

## IN SITU CHARACTERIZATION OF HIGH-TEMPERATURE SHIFT CATALYSTS

Alfons M. Molenbroek<sup>a</sup>, Rune E. Johnsen<sup>a,b</sup>, Kenny Ståhl<sup>b</sup>,

<sup>a</sup>*Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark*

<sup>b</sup>*Department of Chemistry, Technical University of Denmark*

E-mail: [am@topsoe.dk](mailto:am@topsoe.dk)

High-temperature shift catalysts are used in chemical industry to catalyze the water-gas shift reaction in which CO with steam is converted to CO<sub>2</sub> and H<sub>2</sub>. This reaction is an intermediate process in the industrial production of hydrogen used for e.g. the synthesis of ammonia. The product gas from a steam reformer is cooled in two processes: a high-temperature step (320-500°C) over a Cr containing magnetite catalyst and a low-temperature step (~220°C) over a Cu-Al<sub>2</sub>O<sub>3</sub>-ZnO based catalyst that reduces the CO concentration to about 0.1% [1,2].

In this combination of in situ studies, model high-temperature shift catalysts were prepared in order to determine the structure of pure and Cr containing iron oxides under industrially relevant conditions. From XRD it was observed that magnetite is the active phase under shift conditions and that the addition of Cr resulted in smaller crystallite sizes of the activated magnetite catalysts. Quantitative phase analysis using Rietveld refinement, the Avrami- and Arrhenius expressions, resulted in activation energies for the reduction process. It turned out that there is no significant difference in the activation energy for the reduction process between the pure and the Cr containing catalysts.

XAFS, performed at the Cr- and Fe K-edges, showed the short-range order and oxidation states. Dependent on the preparation procedure Cr is present as a mixture of Cr<sup>3+</sup> and Cr<sup>6+</sup> in the calcined catalysts.

TEM images illustrated that elongated particles become more dominant with increasing Cr concentration for the chloride-based synthesis. The particle sizes obtained by TEM are generally in good agreement with crystallite sizes obtained by XRD. STEM studies combined with EDS suggested that the Cr concentration at the surface of the reduced particles was enhanced. Finally, electron diffraction showed transformations of crystallographic axes from Cr containing hematite particles to Cr containing magnetite particles [3].

[1] M.V. Twigg, *Catalyst Handbook*, 2<sup>nd</sup> ed., (Wolfe. Press, London, 1989)

[2] C. Rhodes, G.J. Hutchings, and A.M. Ward, *Catalysis Today* **23**, 43-58 (1995)

[3] R.E. Johnsen, A.M. Molenbroek, and K. Ståhl, *Journal of Applied Crystallography* **39**, 519-526 (2006)