

## POISONING OF FLUID CRACKING ZEOLITE CATALYSTS BY METALS

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### ABSTRACT

One of the most important problems facing users of zeolite fluid cracking catalysts is the poisoning of the catalyst by metal deposits such as vanadium and nickel. We have been investigating these poisoned zeolite catalysts with several spectroscopic tools such as luminescence excitation, emission and lifetime spectroscopies. Each of the two main components of these catalysts (the binder and the lanthanum faujasitic component) has been independently poisoned by both iron and copper. The decrease in the cracking activity parallels the quenching of the luminescence of lanthanum by both metal poisons. From the luminescence data we are able to tell at low loadings (2% by weight) that both copper and iron sinter on streaming. Such metal deposits increase the cracking activity and lead to large coke deposits. Catalytic cracking experiments have been carried out in a flow reactor. Correlations between the spectroscopic data and the cracking data will be discussed.

### INTRODUCTION

For a long time it has been known that metals such as Fe, Cu, Ni and V have detrimental effects on the cracking activity of fluid cracking catalysts (FCC). Iron, copper and nickel metal deposits [1,2] cause increasing amounts of coke to form. On the other hand vanadium is known to destroy the catalytic cracking activity [3,4] of the FCC. It is not well known what the exact surface interactions are in these systems.

It is believed that these metals (Ni, V, Cu, Fe) which are found in the oil feedstocks are not the only factors which cause deactivation of the cracking catalysts. Partial or total blockage of the pore system of the zeolite component of the FCC can cause the destruction of catalytic cracking activity.

Fluid cracking catalysts are composed of 2 parts. One part is the zeolite cracking component. This is usually a hydrogen or rare earth form of a large pore faujasitic zeolite. The second part of the FCC is the binder or scavenger. The binder is typically a clay such as a dealuminated kaolin. One role that the

scavenger can play is to selectively bind to metal deposits [5] thereby reducing the detrimental effects of these metal deposits.

Another route to control the deactivation of FCC materials is to add a passivating agent such as Sb, Sn, Bi or various combinations of these. [6] For the most part this route has been ignored and not studied in great detail.

The purpose of this paper is to show that both iron and copper deposits on real fluid cracking catalysts can be detected by luminescence emission, excitation and lifetime measurements. Microactivity tests of the cracking activity of the FCC materials were also carried out and correlations between the catalytic and photochemical properties of these catalysts have been made.

## EXPERIMENTAL

Sample Preparation. Copper and iron naphthenates were dissolved in benzene and incipient wetness methods were used to impregnate a commercially available fluid cracking catalyst. The naphthenates were obtained from Pfaltz and Bauer and were used without further purification. The catalysts were calcined in air at 540°C for 10 hours and then aged in steam for 10 hours at 730°C in a fluidized bed.

Cracking Activity. The cracking activity of these materials was studied with a flow system which has previously been reported [7]. A Cincinnati feedstock oil with a 260-426°C boiling range was used. About 2.5 grams of 100x325 mesh microspherical catalyst particles were used. The catalysts were tested for an 80-second contact time, at 515°C and at 15 WHSV.

Luminescence Methods. All samples were loaded into 2mm path length quartz cells obtained from Precision Cells, Inc., Hicksville, New York. Spectra were recorded using a double Czerny-Turner monochromator Spex Model 1902 fluorometer. Front face detection was used for all samples. Finally, a rhodamine B solution was used as a quantum counter in order to correct for variations in intensity of the excitation source at different wavelengths.

Lifetime experiments were done with a PRA Model 3000 system. A PRA model LN100 nitrogen laser was used as an excitation source. A monochromator was positioned between the sample and the emission photomultiplier tube. The lifetime data were collected by using multichannel scaling methods with a multichannel analyzer and then transferred to a DEC, PDP-1103 computer for data manipulation. All lifetime data were fit to at least 2 exponential decays and usually to 3 decays.

## RESULTS

Since these fluid cracking catalysts contain lanthanum Y zeolite as an active component it is essential to know what the photochemical behavior of LaY zeolite is. A luminescence emission spectrum for LaY is given in Figure 1.

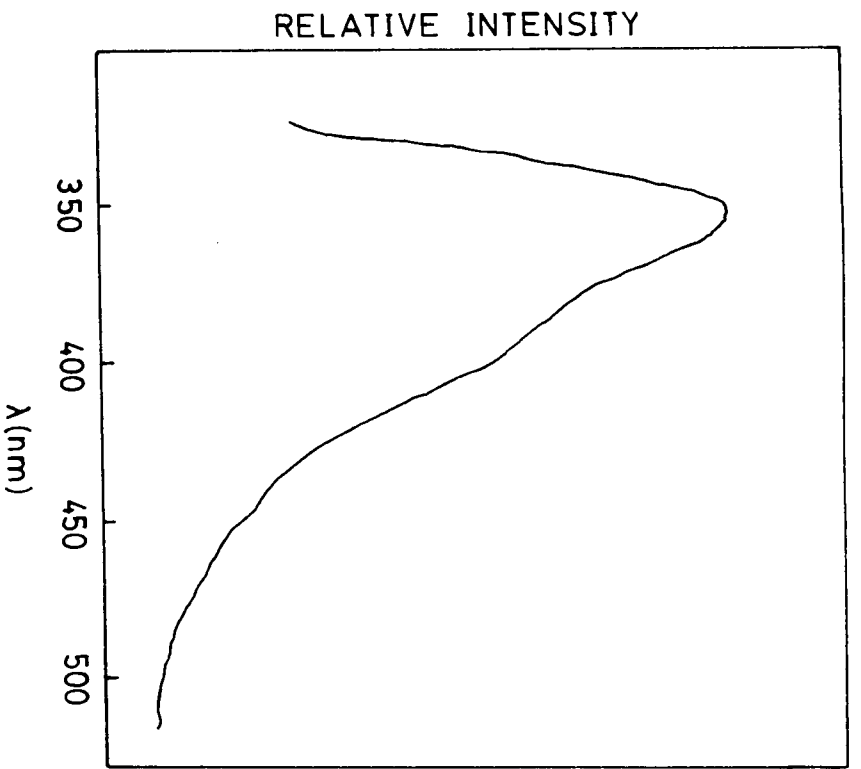


Fig. 1. Luminescence Emission Spectra of LaY.

The luminescence emission spectra of 2% Cu on the fresh catalyst and on the aged catalyst are given in figure 2, as well as the fresh catalyst.

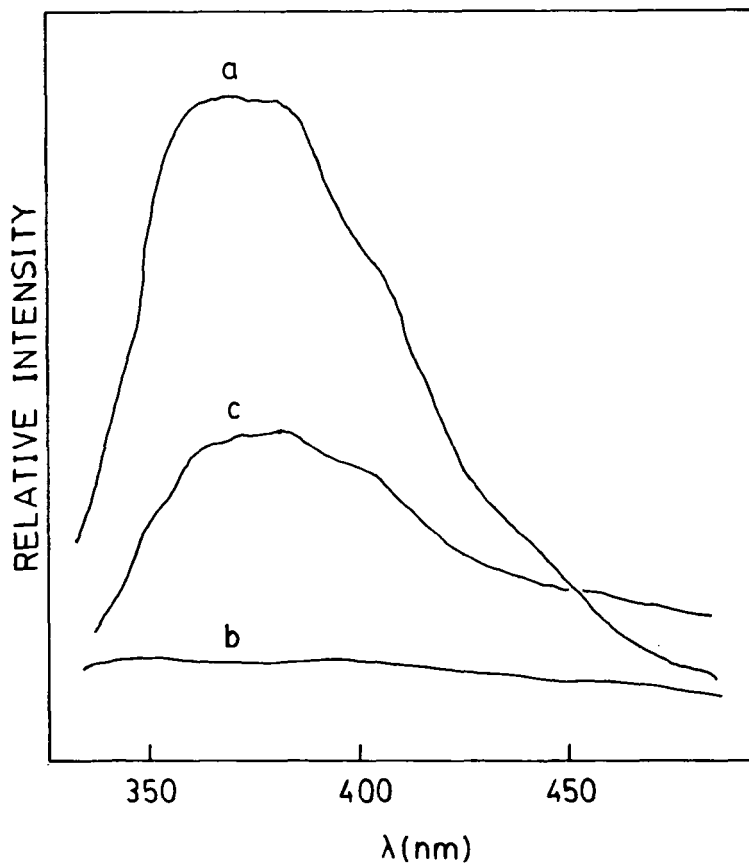


Fig. 2. Luminescence Emission Spectra of (a) fresh catalyst, (b) 2% Cu on fresh catalyst, (c) 2% Cu on aged catalyst.

Similar luminescence emission spectra are given in Figure 3 for 2% Fe on the fresh catalyst, 2% Fe on the aged catalyst, and for the fresh catalyst.

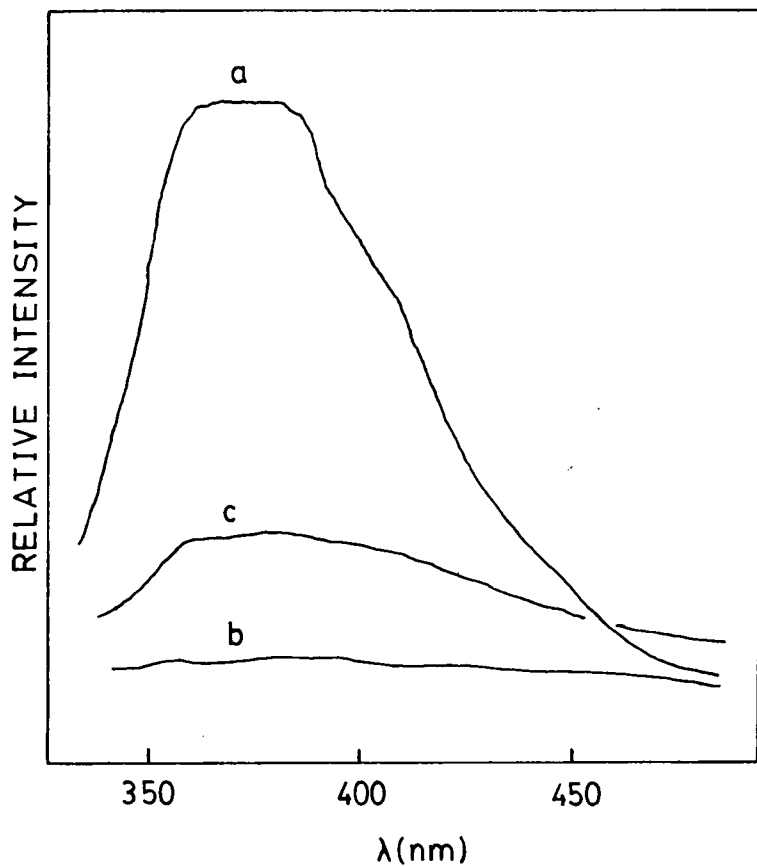


Fig. 3. Luminescence Emission Spectra of (a) fresh catalyst, (b) 2% Fe on fresh catalyst, (c) 2% Fe on aged catalyst.

The effects of increasing amounts of metal, on the cracking conversion are given in Figure 4.

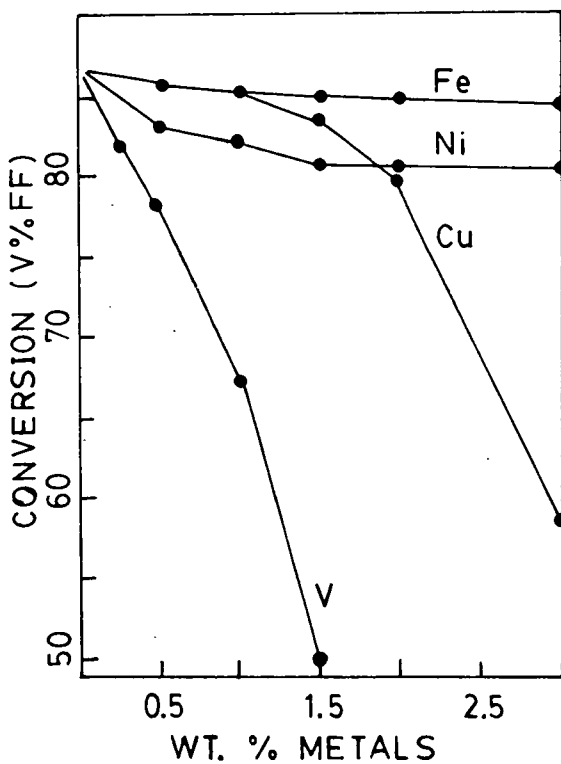


Fig. 4. Effects of Ni, V, Cu and Fe on Cracking Activity.

The effect of metal poisons on the gasoline yield is given in Figure 5.

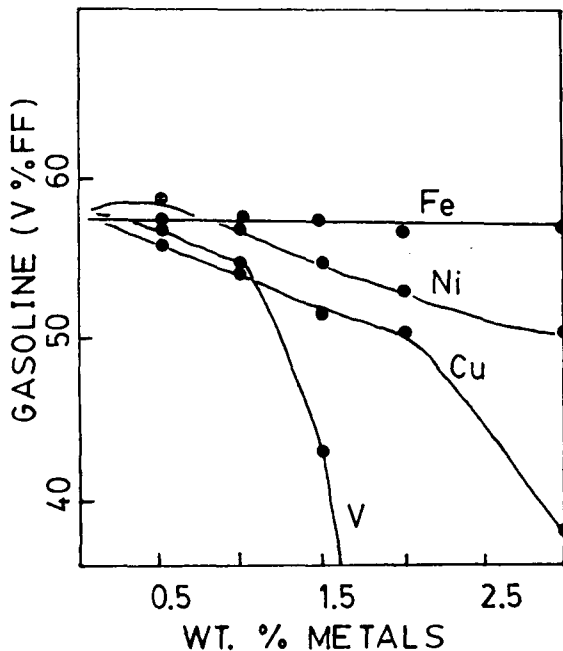


Fig. 5. Effect of Ni, V, Cu, Fe Poisons on Gasoline Yield.

#### DISCUSSION

The luminescence emission spectra of Figures 1, 2a and 3a show several similarities. This emission is due to the LaY component of the catalyst. On the fresh catalyst the emission is very apparent. As both iron and copper deposits are placed on the fresh catalyst, as in Figures 2c and 3c, the LaY emission is quenched. After steam aging the emission intensity for the LaY component of the FCC increases as shown in Figures 2b and 3b. This indicates that the copper and iron deposits are aggregating on the surface and exposing the LaY.

Similar luminescence results have been found for nickel deposits on FCC materials [9]. Further evidence for sintering of the nickel comes from electron microscopy results.

The catalytic cracking activity for nickel, vanadium, copper and iron deposits changes as a function of the amount of metal poison that is deposited. This is shown in Figure 4. For the most part, nickel and iron show parallel behavior with little decrease in overall activity as the weight % of metal is increased. Vanadium on the other hand shows an abrupt decrease in overall conversion even at relatively low amounts of metal poison. Iron starts to resemble vanadium only at high (>2 weight %) loading.

The gasoline yield also changes as a function of the weight % of metal poison as shown in Figure 5. Note that nickel, copper and vanadium deposits drastically decrease the gasoline yield. Iron deposits on the other hand do not change the gasoline yield too much.

## CONCLUSION

It is evident from the data in this paper that luminescence emission spectra can be of great help in the elucidation of poisoning effects of metals on the catalytic activity of fluid cracking catalysts. The luminescence data can be used to determine changes in bond distance [9] during a reaction and as a qualitative tool in the identification of active surface phases. We also point out the good correlation between luminescence emission of the active LaY component and the catalytic cracking activity. Different metal poisons alter the catalysts in various ways depending on the type and amount of metal.

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