

X-Ray Absorption Spectroscopy Characterization of Vanadium on Fluid Catalytic Cracking Catalysts

Hyung S. Woo¹, and George D. Meitzner²

¹ExxonMobil Process Research Laboratories, Baton Rouge, LA 70821

²Lowry Associates, Baton Rouge, LA70821

Introduction

Fluid Catalytic Cracking (FCC) is a major refinery process for conversion of heavy petroleum into gasoline and diesel range liquids. The catalyst consists of a mixture of aluminum oxide, silicon dioxide, and rare earth exchanged zeolite. The zeolite substantially controls the catalytic activity and selectivity. Vanadium from the feed deposit onto the zeolite and ultimately damages it by accelerating decrystallization of the zeolite. Observation of vanadium zeolite interaction has been difficult using x-ray absorption spectroscopy (XAS) due to the interference between the rare earth L edges and the vanadium K edge. Also because of the severe conditions characteristic of FCC operation *in situ* observation has not been made. There are a number of hurdles that need to be overcome in order to characterize vanadium, and this work describes requirement of the reactor and detection scheme used to characterize vanadium under FCC regenerator conditions.

Materials and Methods

A fluorescence *in situ* reactor was used to facilitate XAS measurement of vanadium under FCC regenerator condition. Figure 1 shows a schematic of the reactor used. The reactor is built with corrosion resistant alloy to withstand corrosive nature of FCC regenerator flue gas. The fluorescence detection combined with a Ti fluorescence windows is used to enhance the quality of spectra due to dilute vanadium concentration and allow fluorescence detection at FCC regenerator condition. Because of x-rays from rare earths contained in FCC catalysts interferes with vanadium signal, an energy discriminating 13 element Ge x-ray detector was used. The experiments were conducted at beamline x-10c at National Synchrotron Light Source. FCC catalysts studied were equilibrium catalysts from commercial operation FCC unit as well as laboratory prepared FCC catalysts.

Results and Discussion

The separation of the La L_{III} edge at 5483 eV and the V K edge at 5465 eV was accomplished by discriminating the corresponding fluorescence lines at about 4646 eV and 4950 eV. The top trace in Figure 2 shows the fluorescence yield spectrum of La(VO₃)₃ measured without discrimination. The middle trace shows the V K_α yield and the lower trace shows the La L_{a1,2} yield. The energy discrimination scheme allows for a clear observation of vanadium in the presence of lanthanum, a major component of rare earth used in FCC catalysts. Figure 3 shows vanadium K edge spectra from commercial FCC equilibrium catalysts held at 750 °C in a gaseous mixture of N₂/H₂O/CO₂/O₂ (labeled excess O₂) and N₂/H₂O/CO₂/CO/O₂ (labeled excess CO) simulating FCC regeneration conditions. The spectra show that vanadium state is quite different between condition with excess O₂ and excess CO despite the presence of O₂ under excess CO condition.

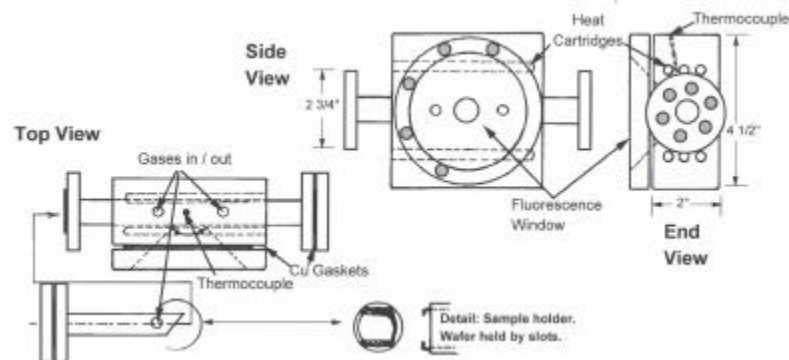


Figure 1. Schematic of *in situ* XAS cell

Significance

The combined use of *in situ* fluorescence reactor and x-ray energy discrimination allows for clear observation of vanadium chemistry of a commercial FCC catalyst in the presence of rare earth. This method allows for detailed investigation of vanadium through its life cycle in a FCC unit from vanadium present in a feed to its interaction with FCC catalyst in riser, stripper and regenerator sections of a FCC unit.

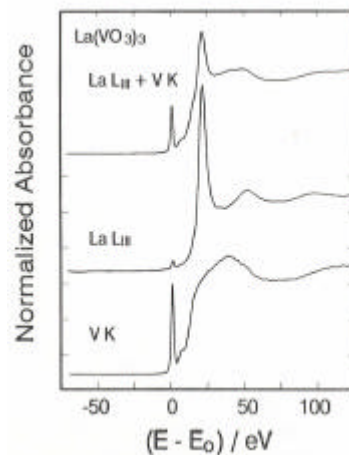


Figure 2. Coincident V and La edges were discriminated by windowing corresponding fluorescence lines.

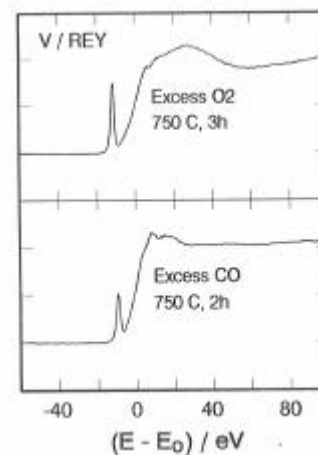


Figure 3. Vanadium in a rare earth containing FCC equilibrium catalyst is modified by reducing flue gas.