Reduction and Carburization of Iron Oxides for Fischer-Tropsch Synthesis

Nielsen, Monia Runge; Moss, Asger Barkholt; Bjørnlund, Anton Simon; Liu, Xi; Knop-Gericke, Axel; Klyushin, Alexander Yu; Grunwaldt, Jan-Dierk; Sheppard, Thomas L.; Doronkin, Dmitry E.; Zimina, Anna

Total number of authors:

15

Publication date:

2020

Document Version

Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Nielsen, M. R., Moss, A. B., Bjørnlund, A. S., Liu, X., Knop-Gericke, A., Klyushin, A. Y., Grunwaldt, J-D., Sheppard, T. L., Doronkin, D. E., Zimina, A., Smitshuysen, T. E. L., Fam, Y., Damsgaard, C. D., Wagner, J. B., & Hansen, T. W. (2020). *Reduction and Carburization of Iron Oxides for Fischer-Tropsch Synthesis*. Abstract from Microscopy and Microanalysis 2020, Milwaukee, Wisconsin, United States.

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.

Reduction and Carburization of Iron Oxides for Fischer-Tropsch Synthesis

Monia Runge Nielsen¹, Asger Barkholt Moss^{1,2}, Anton Simon Bjørnlund^{1,2}, Xi Liu^{3,4}, Axel Knop-Gericke^{5,6}, Alexander Yu. Klyushin^{5,7}, Jan-Dierk Grunwaldt^{8,9}, Thomas L. Sheppard^{8,9}, Dmitry E. Doronkin^{8,9}, Anna Zimina^{8,9}, Thomas Eric Lyck Smitshuysen², Yakub Fam¹, Christian Danvad Damsgaard^{1,2}, Jakob Birkedal Wagner¹, Thomas Willum Hansen¹

¹DTU Nanolab, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

²Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

³SynCat@Beijing, Synfuels China Technology Co., Ltd, Beijing, 101407, China

⁴School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 200240, Shanghai, China

⁵Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, D-14195 Berlin, Germany

⁶Research Group Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, D-45470 Mülheim, Germany

⁷Research Group Catalysis for Energy, Helmholtz-Zentrum Berlin for Materials and Energy (BESSY II), D-12489 Berlin, Germany

⁸Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany

⁹Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, D-76344 Eggenstein-Leopoldshafen, Germany

Fischer-Tropsch Synthesis (FTS) is the chemical reaction in which a mixture of carbon monoxide and hydrogen (syngas) is converted into mainly hydrocarbons which are subsequently used for making liquid fuels and chemicals. Iron and cobalt are the most commonly used catalysts in industrial FTS [1]. Compared to cobalt, iron is cheaper as it is one of the most abundant elements in the crust of the earth. Iron catalysts are less active but also less impacted by operating conditions, i.e. pressure and temperature.

The activation of an iron-based FTS catalysts typically consists of two steps: reduction in hydrogen followed by carburization in either CO or syngas mixture. Alternatively, both steps can be carried out simultaneously in syngas. A combination of different complementary *in situ* techniques was used to gain insight into the behavior of Fe-based FTS catalysts during these steps. *In situ* XRD was used to identify the crystalline phases present during both steps. From the XRD data, an increase in reduction rate was observed with increasing temperature. *In situ* X-ray diffraction experiments in H₂ at a flow of 2 Nml/min corresponding to a H₂ partial pressure of 14 mbar at the sample show the temperature dependence of the reduction process. Metallic iron is present already at around 400°C and at 700°C the sample is fully reduced. However, these experiments do not provide any information on how the reduction properties depends on the structure.

To further investigate the structural effects of the reduction process, environmental transmission electron microscopy (ETEM) was used [2]. The experiments were carried out at low pressure using an aberration corrected FEI Titan 80-300 E-cell, operated at 300 kV. The sample was dispersed in ethanol and sonicated for 15 min. prior to drop casting onto a through-hole Wildfire heating chip from DENSsolutions. Iron oxide was reduced *in situ* in hydrogen at temperatures up to 500°C at various pressures in the range 1.3-3.8 mbar. High-pressure studies were carried out using the Climate closed gas-cell holder from DENSsolutions, with a gas flow up to 0.9 Nml/min and a maximum pressure of 1 atm. In order to minimize the effect of the electron beam, the beam was turned off while ramping the temperature between each image/diffraction/spectrum acquisition.

Both oxides and metallic iron were observed during the reduction using *in situ* XRD. These were further confirmed when reducing iron oxide in the ETEM. With a pressure of 1.3 mbar H₂ at a flow of 2 Nml/min, iron oxide was reduced to metallic iron at 500°C as confirmed by electron energy-loss spectroscopy (EELS), Figure 1. With limited beam influence, hematite was completely reduced at 500°C. At 450°C, imaging and diffraction indicated a clear dependence on agglomerate size, Figure 2. At this temperature, diffraction patterns from the larger agglomerate in Figure 2a indicate the presence of both metallic iron as well as hematite while under the same conditions, the smaller agglomerate in Figure 2b show only metallic iron. A possible explanation could be the presence of water produced during the reduction process.

In conclusion, in the ETEM, complete reduction to metallic was demonstrated and an effect of agglomerate size was apparent. Both ETEM and high pressure experiments indicate that smaller agglomerates reduce at lower temperatures than larger agglomerates.

Figure 1: EELS data from the reduction of hematite at increasing temperatures, showing the oxygen K-edge (~ 532 eV) and the iron L-edge (~ 708 eV). The data is normalized at the peak intensity at the Fe L₃-edge.

Figure 2: Two agglomerates of different size with corresponding electron diffraction patterns acquired at 450°C, showing a) both the presence of hematite and b) metallic iron. The images and diffraction patterns were acquired under the same conditions.

- [1] B. H. Davis, *Catal. Today* 84, (2003) 83-98.
- [2] T. W. Hansen, J. B. Wagner, R. E. Dunin-Borkowski, *Mater. Sci. Technol.* 26, (2010) 1338-1344.