In situ characterization of Pd2Ga catalysts for methanol synthesis by Electron Microscopy and X-ray Diffraction

Fiordaliso, Elisabetta Maria; Sharafutdinov, Irek; Gardini, Diego; Kehres, Jan; Gundlach, Carsten; Thomas, D.; Hansen, Thomas Willum; Chorkendorff, Ib; Wagner, Jakob Birkedal; Damsgaard, Christian Danvad

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

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Catalysis for Sustainable Energy

In situ characterization of Pd_2Ga intermetallic compounds for methanol synthesis

E. M. Fiordaliso[1], I. Sharafutdinov[2], D. Gardini[1], J. Kehres[2], C. Gundlach[3], D. Thomas[4], T. W. Hansen[1], I. Chorkendorff[2], J. B. Wagner[1], C. D. Damsgaard[1,2]

[1]Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark
[2]Center for Individual Nanoparticle Functionality, Department of Physics Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark
[3]Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark
[4]Max II laboratory, University of Lund, SE-22100 Lund, Sweden

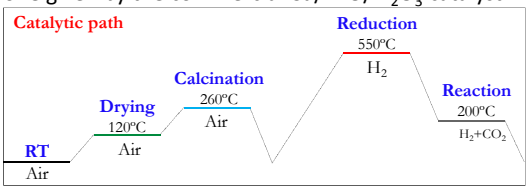
Introduction

Methanol (CH_3OH) is a chemical produced in 40 million tons per year[1] and amongst many applications, it can be used as a fuel or energy carrier. The synthesis is generally carried out from H_2 and CO at pressures up to 100 bar using a $Cu/ZnO/Al_2O_3$ catalyst. New materials able to synthesize methanol from H_2 and CO_2 at low pressure, such as Ni-Ga and Pd-Ga intermetallic compounds, have been predicted by DFT calculations and tested in a reactor [2,3]. In this study Pd_2Ga nanoparticles are investigated by complementary techniques such as XRD, TEM and ETEM, providing information on catalytic properties, size, morphology and crystal phase as summarized in the table.

	Reactor	XRD	TEM	ETEM
Size distribution	No	(Yes)	Yes	Yes
Morphology	No	No	Yes	Yes
Crystal phase	No	Yes	Yes	Yes
Selectivity	Yes	(Yes)	No	No
Activity	Yes	(Yes)	No	No
Pressure	1 - 10 bar	10^{-6} - 1 bar	HV	5 mbar
Flow	5 Nl/min	100 Nml/min	-	10 Nml/min

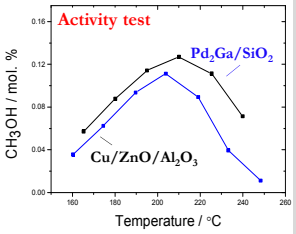
Catalytic path and test of Pd_2Ga/SiO_2 (1 bar)

A high surface area (HSA) silica is impregnated with a solution of Pd and Ga nitrates in nitric acid. The catalyst is dried and calcined in air then reduced at 550°C in H_2. Methanol synthesis from H_2 and CO_2 is carried out in the range 160-250°C and the products are measured by gas chromatography. The yield from Pd_2Ga/SiO_2 catalyst is found to be higher than the one given by the commercial $Cu/ZnO/Al_2O_3$ catalyst.



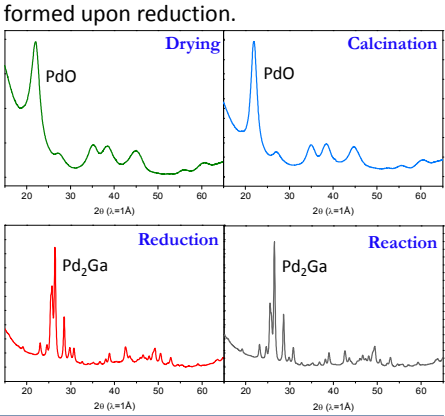
Methanol synthesis reaction:

$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O$



Investigation by *In-situ* XRD (1 bar)

XRD patterns using synchrotron radiation are acquired at the 711 beam line of the *Max II Laboratory* (Lund, Sweden) during each step of the catalytic path to study the crystal phase and the alloy formation. During drying and calcination a PdO phase is observed (Ga_2O_3 is amorphous) and the active phase for the methanol synthesis is formed upon reduction.



Sample preparation for TEM

1. *Model system* (2-D)

$Pd(NO_3)_2 + Ga(NO_3)_3 + HNO_3 + H_2O$

Impregnation on SIMPore grid

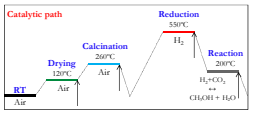
2. *Real system* (3-D)

$Pd(NO_3)_2 + Ga(NO_3)_3 + HNO_3 + H_2O$ on HSA silica

Deposition on Au/SiO_2 grid

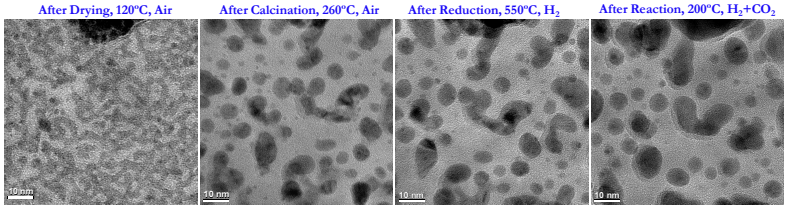
TEM of identical location (HV)

The catalytic path is carried out at 1 bar in a furnace (Anton Paar XRK 900) connected to a gas system and containing a ceramic holder for 6 TEM grids. After each step of the path (see arrows in the figure) the grids are trasferred to the TEM (HV), where images of identical locations are acquired in order to follow the evolution of the catalysts through the path.



Ceramic holder
Furnace ↔ TEM transfer of grids

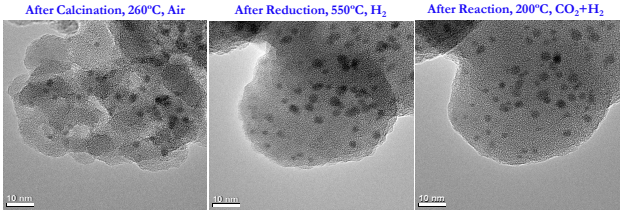
1. TEM of identical location the *model catalyst*



Images acquired at 200 kV, 285000 Magnification, Fei Technai

Between drying and calcination XRD shows that there is no changes in the crystal phase, whereas TEM images reveal a significant morphological change of the catalyst. During calcination the nanoparticle formation takes place and the size distribution is determined.

2. TEM of identical location for the *real catalyst*



Images acquired at 200 kV, 285000 Magnification, Fei Technai

The supported nanoparticles are very stable through the catalytic path, although sintering of the support is observed. The particle size is smaller than for the model catalyst because of the interaction with the HSA silica support.

Sample preparation for ETEM

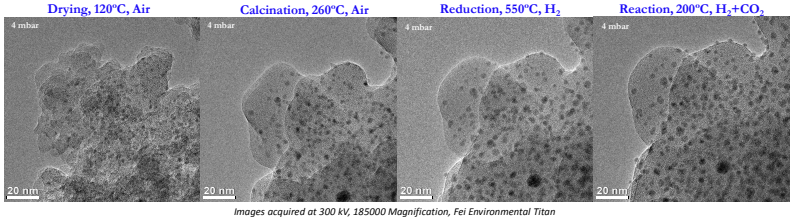
1. Real system (3-D)

$Pd(NO_3)_2 + Ga(NO_3)_3 + HNO_3 + H_2O$ on HSA silica

Deposition on Protochips

ETEM (4 mbar)

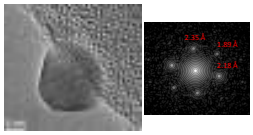
The test of the Pd_2Ga/SiO_2 nanoparticles in the reactor and the *In situ* XRD measurements are carried out at 1 bar, whereas the TEM images are acquired in vacuum. Repeating the whole catalytic path at 4 mbar in the ETEM enables to bridge the pressure gap between XRD and TEM and allows monitoring the catalyst evolution *in situ* and in real time.



Images acquired at 300 kV, 185000 Magnification, Fei Environmental Titan

During each step the beam is parked outside the areas selected for imaging, to avoid beam induced effects. The results are consistent with the observations in TEM (HV) for the supported catalyst, showing that the Pd_2Ga/SiO_2 is a stable system and that pressure does not play an important role in the particle formation and evolution.

Particle analysis



HRTEM image show view along the [0 1 3] zone axis of Pd_2Ga

Conclusions

- Pd_2Ga intermetallic compounds have been investigated by complementary techniques (Reactor measurement, XRD, TEM and ETEM).
- The test of the catalyst in the reactor shows that the methanol yield from Pd_2Ga/SiO_2 is higher to the one given by $Cu/ZnO/Al_2O_3$.
- XRD shows that the Pd_2Ga phase is formed upon reduction.
- Morphological changes and nanoparticle formation are observed by TEM imaging of identical locations and by ETEM experiments.
- Further investigation is required in order to further optimize the Pd_2Ga alloys for the methanol synthesis reaction from CO_2.

Contact: Elisabetta M. Fiordaliso
e.fiordaliso@cen.dtu.dk

References
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