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## **In situ Ni K-edge XANES study of the reducibility of Ni in FCC catalysts**

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The majority of the Ni in an aged equilibrated catalyst (ECAT) from the resid UOP fluid catalytic cracking (FCC) unit in the Pertamina EXOR-1 refinery (with 12,000 ppm Ni) is present primarily as a NiAl<sub>2</sub>O<sub>4</sub> phase. No appreciable Ni reduction occurs below 500°C in a flow of H<sub>2</sub>. In situ Ni K-edge XANES has been used to follow the reduction kinetics of this NiAl<sub>2</sub>O<sub>4</sub> phase. Reduction in H<sub>2</sub> is described by pseudo-second-order kinetics. An apparent activation energy is estimated to be 26 kcal/mol. This value is compared to that of 4.3 kcal/mol for NiO reduction and 32 kcal/mol for NiAl<sub>2</sub>O<sub>4</sub> reduction. Less than 10% of the Ni is estimated to go through a redox cycle in an FCC unit, resulting in a negligible impact on the hydrogen in coke calculation.

**Keywords:** catalysis; FCC; Ni K-edge XANES; in situ studies; Ni oxidation state.

### **1. Introduction**

Fluid catalytic cracking (FCC) is a process for the conversion of vacuum gas oils, atmospheric residues (resids), and other heavy feedstocks into high-octane gasoline and light fuel oils. In a typical FCC unit, the cracking reactions are carried out in a riser reactor. Simultaneous to the desired reactions, coke, with a low ratio of hydrogen to carbon, deposits on the catalyst. The spent catalyst and converted products are separated, and the catalyst passes to a separate chamber, the regenerator, where the coke is burned to regenerate the catalyst. This regenerated catalyst then passes to the bottom of the riser, where the cycle begins again.

The feeds used in an FCC unit typically contain high levels of contaminant metals, particularly Ni and V. These metals are deposited on the catalyst and accumulate over time. Nickel promotes undesirable dehydrogenation reactions in the FCC riser. The dehydrogenation activity is dependent on the quantity, age, and chemical form of the Ni, and it tends to lose its initial activity as a result of processing conditions (Cimbalo *et al.*, 1972, Campagna *et al.*, 1983, Cadet *et al.*, 1991, Chester, 1987, Hettinger *et al.*, 1983, Tatterson, 1988, Nielsen *et al.*, 1993, Palmer *et al.*, 1987, Mitchell, 1980). However, most of the studies performed were on catalysts with a relatively low Ni concentration. In ECAT samples from the UOP resid FCC unit in the Pertamina EXOR-1 refinery, the levels of Ni have reached as high as 12,000 ppm.

An important parameter in estimating FCC performance is the amount of hydrogen in coke. This value is calculated from flue

gas analysis using an oxygen balance. If the Ni deposited on the spent catalyst were to go through a redox cycle, then the missing oxygen would not be totally due to water formation but would also be due to oxidizing the reduced Ni. For the high Ni-containing ECAT studied, this amount would become a significant fraction of the oxygen and thus lead to erroneous conclusions on the operation of the FCC unit. An understanding of the contribution of high Ni loadings to calculated H<sub>2</sub> in coke is imperative to ensure that the unit operates effectively without using a passivating additive.

Nickel K-edge XANES has been used to investigate the chemical and structural changes occurring during simulated redox cycles. Previous studies have shown XAS to be a valuable tool in studying Ni in FCC catalysts (Woolery *et al.*, 1996, Woolery *et al.*, 1998). These studies showed that both dispersed NiO and NiAl<sub>2</sub>O<sub>4</sub> are present and that the relative concentration of these species varies with catalyst type and unit operating conditions.

### **2. Experimental**

The Ni K-edge XANES data were collected on beamline X18B at the NSLS, Brookhaven National Laboratory, using a channel-cut Si(111) monochromator. Spectra of the FCC catalysts were collected using fluorescence detection. The FCC samples were ground to a fine powder and pressed into a stainless steel sample holder and held at 45° to the incident beam. The sample holder was placed in a quartz reactor designed for in situ x-ray absorption measurements. After a helium purge at room temperature, the in situ studies were performed by flowing 100% H<sub>2</sub> over the sample. The data were recorded at the specified temperatures. The Ni K-edge XANES data for NiO and NiAl<sub>2</sub>O<sub>4</sub> were collected in transmission.

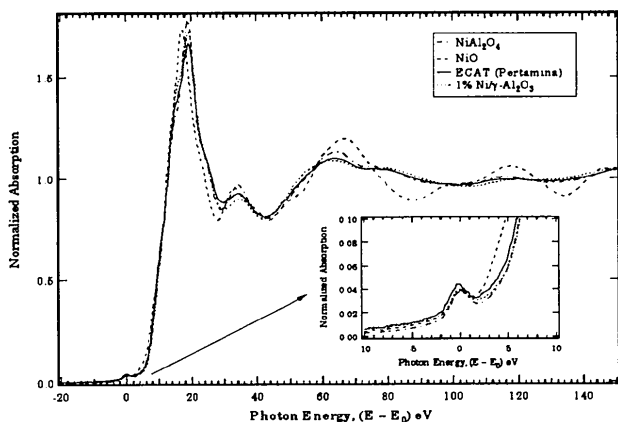
Spectra were processed using BAN. The energy scale was established by setting the maximum of the first derivative of the Ni foil spectrum to 0.0 eV, thereby establishing 8333.0 eV as the zero energy. The background was approximated by a least-squares fit of the pre-edge region (–90 to –30 eV) and was subtracted from the spectrum. The spectra were then normalized to unity absorption by dividing by a least-squares fit to the region 100 to 200 eV above the absorption edge. This normalization procedure is thought to give a qualitative comparison between samples.

The 1 wt-% Ni on  $\gamma$ -alumina was prepared by incipient wetness techniques using a solution prepared from Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O followed by calcination at 500°C for 2 hr. The NiAl<sub>2</sub>O<sub>4</sub> was prepared from NiO and Al<sub>2</sub>O<sub>3</sub> (Sridhar *et al.*, 1994).

### **3. Results and Discussion**

Figure 1 shows the Ni K-edge XANES of bulk NiO, NiAl<sub>2</sub>O<sub>4</sub>, 1% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and a regenerated Pertamina ECAT sample (12,000 ppm Ni). The XANES spectra of NiAl<sub>2</sub>O<sub>4</sub>, 1% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the ECAT are similar and quite distinct from that of NiO, indicating that the Ni in the ECAT sample is present mainly as a NiAl<sub>2</sub>O<sub>4</sub>-type phase. The Ni in NiAl<sub>2</sub>O<sub>4</sub> is present in a mix of octahedral and tetrahedral sites but the majority is

octahedral (Wells, 1986). Similarly the Ni in the 1% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample is also present as a mix of coordination environments (Scheffer *et al.*, 1987). For the preparation conditions of this study, only a few percent of the Ni are expected to be tetrahedral. The similarity and low intensity of the 1s $\rightarrow$ 4d pre-edge peak (inset of Figure 1) are consistent with most of the Ni being in octahedral sites in all the compounds. The spectrum of this high-Ni ECAT is quite similar to those previously published for an ECAT with only 3,300 ppm Ni (Woolery *et al.*, 1996, Woolery *et al.*, 1998). These authors concluded that the majority of the Ni was present as NiAl<sub>2</sub>O<sub>4</sub>.



**Figure 1**  
Ni K-edge XANES data of Ni reference materials and Pertamina ECAT. Inset shows an enlargement of the pre-edge peak.

To estimate the amount of reducible Ni and to explore the kinetics of Ni reduction in the Pertamina ECAT sample, two series of experiments were performed. First, samples of catalyst were reduced at 700°C for periods of 3, 15, 45, and 120 min in a flow of 100% H<sub>2</sub>. Second, samples of the catalyst were reduced in 100% H<sub>2</sub> at 500, 600, and 700°C for 2 hr at each temperature. Figure 2 shows the Ni K-edge XANES data on the catalyst reduced at 700°C for varying lengths of time. Clearly, the resulting spectrum after reduction is quite different from that of the original ECAT and indicates the presence of reduced Ni. The amount of reduction was estimated by fitting the XANES data to a linear combination of the spectra of the original regenerated catalyst and Ni foil. The fit was optimized to give the best fit over the edge region itself. The calculated amount of reduction gave a reasonable fit to a second-order kinetic model (inset of Figure 2):

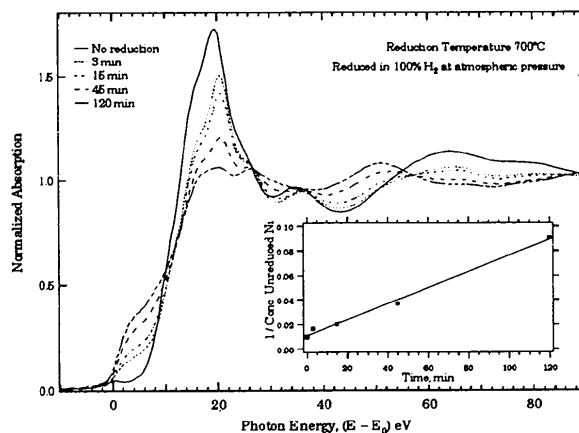
$$-r_{Ni} = -dC_{Ni}/dt = kC_{Ni}^2$$

$$1/(C_{Ni})_t - 1/(C_{Ni})_0 = kt$$

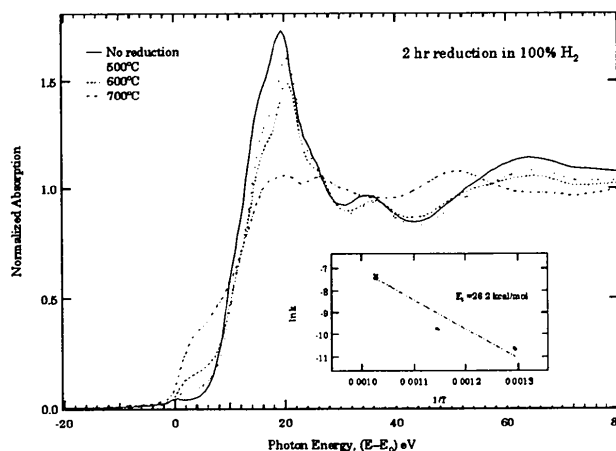
where  $r_{Ni}$  = reaction rate for Ni reduction,  $C_{Ni}$  = concentration of unreduced Ni, and  $k$  = rate constant.

The Ni K-edge XANES of the Pertamina ECAT that was reduced for 2 hr at varying temperatures is shown in Figure 3. Once again, the spectra indicate the presence of reduced Ni. The Arrhenius plot, assuming second-order kinetics, is shown in the inset of Figure 3. The slope gives an apparent activation energy of reduction of 26 $\pm$ 4 kcal/mol. This value is significantly higher than that for the reduction of NiO (4.3 kcal/mol) but is in close

agreement with the value obtained for bulk NiAl<sub>2</sub>O<sub>4</sub> (32 kcal/mol) (Sridhar *et al.*, 1994). These kinetic data add support to the spectral fingerprint, which indicated that the Ni is present in these catalysts as NiAl<sub>2</sub>O<sub>4</sub>.



**Figure 2**  
Ni K-edge XANES of Pertamina ECAT as a function of reduction at 700°C for the stated amounts of time. Inset shows a linear relationship between the concentration of unreduced Ni vs. time, indicating second-order kinetics.



**Figure 3**  
Ni K-edge XANES of Pertamina ECAT as a function of reduction for 2 hr at the stated temperatures. Inset shows an Arrhenius plot assuming second-order kinetics.

If these data are extrapolated to typical cracking process conditions, less than 10% of the ECAT Ni is likely reduced. This extent of reduction has an insignificant effect on the calculation of H<sub>2</sub> in coke.

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