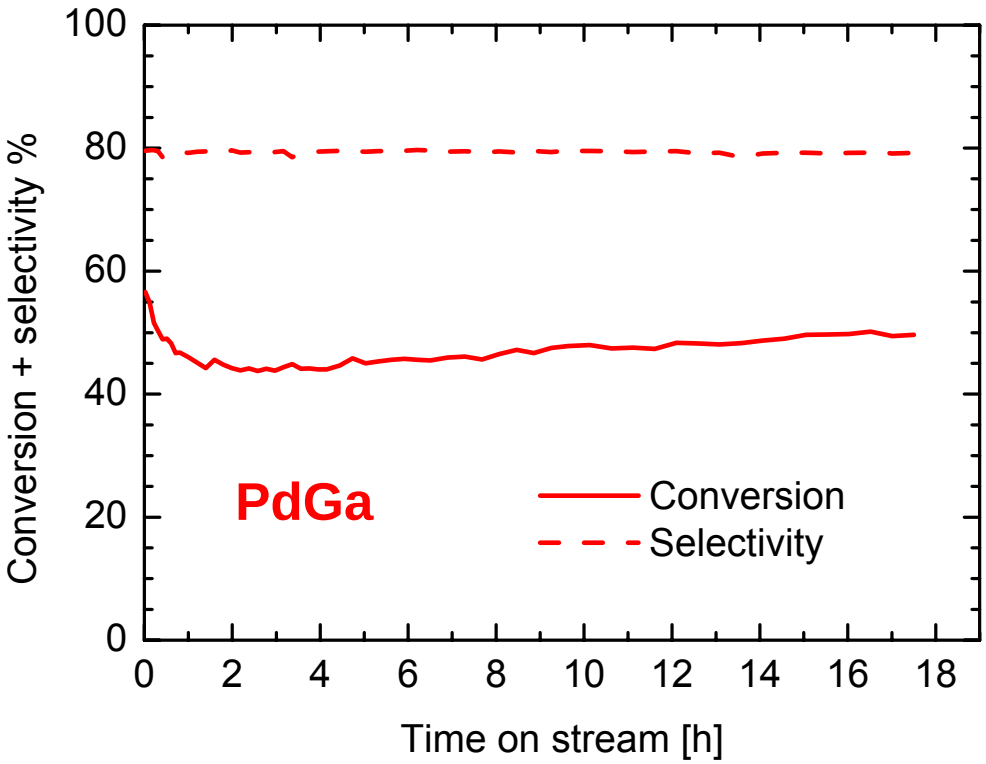
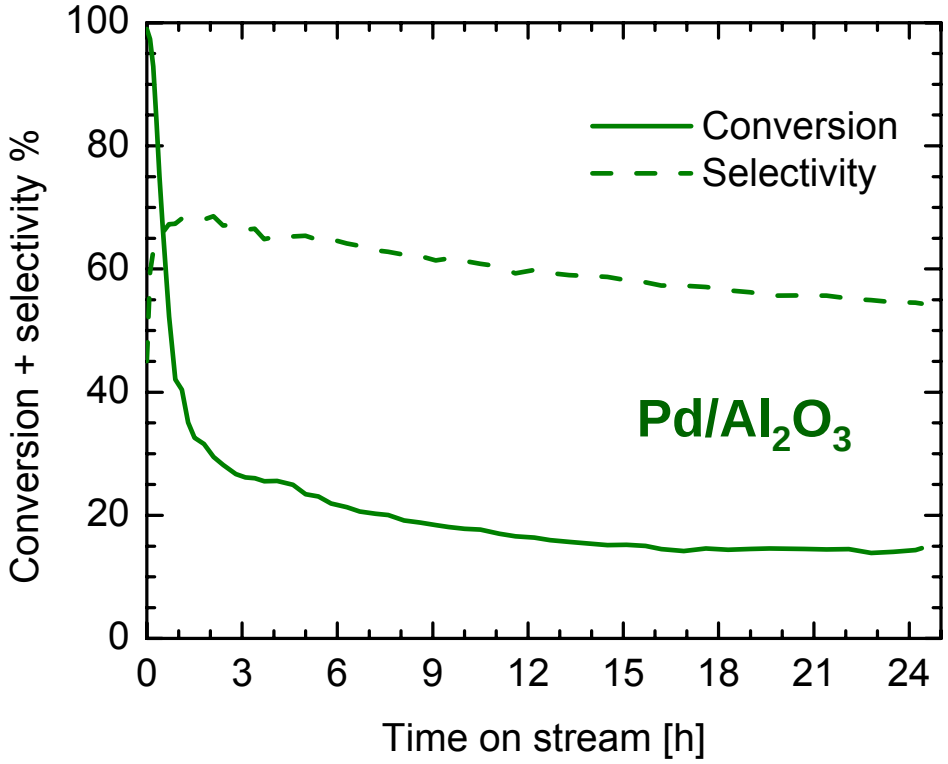
Long-term stability of Pd intermetallic compounds

Isothermal experiments at 398 K





in 2% C_2H_2 + 4% H_2

PdGa: 50 mg, Pd/Al_2O_3: 0.5 mg

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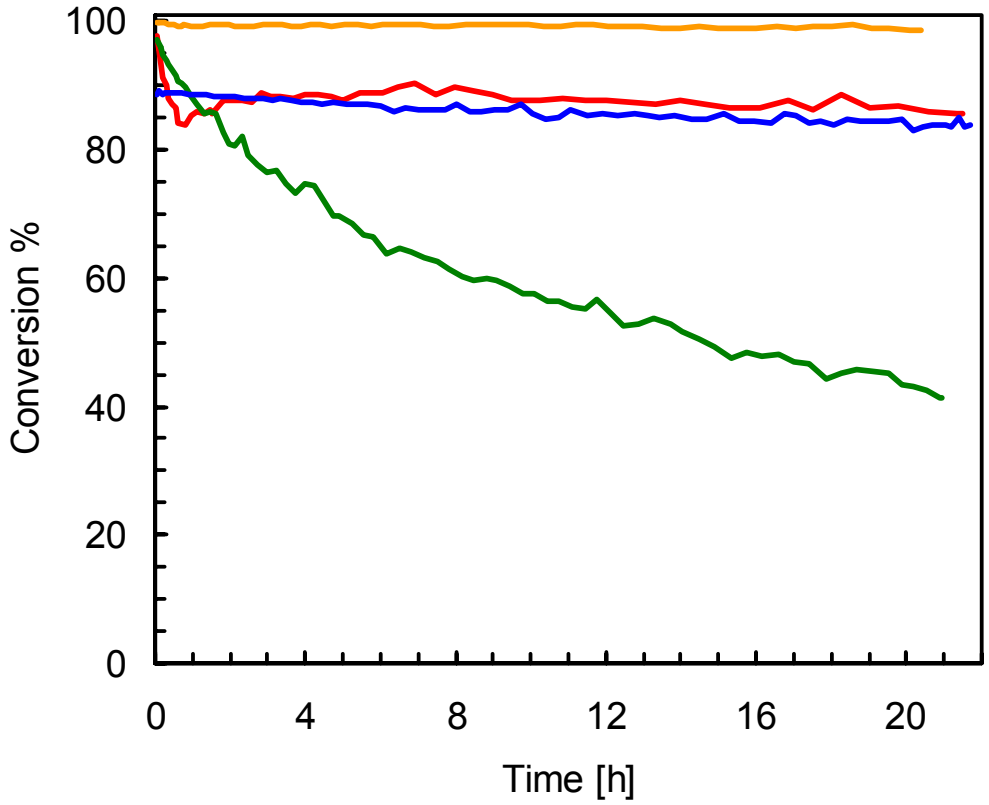
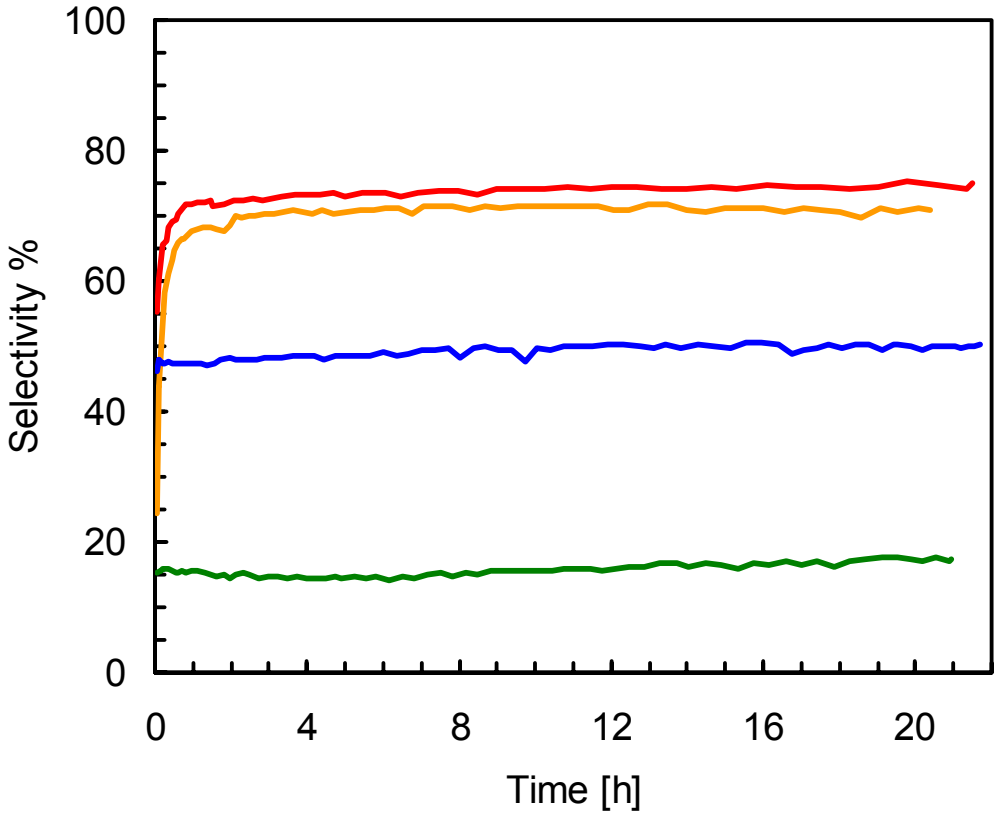
Long-term stability of Pd intermetallic compounds

Isothermal experiments in ethylene excess at 473 K

0.5% C_2H_2 + 5% H_2 + 50% C_2H_4





PdGa: 40 mg

Pd/Al_2O_3: 0.15 mg

Pd_3Ga_7: 100 mg

$Pd_{20}Ag_{80}$: 200 mg

Conclusion

Active-site isolated Pd-Ga intermetallic compounds show

- high structural stability and no hydride formation
- higher selectivity in acetylene hydrogenation compared to Pd and Pd based alloys
- catalytic long-term stability

➢ Isolation of active sites through selection of Pd-Ga intermetallic compounds leads to superior catalysts

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Ute Wild

Group Surfaces Analysis, Inorganic Chemistry, FHI

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