

## An investigation on N chemistry of FCC

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### Introduction

Increasing environmental awareness at a global level is leading to more stringent regulations to limit hazardous emissions to the atmosphere. NO<sub>x</sub> (mixed nitrogen oxides) and SO<sub>x</sub> (mixed sulphur oxides) emissions from fluid catalytic cracking (FCC) units have been under scrutiny for some time now, especially in North America and Europe [1]. More recently, however, hydrogen cyanide (HCN) emissions (present in FCC flue gas at levels up to about 150ppm) have drawn concerns in the US and some parts of Europe. Controlling flue gas emissions of this species is an emerging challenge for refiners operating FCC units [2].

A comprehensive understanding of emissions from FCC regenerators will greatly assist design considerations and implementation of emission control techniques. However, the origin of N species in FCC flue gas has been poorly understood and public domain information is very limited. The aim of this work is to understand the origin of HCN and its relationship with other nitrogen containing gases, and to probe the dominant mechanistic pathways for the reduction of N pollution from FCC units.

### Materials and Methods

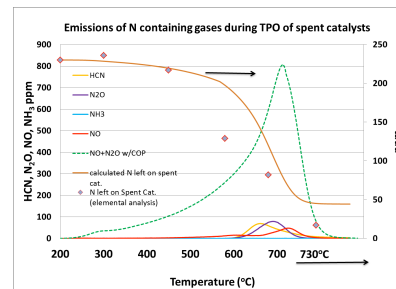
Deactivated “spent” FCC equilibrium catalysts (refer to spent catalyst in the paper) were retrieved from commercial FCC units or prepared in the lab. The catalytic additives used in this study were commercially available CO promoters as well as new additives prepared by INTERCAT<sub>JM</sub>. Model gases (CO, O<sub>2</sub>, NO, NH<sub>3</sub>, HCN balanced with N<sub>2</sub>/He) were supplied by Praxair.

Temperature programmed oxidation (TPO) of spent FCC catalysts and model gas reactions were carried out to study FCC regenerator chemistry. A typical procedure was as following: 2 g of sample were loaded in a quartz reactor, held isothermally at 150°C for 15min, followed by ramping the bed temperature to 730°C at 10 or 15°C/min under a carrier gas containing desired gases (for instance, 2 - 4%O<sub>2</sub>/N<sub>2</sub> and 2.5% H<sub>2</sub>O for TPO of spent catalysts), then holding at 730°C for 30min. Effluent gas was monitored by an MKS multi-gas analyzer. N species monitored include NO, N<sub>2</sub>O, NO<sub>2</sub>, HCN, NH<sub>3</sub>, HCN, HNO<sub>3</sub> and HCNO.

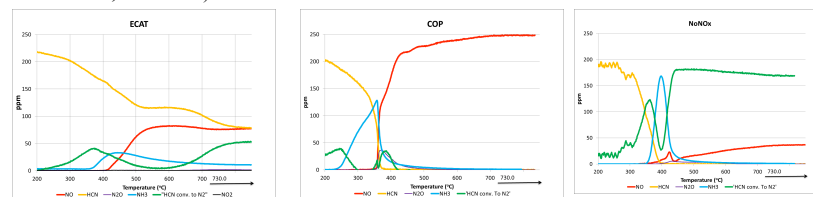
### Results and Discussion

Figure 1 shows emission profiles obtained from TPO of a spent catalyst with and without the addition of a Pt based additive, a commercial product used as FCC CO combustion promoter (COP). The samples for N elemental analysis were obtained by quenching TPO at desired temperatures. The calculated N left on the spent catalyst was based on the N emission with the addition of COP. Since the calculated N is close to the values from elemental analysis, it is convincing that most of the N in coke combusted during TPO in the presence of COP was released as NO<sub>x</sub>. For TPO without COP, HCN was observed in addition to N<sub>2</sub>O and NO, and 90% of N in coke was converted to N<sub>2</sub> based on N balance. Apparently, the formation of N-containing species started at temperature below 300°C, same temperature at which CO/CO<sub>2</sub> started to form (not shown here). Thus, the N species especially N<sub>2</sub> in the effluent gas are mostly resulted from secondary reactions (once formed, N<sub>2</sub> is stable since negligible NO

was formed during the TPO of N<sub>2</sub> and O<sub>2</sub> in the presence of COP). The compositions of N species in the flue gas depend on the nature of catalysts/additives and operation conditions.



**Figure 1.** N emission profiles during TPO of a spent FCC catalyst (3%O<sub>2</sub>/N<sub>2</sub>, 2%H<sub>2</sub>O, 50mL/min, 15°C/min).



**Figure 2.** Temperature programmed reaction of HCN with O<sub>2</sub> and H<sub>2</sub>O on an equilibrium FCC Catalyst (ECAT, left); COP (middle); and a newly developed NO<sub>x</sub> additive –NoNO<sub>x</sub> (right).

HCN conversion in the presence of O<sub>2</sub> and H<sub>2</sub>O is one of the model reactions carried out in this study assuming HCN/NH<sub>3</sub> is the primary product during coke burnoff as suggested from coal combustion studies. As shown in Fig. 2, HCN can survive under FCC regenerator conditions even with excess O<sub>2</sub> – indicating HCN conversion is under kinetic control. The effects of additives are significantly different as exemplified by two additives. Oxidation of HCN to NO<sub>x</sub> on COP could be the mechanism resulting in increased NO<sub>x</sub> emission when COP is used in the units. At the same time, converting HCN to N<sub>2</sub> appears to be a major pathway reducing N emission.

### Significance

This work will generate a more comprehensive understanding on the FCC N chemistry, providing fundamental basis for refiners when taking measures to meet emissions regulations.

### References

1. Niccum, P. K. and Santner C. R. in “Handbook of Petroleum Refining Processes” (Myers, R. A. Ed.) P146. McGraw Hill, New York, 1996.
2. Mo, X.; De Graaf, B.; Diddams, P. Petroleum Technology Quarterly 2013, Q2, 81 – 84.