Characterization and Performance of Pd/CeO_2 Catalysts as a Powder in Fixed-bed Reactor and as a Coating in a Stacked Foil Microreactor for the Methanol Synthesis

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Xuyen Kim Phan[1], John Walmsley[2], Hamidreza Bakhtiary-Davijany[1], Rune Myrstad[2], Peter Pfeifer[3], Anders Holmen[1] and Hilde J. Venvik[1]

1. *Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Sem Sælands vei 4, N-7491, Trondheim, Norway*
2. *SINTEF Materials and Chemistry, Sem Selands vei 2A, N-7465 Trondheim, Norway*
3. *Karlsruhe Institute of Technology, Institute for Micro Process Engineering, D-76344 Eggenstein-Leopoldshafen, Germany*

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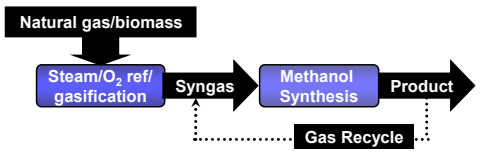
Introduction

Solution for Remote Natural Gas Fields or Biofuels?



Microstructured reactors have recently been proposed as alternatives to the conventional reactor technology in compact applications due to their heat and mass transfer properties

Objectives

- Explore the properties of Pd-based catalyst coatings for methanol synthesis in microstructured reactors
  - Reaction mechanism over Pd to facilitate unconventional synthesis gas [1]
  - High activity potential with particular supports [2] ?

Experiments

Reactors and reaction conditions

- 14 structured and coated foils stacked and sealed inside alloy 800 housing graphite (Frentzelit) [4]

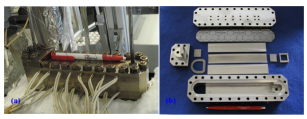


Figure 1: The stacked foil microreactor (SFMR) under operation (a), opened (b).

- SS tube fixed-bed reactor (FBR, Φ=10mm).
- Reduction at 1 bar and 300 ºC in 10 vol.% H_2 in N_2.
- Methanol synthesis at 220-350 ºC and 80 bar ($H_2/CO/CO_2/N_2$ = 65/25/5/5).

Preparation of Pd/CeO_2 catalysts:

- 10 wt% Pd/CeO_2 foil coatings:
  1. CeO_2 sol-gel prepared from cerium ammonium nitrate[2],
  2. CeO_2 sol-gel dripped uniformly over microchannels, followed by drying (70 ºC, overnight) and calcination (500 ºC, 5 h, air).
  3. CeO_2 layer dripped with $PdCl_2$ solution until 10 wt. %, dried and calcined as before.
- 10 wt% Pd/CeO_2 50-120 µm catalyst particles:
  - Deposition – precipitation, using CeO_2 nanopowder (Sigma Aldrich, d < 25 nm) and $PdCl_2$ solution as precursors.

Characterization

- S_{BET} by N_2 adsorption (-196 ºC Micromeretics Tristar 3000).
- XRD Bruker AXS D8 Focus (CuKα, 20-90º, 0.03º step, 0.6s/step..
- Volumetric CO chemisorption at (313 K) of prereduced sample. D, %, calculated assuming Pd/CO=1
- SEM (Zeiss Ultra 20 kV) and SEM EDS (Bruker Quantex).
- TEM (JEOL 2010F, 200 kV) and TEM EDS (Oxford Instruments INCA).

Results and discussion

Pd/CeO_2 catalyst activity and stability

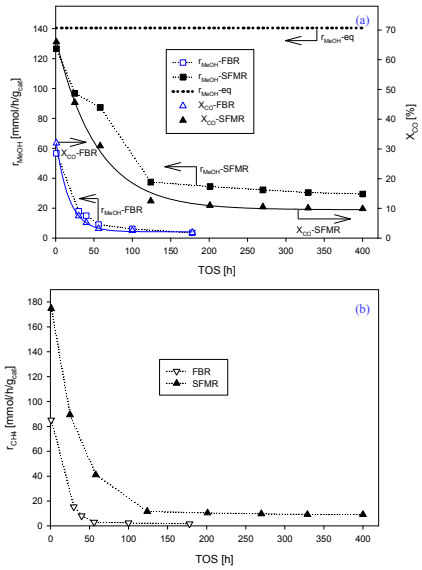


Figure 2: CO conversion and rate of CH_3OH (a) and CH_4 by-product (b) formation with time on stream (TOS) for Pd/CeO_2 powder catalyst (FBR) and Pd/CeO_2 foil coating in SFMR. T = 300 ºC, contact time W/F = 110 [ms·g_{cat}/cm^3], pressure 80 bar and syngas composition $H_2/CO/CO_2/N_2$ = 65/25/5/5.

Pd/CeO_2 powder catalyst characterization

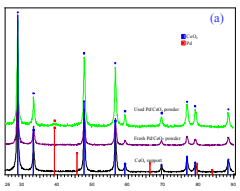


Figure 3: XRD diffractograms (a) of the CeO_2 support and the Pd/CeO_2 powders before and after testing in FBR and bright-field TEM micrographs (b) of the fresh Pd/CeO_2 powder at different magnifications.

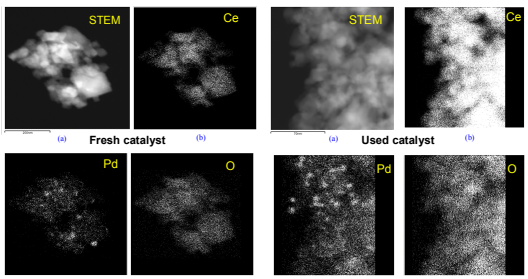


Figure 4: Dark-field STEM micrograph (a) and complementary EDS Ce (b), Pd (c), and O (d) mapping of the fresh (left panels) and used (right panels) Pd/CeO_2 powder catalyst.

	S_{BET} [m^2/g][a]	d_{pore} [nm][b]	Pore volume [cm^3/g][b]	D [%][c]	dp [nm][d]
CeO_2	32	21	0.178	-	-
Pd/CeO_2	52	14	0.183	32	3.4

[a] BET surface area.
[b] Average pore size and pore volume calculated by using BJH method.
[c] Pd dispersion calculated from CO chemisorption at 313 K.
[d] Pd particle size based on CO chemisorption at 313 K.

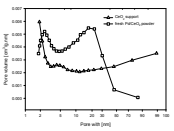


Figure 5: BET and chemisoption data

Pd/CeO_2 foil coating characterization

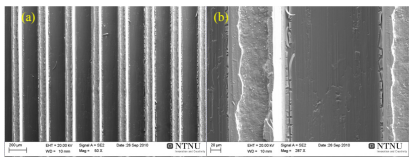


Figure 6: SEM pictures of the fresh Pd/CeO_2 coated foil at low (a) and high (b) magnification.

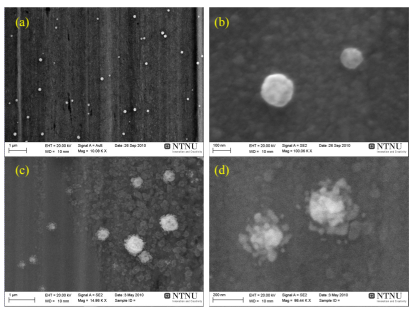


Figure 7: SEM pictures of the fresh (a-b) and the used (c-d) Pd/CeO_2 coated foil at 10^4-10^5 magnification.

Conclusions

- The Pd/CeO_2 catalysts show extremely high initial activity but deactivate significantly
- Transition from high S_{CH4} and low S_{CH3OH} to decreased CH_4 formation and improved S_{CH3OH} upon stabilization.
- Activity of Pd/CeO_2 foil coating (sol-gel synthesis) substantially better than of Pd/CeO_2 particles (deposition-precipitation)
- Significantly higher Pd dispersion of Pd/CeO_2 powder than of Pd/CeO_2 foil coating
- Effects attributed to the Pd nanoparticles being covered by a ceria during the preparation and subsequent reduction [6]

References

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