# *In situ* reduction of various iron oxides to form high-surface-area Fe-metal catalysts as studied by high-resolution powder diffraction

Richard Harlow, Mike Guise, William Holstein, and Glover Jones
*The DuPont Company, CRD-E228/316d, Wilmington DE 19880-0228 USA*

## Introduction

Fe-metal catalysts have been used for years in the Haber process for the conversion of $H_2$ and $N_2$ into $NH_3$. Originally made by reducing various iron ores with $H_2$, these catalysts are relatively inexpensive and hence have found wider application as general reduction catalysts. Over the years, technologies for improving the activity of the Fe catalyst have been developed: doping of the iron oxide with other elements, cofeeding other gases with the $H_2$, pre-treatment of the oxide by thermal annealing/melting, variations in the temperature and pressure of the reduction gas, etc. While it is possible to study all of these effects on the activity of the Fe-catalyst, activity measurements are very time consuming. Studies of the *in situ* reduction of various iron oxides (natural ores, by-product oxides, and commercial precursors) on the powder diffraction beamline of sector 5 (DND-CAT) were thus initiated. When early experiments suggested a correlation between activity and the breadth of the Fe(110) peak in the catalyst, the study was expanded into a general survey covering many aspects of Fe catalyst engineering.

## Methods and Materials

While *in situ* experiments have be done on commercial instruments, the powder diffraction setup at DND offers many advantages. Shorter wavelengths allow (1) penetration into the large particles of catalyst, which helps to keep sample preparation to a minimum and (2) use of large sample volumes to minimize preferred orientation effects so that quantitative analyses could be performed on both the oxide precursor phases and on the reduction products at any point in the reaction. High-resolution geometry [Ge(220) analyzer with vertical Soller slits in the reflected beam path] minimized both the effects of sample mis-positioning with heating and the instrumental part of the peak breadth. The latter was particularly important because the broadening of the Fe peak was found to be correlated with activity. The sharp diffraction lines from the Be tube, which was used as a giant "capillary" reaction vessel, served as internal standards to monitor small wavelength shifts and as checks for gross variations in intensity.

For all of the catalyst precursors studied, three pieces of basic information were generally obtained: (1) a quantitative phase analysis of the precursor primarily to determine the $Fe^{+2}/Fe^{+3}$ ratio but also to spot contaminant phases, (2) the time required to complete the reduction, and (3) the full width half maximum (FWHM) of the Fe(110) peak. Particle sizes of the catalyst precursors were carefully controlled because initial experiments demonstrated that the reduction times were very dependent on the size, bolstering the notion that the reduction is diffusion limited. Furthermore, the reduction is position dependent: the catalyst closest to the gas inlet reduces first and that closest to the exit reduces last. Thus, it was necessary to control the position of the Be tube in the beam rather carefully. The dependency on the position in the tube could be followed by using only part of the 8 mm beam to strike different positions of the Be tube.

## Results

Many of the experiments run to date have been guided by years of folklore and a large volume of literature. Results of the survey to date confirm the following engineering beliefs:

(1) A reduction temperature of approximately 400°C is optimal, balancing the time required for complete reduction while maintaining a broad FWHM for the Fe(110) peak. Higher temperatures reduce the reduction time but sharpen the Fe peak substantially.

(2) Doping the iron oxide with a small amount of $Al^{+3}$, approximately 1%, increases the reduction time and the FWHM by roughly 20-30%. In the case of magnetite, the Al dopes into the Fe sites in the structure as evidenced by the shift in the magnetite peaks. In general, the high accuracy of the peak positions can be used to determine whether dopants substitute into the iron oxide phases (magnetite, $Fe_3O_4$; hematite, $Fe_2O_3$; wuestite-like phases, $Fe_xO$). If not, the signal/noise ratio is sufficiently high to determine whether the dopants form separate crystalline phases. Silicon is one additive that does not substitute into the iron oxide phases, but its presence does not result in any observable crystalline peaks (amorphous?).

(3) The addition of 3% $NH_3$ to the $H_2$ reduction gas stream also lengthens the reduction time and broadens the Fe peak by 20-30%. Additional $NH_3$ has only minor effects.

(4) Higher $H_2$ flow rates not only reduce the reduction time, but they increase the FWHM of the Fe peak.

Results which appear to be at odds with folklore also abound. (1) The $Fe^{+2}/Fe^{+3}$ ratio in the precursor oxide has little effect on the reduction time and no measurable effect on the FWHM. (2) The reduction of $Fe_3O_4$ to Fe metal occurs without the formation of any visible amount of intermediate FeO. When both FeO and $Fe_3O_4$ are initially present, the FeO appears to reduce somewhat faster than the $Fe_3O_4$ only because its average particle size is much smaller (wuestite peaks are generally quite broad).

## Discussion

These preliminary experiments have demonstrated the value of *in situ* powder diffraction experiments at the Advanced Photon Source for studying catalysts under a wide variety of conditions. More details of the Fe catalyst survey will be forthcoming shortly.

## Acknowledgments