Investigating the Aluminum chemistry of individual zeolite domains in single FCC particles using Scanning Transmission X-ray Microscopy

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Introduction
Fluid Catalytic Cracking (FCC) particles are a major class of petrochemical catalysts that account for 40-45% of global gasoline production. One of the main components of FCC particles are acidic, polycrystalline zeolites, which make up 20-50% of the particle. The rest of the particle consists of matrix, binder and filler material, typically alumina, silica and clay. These micro-porous aluminosilicate zeolites provide an advantageous shape and size selectivity while acidic sites on the framework perform cracking leading to favorable product distributions. Acidity in zeolites arises from the presence of aluminum in the silicon oxide framework where the charge balance is made up of Bronsted acidic protons. The acidity and thus the cracking capability of zeolites are inextricably linked to the concentration, amount and stability of aluminum in the zeolitic framework.

The FCC process consists of continual cracking and regeneration cycles during both of which FCC particles are under severe physical and chemical stress. In regeneration, FCC particles are subject to steam treatment under high temperature (≥ 700°C). These harsh conditions promote the migration of aluminum from the lattice framework into extra- and non-framework positions [1]. This process significantly alters the chemical environment of the aluminum leading to a reduction in the particles cracking capability. Furthermore, if the dealumination process remains unchecked, zeolite domains may collapse thereby neutralizing their beneficial shape and size selective properties [2]. In order to increase the stability of zeolites in FCC particles, Rare Earths such as Lanthanum or Cerium may be incorporated into the zeolite in order to stabilize framework aluminum. Due to the complex structure of FCC particles, zeolite dealumination has almost exclusively been studied in the context of model zeolites. However, to build an accurate description of aluminum migration from zeolites in FCC particles, where particle heterogeneities, the presence of metals and the active matrix structure may all play important roles in promoting or inhibiting dealumination, it is important to investigate particles that have experienced as close to in operando conditions as possible. Here we report a study of the silicon and aluminum chemistry of industrially deactivated FCC particles using synchrotron based soft X-ray Scanning Transmission X-ray Microscopy (STXM) [3].

Materials and Methods
FCC particles were obtained from an industrial FCC unit where only one catalyst type had been in continual use. This catalyst fraction was separated based upon skeletal density using a sink-float method. The age of the catalyst is related to the catalyst density because of the continuous incorporation of metal onto the FCC particles. FCC particles from the densest fraction (high metal loading) and Fresh particles were microtomed into 500 nm thin-sections onto formvar coated, 50 mesh copper grids. These samples were examined using STXM at the Spectromicroscopy (SM) beamline ID10-1 at the Canadian Light Source synchrotron. The samples were studied at the Al K, Si K, La M, and the Fe L edges.

Results and Discussion
In spite of x-ray spectroscopic identification, the detection of zeolite domains remains challenging due to the complex aluminum environment of the FCC particle as a whole. The identification of Rare-Earth stabilized zeolites using La specific elemental maps is possible, as shown in figure 1 (left). This selective visualization allows for the determination of physical properties such as domain size to be mapped for each individual domain (figure 1, right). Furthermore by examining the Al and Si K edge jump, the silicon to aluminum ratio may be ascertained for individual zeolite domains. One is further able to understand the chemical changes that occur to the aluminum present in the zeolite domains via Al K edge XANES. Thus, we are able to form an understanding of the amount and nature of aluminum present in zeolite domains and the rest of the FCC particle. Furthermore, by doing spatial mapping of each individual domain, and performing the studies across particles at different life stages, we are able to understand any spatially heterogeneous effects that may be present during aluminum migration from zeolite domains.

Significance
This study shows, for the first time, the spatial and temporal dynamics of aluminum chemistry during deactivation of zeolite domains in single FCC catalyst particles at an individual zeolite domain scale.

Figure 1. (Left) A false colored map showing Lanthanum (i.e. zeolite domains) overlaid on the FCC particle section. (Right) Highlight and zoom in of individual zeolite domains.

References