



# Characterization of iron contamination on equilibrium fluid catalytic cracking catalyst particles

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## ABSTRACT

Iron poisoning is a well-known problem for fluid catalytic cracking catalysts. To better understand this issue, several characterization techniques were used to examine a catalyst sample from a commercial unit. Under SEM-EDX, most cross sections of the catalyst particles exhibited iron nodule rims enriched with Fe, other contaminant metals, and Si. Scanning TEM X-ray mapping further confirmed that, compared to the inside of a catalyst particle, the surface layer was enriched in Si and contaminant metals, while depleted in Al. This catalyst had high frequency-dependent magnetic susceptibility, suggesting that some or all of the iron-bearing species should be in the nanometer size range. In TEM, the nodules were found to consist of Fe-bearing nanoparticles, imbedded in an amorphous matrix. The nanoparticles were also enriched in Mg, Ni or Ca, while the matrix was dominated by Si and minor Al. Selected area electron diffraction pattern indicated that these iron enriched nanoparticles had the spinel structure. These results should shed light on iron poisoning issues in FCC units.

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## 1. Introduction

Fluid catalytic cracking (FCC) catalysts are the workhorse of current oil refinery, responsible for a significant portion of the global gasoline production. The severe detrimental effects of added iron on the performance of FCC catalysts either in the field or in the lab are well recognized [1–7]. There are mainly two effects, and they are not necessarily contemporaneous. (1) Increased iron deposition may induce surface roughening, even the formation of nodules, which may affect the catalyst apparent bulk density (ABD) and also fluidization [6]. (2) Iron contamination can trigger irreversible catalyst deactivation, causing loss in conversion and deteriorated product selectivity, including increased coke and hydrogen formation [1–5,7]. In advanced stages, it has been proposed that iron contamination mixed with Si, Ca, Na and perhaps other contaminants can form a dense skin layer via a vitrification process and block surface pore entrances, causing reactant molecule accessibility loss and diminishing catalyst cracking capability [4,7–11].

In order to understand iron poisoning issue, many techniques have been utilized to characterize equilibrium catalysts (Ecats) from commercial units, including scanning electron microscopy

(SEM) [6,10–14], energy dispersive X-ray spectroscopy (EDX or EDS) [10–14], Auger electron spectroscopy (AES) [12], electron paramagnetic resonance spectroscopy (EPR) [12], transmission electron microscopy (TEM) [10,11], magnetic susceptibility [11], atomic force microscopy (AFM) [13], X-ray photoelectron spectroscopy (XPS) [13,14], electron probe microanalyzer (EPMA) [14], and optical microscopy [14]. Recently, several non-invasive methods based on X-ray probe were developed by Weckhuysen's and van Bokhoven's groups to study whole individual catalyst particles, including X-ray fluorescence tomography [15,16], transmission X-ray nanotomography [8,9,17], X-ray ptychography [16,18], and Tomographic X-ray Absorption Spectroscopy [19]. Despite these efforts, the exact mechanism of iron poisoning is still not well understood. For example, most chemical imaging methods based on X-ray probe [8,9,15,17,18] or X-ray emission detection (EDX [10] or EPMA [14]) focused on iron distribution only and showed iron contamination as a patch of material. However, with TEM, iron-rich small crystalline particles (supposedly maghemite) were reportedly observed in the nodules [10,11]. Moreover, not much work has been reported to understand the role of surrounding matrix in which iron species is present. Wieland and Chung [11] argued that iron rich particles did not block the pore entrances or limit diffusional access to the catalyst. Instead, the more likely reason for poor catalyst performance was the formation of vitrified regimes resulting from iron-alkali (primarily calcium and sodium)

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eutectics formation. Yaluris et al. [14] made a similar proposal, but proposed that silicon was likely also involved in the eutectics. More recently, van Bokhoven's group reported that a dense amorphous silica–alumina (ASA) shell formed due to amorphization of zeolites close to the particle exterior, and that iron contaminant contributed to the formation of this ASA envelope [16,19].

In this report, we examined the oldest fraction of an iron poisoned Ecat from a commercial unit with several techniques, including SEM-EDX, frequency dependent magnetic susceptibility, and TEM. The results clearly show that the nodules and the surrounding areas consist of iron enriched crystalline nanoparticles, imbedded in a silicon enriched amorphous matrix, indicating that both Fe-bearing species and Si-enriched matrix have to be considered together to understand iron poisoning issues for FCC catalysts.

## 2. Materials and methods

### 2.1. Sample

The Ecat used in this study was obtained from a commercial FCC unit that suffered typical iron poisoning symptoms due to high iron content in the feed. Since the Ecat was a mixture of base catalyst particles with different age and additives, density separation [20] was performed to obtain four clean fractions of the base catalysts. From the first to the last fraction, the iron content increased ( $\text{Fe}_2\text{O}_3$  wt.% was 1.63, 1.64, 2.23 and 2.43), and the corresponding diffusion coefficient measured by iGC method developed by Grace [21] decreased (iGC index was >100, 82, 69 and 46), consistent with the observed iron poisoning issues in the unit. The last fraction was used in this study, and its chemical composition measured by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) is shown in Table 1. Clearly, this sample has very high iron content (for comparison,  $\text{Fe}_2\text{O}_3$  wt.% for the fresh catalyst is about 0.4), and other metal contaminants such as Ni, V, Ca and Mg. The Si to Al atomic ratio is calculated to be about 0.6.

### 2.2. SEM-EDX imaging and elemental mapping

For imaging whole particles, individual catalyst particles were attached to an aluminum stub with carbon tape. For imaging and mapping particle cross section, particles were placed in an epoxy, and the resin was cured overnight at room temperature. The sample stub was then cut with a diamond blade, and polished to a smooth surface with 6  $\mu\text{m}$  and 0.25  $\mu\text{m}$  diamond pastes. For better conductivity, a thin Pd-Au coating was applied to the samples.

Back-scattered electron (BSE) images were obtained by using a Hitachi SU3500 SEM, and line scanning and elemental mapping were acquired with an EDAX Octane Elite EDX detector with TEAM software at 25 kV. Quantitative elemental analysis with standard-

less method and chemical phase analysis were conducted automatically by the software. For quantitative analysis, all major elements had to be considered, including C from epoxy and contamination, in order to get accurate results. For phase analysis, however, only Si, Al, Ca, Mg and Fe were considered for simplicity. For more technical details about these methods, readers are encouraged to read the book by Friel et al. [22].

### 2.3. Magnetic susceptibility

Magnetic susceptibility of the sample was measured with a MS3 meter coupled with a dual frequency (0.465 kHz and 4.65 kHz) laboratory sensor MS2B from Bartington. More details about using magnetic susceptibility to characterize FCC catalysts will be reported later.

### 2.4. TEM

To prepare the sample for TEM, catalyst particles were imbedded in low viscosity epoxy in capsule and centrifuged to ensure close packing of grains. After epoxy was cured overnight at room temperature, the capsule was cut with a diamond blade. The cut surface was ground with 240, 320, 400, and 600 grit carbide paper and finally polished with 1.0  $\mu\text{m}$  alumina. The polished surface was cleaned in water with ultrasound, and glued to a glass slide with Crystalbond adhesive. The other end was then cut off, and the sample was ground down to <30  $\mu\text{m}$ , and polished. Afterward, Crystal bond was removed with acetone to leave the thin section free standing. This section was glued to a 3 mm Cu TEM grid with 1 mm inner diameter in area of interest with quick cure epoxy. After the perimeter of the grid was scored with a razor blade, the sample was placed inside a Gatan PIPS II ion mill using a liquid nitrogen cooled stage. Ion milling proceeded at 3 kV and 5° for ~1 h, 2 kV for 2 min, and finally 0.5 kV and 2° for 1 min, and was normally terminated just as the epoxy was removed from the surface of the Ecat. After thinning, the sample was coated with ~5 nm amorphous C.

TEM examinations were conducted with a Philips CM300 FEG TEM/STEM equipped with an Oxford light element EDX detector using Emispec ES Vision 4 software. Images in conventional TEM mode were collected using a Gatan 4k Orius CCD camera. These high-resolution lattice images revealed the crystalline or amorphous nature of the rim and core materials. Selected area electron diffraction (SAED) patterns were collected in specific areas that allow for the crystal structure of the phases to be identified. Ring patterns were radially averaged in order to directly compare SAED patterns with patterns calculated by the Crystal Diffract program based on published unit cell data from the International Crystal Structures Database. Scanning TEM (STEM) methods generated both high-angle annular dark field (HAADF) images and EDX intensity maps. The intensity in the HAADF images is a function of mean atomic number, density and thickness. Intensity in the EDX maps is a function of element concentration, density and thickness. Interpretations of HAADF and EDX images have to consider local changes in thickness inherent in TEM samples with variable porosity. Due to this limitation, no quantification for EDX results were attempted.

## 3. Results

### 3.1. Enrichment of Si and contaminant metals on catalyst surface

For iron poisoned catalysts, formation of nodules is frequently observed on the catalyst surface. For the current sample, nodules are obvious on most particles as shown in Fig. 1A. This is not sur-

**Table 1**  
Chemical composition of the studied sample by ICP-AES.

$\text{Al}_2\text{O}_3$ , Wt.%	54.35
$\text{La}_2\text{O}_3$ , Wt.%	2.01
$\text{Na}_2\text{O}$ , Wt.%	0.27
$\text{Fe}_2\text{O}_3$ , Wt.%	2.43
$\text{TiO}_2$ , Wt.%	0.69
MgO, Wt.%	0.66
CaO, Wt.%	0.91
$\text{P}_2\text{O}_5$ , Wt.%	0.09
Sb, ppm	403
Ni, ppm	1864
V, ppm	2300
$\text{SiO}_2$ , Wt.% <sup>a</sup>	38.17

<sup>a</sup>  $\text{SiO}_2$  was not measured directly by ICP-AES, rather calculated based on 100% weight content.

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