Microstuctural Studies Of The Chromia Stabilized Iron Oxide Water Gas Shift Catalyst

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Iron oxide in the form of magnetite (Fe_3O_4) is the primary catalyst for the high temperature (310–450°C) water gas shift (WGS) catalyst [1]. In use, pure Fe_3O_4 catalysts rapidly lose activity due to a reduction in surface area caused by sintering. Hence a structural stabilizer, usually Cr_2O_3, is added to industrial WGS catalysts. Various Fe_3O_4/Cr_2O_3 catalyst compositions have been tried, and whilst 14wt% Cr_2O_3 produces the greatest resistance to sintering, a concomitant reduction in activity per unit area means that an 8wt% Cr_2O_3 addition has been accepted as a compromise. Such stabilized catalysts can operate for 2-10 years before sintering produces a reduction in activity sufficient to require catalyst replacement. Despite the industrial significance of the WGS catalyst, some controversy still exists over how the stabilization effect is achieved. Some researchers [2] believe the stabilization is effected by discrete Cr_2O_3 grains that physically block the sintering of neighbouring Fe_3O_4 particles. Others [3] insist that the chromium exists in solid solution in the Fe_3O_4 lattice, although they have not proposed a mechanism by which stabilization occurs. In an attempt to resolve this controversy, we have studied a freshly reduced Fe_3O_4/Cr_2O_3 catalyst by electron diffraction, HREM, STEM-EDS and X-ray photoelectron spectroscopy (XPS).

The Fe_2O_3/Cr_2O_3 catalyst precursor was prepared by co-precipitation from a solution of mixed metal nitrates. Reduction of the precursor to the freshly activated Fe_3O_4/Cr_2O_3 catalyst ($42m^2g^{-1}$) was carried out according to the procedure described by Lywood and Twigg [4]. The nominal bulk Cr:Fe ratio in the catalyst was designed to be 8:92, however XPS analysis yielded a Cr:Fe ratio of 23:27 suggesting a significant surface enrichment in Cr.

The Fe_3O_4/Cr_2O_3 catalyst (Fig.1) was found to consist of dense agglomerates of irregular crystallites ranging between 10-60nm in size. All the rings in the corresponding selected area electron pattern could be attributed to the Fe_3O_4 phase. A typical lattice image from the [1-14] zone axis of a magnetite crystallite is shown in Fig.2. A careful survey of the sample by STEM-EDS analysis failed to identify any discrete Cr_2O_3 grains suggesting that the physical barrier model is not correct. Bulk analyses where the probe was rastered to encompass a large area of sample gave a Cr content of 8.2±0.8wt%, which is close to the nominal value of 8wt%. Point analyses were also taken through the centre and close to the very edge of 100 crystallites using a 1nm probe. A summary of the results obtained is presented in Fig.3. There is a considerable variation in Cr content from grain-to-grain in the material and there is a clear difference in the Cr distribution from the centre-to-edge of individual grains (Fig.4). The average centre composition was 6.3±2.3wt% whereas the average edge composition was 10.7±4.8wt%. This difference directly confirms the existence of a Cr surface segregation effect. No specific correlations could be found between the measured centre and edge compositions of individual grains (i.e. a low Cr content at the interior of a particle did not necessarily mean a high Cr content at the edge).

The Cr^{3+} ion can exist in solid solution within the magnetite lattice. The d^3 electron configuration gives it a maximum crystal field stabilization energy factor ($\Delta=1.2$) meaning that it will exclusively occupy octahedral interstices in the oxygen sub-lattice. The inhomogeneous Cr distribution noted (i) from grain-to-grain and (ii) within individual grains occurs as a consequence of the co-precipitation procedure employed, since the different metallic species involved will come out of solution over a range of pH values. A feasible explanation for the stabilization of Fe_3O_4 by Cr^{3+} may be invoked by taking the Cr surface segregation effect into account. The melting temperatures of Cr_2O_3 and Fe_3O_4 are 2603K and 1870K respectively. By virtue of the stronger Cr-O bond, the melting point of a Fe-Cr-O oxide will progressively increase with increasing Cr content. The Cr enriched surface skin that encapsulates each catalyst grain, being more thermodynamically stable than the iron-rich core, will thus very effectively reduce ion diffusion and sintering effects at the WGS reaction temperature.

[1] Lloyd L, Ridler DE and Twigg MV, Catalyst Handbook, (1989), 2nd Edition.
[2] Chinchen GC, Logan RH and Spencer MS, Appl.Catal,**12**, (1984), 69.
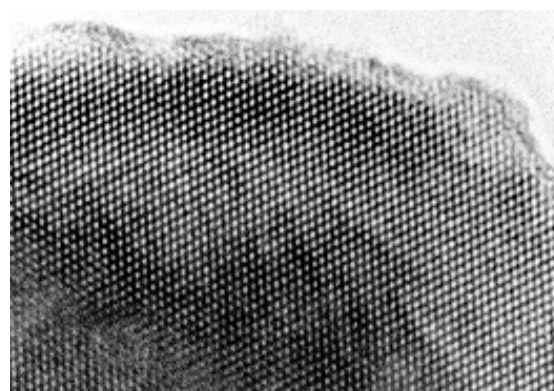[3] Robbins M, Wertheim GK, Sherwood Rc and Buchanan DNE, J.Phys.Chem.Sol.,**32**, (1971),717.
[4] Lywood JW and Twigg MV, European Patent Application, 0361648, (1990).
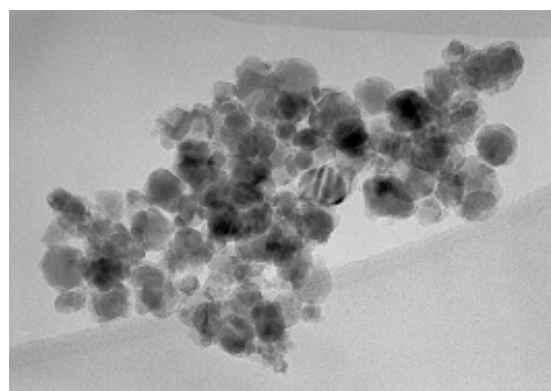
100nm

Figure 1   Bright field micrograph of the Fe_3O_4/Cr_2O_3 WGS catalyst

10nm

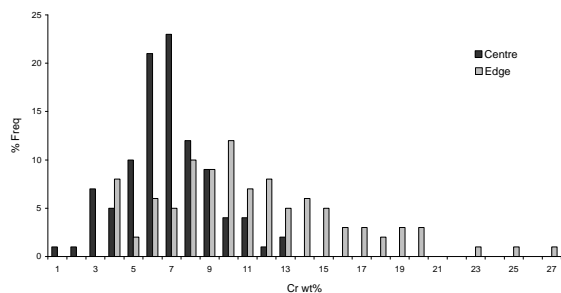**Figure 2** [1-14] HREM image of a single Fe_3O_4/Cr_2O_3 grain.

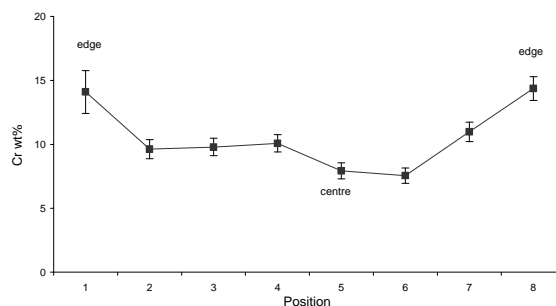**Figure 3** Histogram showing Cr content distribution measured at centre and edge of individual catalyst particles.

Figure 4 Cr content measured as a function of position across the single Fe_3O_4/Cr_2O_3 catalyst particle.