



Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation

Gardini, Diego; Mortensen, Peter Mølgaard; Carvalho, Hudson W. P.; Damsgaard, Christian Danvad; Grunwalst, Jan-Dierk; Jensen, Peter Arendt; Jensen, Anker Degn; Wagner, Jakob Birkedal

Published in:

Microscopy and Microanalysis

Link to article, DOI:

[10.1017/S1431927614004012](https://doi.org/10.1017/S1431927614004012)

Publication date:

2014

[Link back to DTU Orbit](#)

Citation (APA):

Gardini, D., Mortensen, P. M., Carvalho, H. W. P., Damsgaard, C. D., Grunwalst, J-D., Jensen, P. A., ... Wagner, J. B. (2014). Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation. *Microscopy and Microanalysis*, 20(Suppl. 3), 458-459. DOI: 10.1017/S1431927614004012

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation

D Gardini¹, P M Mortensen², H W P Carvalho³, C D Damsgaard^{1,4}, JD Grunwaldt³, P A Jensen², A D Jensen² and J B Wagner¹.

1. Technical University of Denmark, Center for Electron Nanoscopy, DK-2800 Kgs. Lyngby, Denmark.
2. Technical University of Denmark, Department of Chemical and Biochemical Engineering, DK-2800 Kgs. Lyngby, Denmark.
3. Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, 76131 Karlsruhe, Germany.
4. Technical University of Denmark, Center for Individual Nanoparticle Functionality, Department of Physics, DK-2800 Kgs. Lyngby, Denmark.

digar@cen.dtu.dk

Keywords: STEM-EDX, catalysis, bio-oil

Hydrodeoxygenation (HDO) is proposed as an efficient way to remove oxygen in bio-oil, improving its quality as a more sustainable alternative to conventional fuels in terms of CO₂ neutrality and relative short production cycle [1].

Ni and Ni-MoS₂ nanoparticles supported on ZrO₂ show potential as high-pressure (100 bar) catalysts for purification of bio-oil by HDO. However, the catalysts deactivate in presence of sulfur, chlorine and potassium species, which are all naturally occurring in real bio-oil.

The deactivation mechanisms of the Ni/ZrO₂ have been investigated through scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Catalytic testing has been performed using guaiacol in 1-octanol acting as a model compound for bio-oil.

Addition of sulphur (0.3 vol% octanethiol) in the feed resulted in permanent deactivation of the catalyst by formation of a catalytically inactive Ni-S phase, as suggested by the very similar spatial distribution of nickel and sulphur signals in STEM-EDX elemental maps (Figure 1) and confirmed by XRD and X-ray absorption spectroscopy (XAS) techniques.

Deactivation by chlorine (0.3 vol% chlorooctane) co-feeding was found to be reversible, as the catalyst could regain close to its initial deoxygenation activity upon restoration of a clean feed. SEM-EDX investigations excluded the presence of chlorine species; however, XRD analysis revealed sintering of nickel nanoparticles (Figure 2).

Impregnating KCl and KNO₃ on two different batches of catalysts decreased permanently their deoxygenation activity, suggesting the adsorption of potassium at low coordinated nickel sites [2]. The high mobility of potassium under the electron beam [3] prevented the spatial distribution study of this element through STEM-EDX. Moreover, nickel sintering was observed in the KCl poisoned sample and was ascribed once again to the formation of mobile Ni-Cl species upon reaction of HCl with surface oxides [4].

Furthermore, environmental transmission electron microscopy (ETEM) has been used in order to investigate the oxidation of Ni-MoS₂/ZrO₂ catalyst active phase as a function of different HDO reaction conditions and using methanol as a model molecule for bio-oil.

References

- [1] P. M. Mortensen *et al*, Appl. Catal. A: Gen. **407** (2011) p. 1-19.
- [2] H. S. Bengaard *et al*, J. Catal. **209** (2002), p. 365-384.
- [2] S. Hodson and J. Marshall, J. Microsc. **93** (1971), p. 49-53.

[3] Y. Ohtsuka, J. Mol. Cat. **54** (1989), p. 225-235.

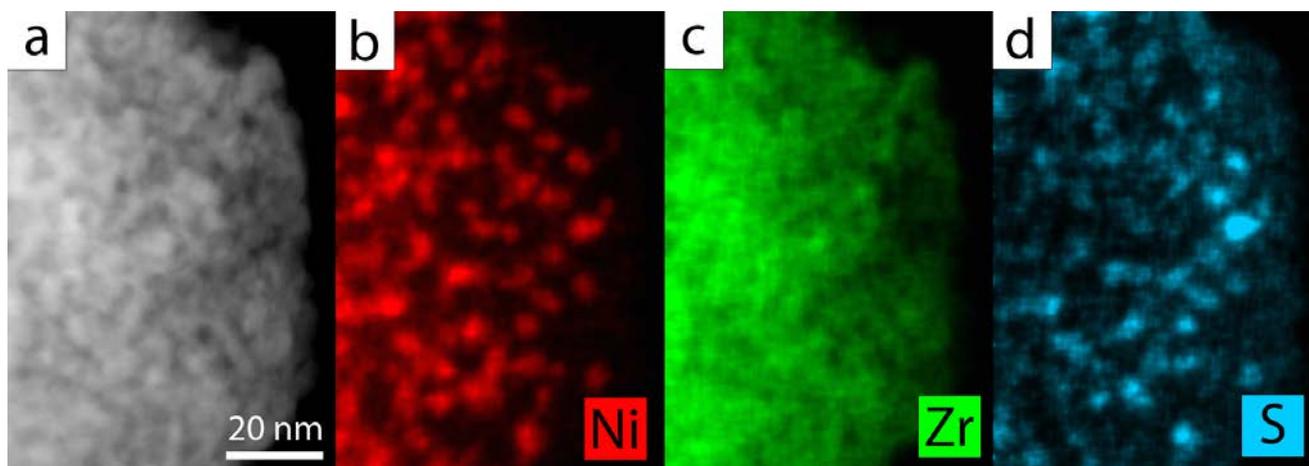


Figure 1 (a) STEM-HAADF micrograph of a portion of a sulfur poisoned Ni/ZrO₂ catalyst with (b) nickel, (c) zirconium and (d) sulfur EDX elemental distributions.

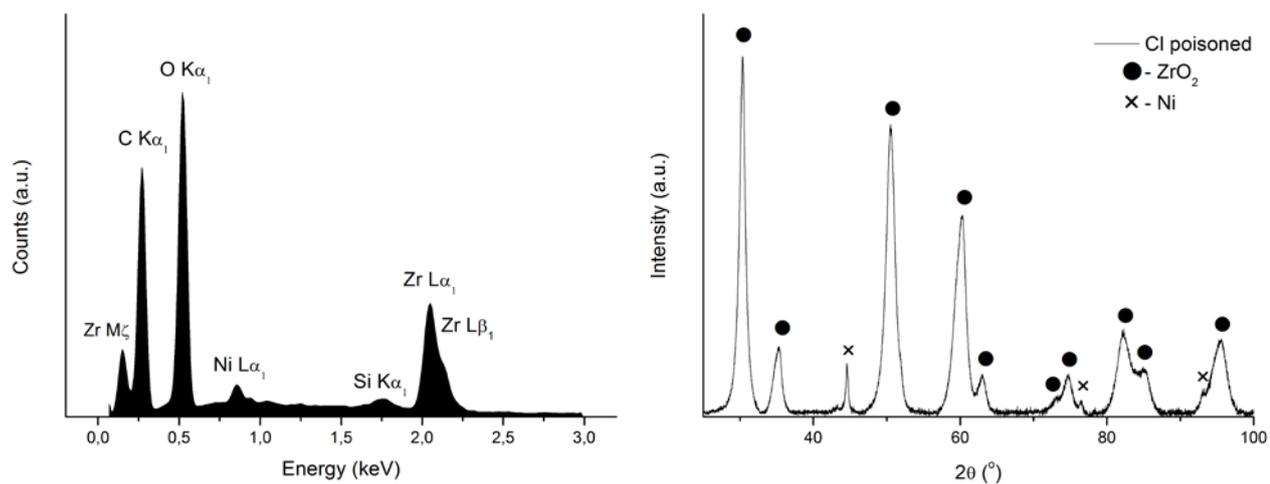


Figure 2 (Left) SEM-EDX spectrum of the chlorine poisoned catalyst and (right) X-ray diffraction pattern of the same catalyst.