Understanding the chemistry of NO_x reduction in the FCC regenerator by lambda sweep test

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Introduction

NO_x emissions from the fluid catalytic cracking units (FCCU) are being limited by regulatory agencies to an increasing degree. NO_x is formed in the FCCU regenerator, where coke is burned off to provide process heat and rejuvenate the catalyst. Typical levels of NO_x in the flue gas from fluid catalytic cracking regeneration units vary between 50 and 150 ppm, depending upon feed nitrogen content and regenerator conditions. Use of low NO_x CO oxidation promoter is a simple, cost-effective way in existing FCC units to promote coke combustion and reduce CO and NO_x emission, without significant modifications in the regenerator design or the unit operating conditions.

In order to develop better low NO_x CO promoter, it is essential to understand the chemistry of NO_x formation in the FCC regenerator. Pathways for conversion of nitrogen-containing species proposed earlier [1-2] include formation of N_2 via NO+CO, NO+coke, NO+reduced ceria OSC, and NH_3-SCR, once NO_x is formed, as well as oxidation of HCN and NH_3. However, during coke-burn experiments, a rather complex reaction network is involved which does not lend itself towards dissection of these individual pathways. In this paper, we study the discrete NO_x reaction pathways by the lambda sweep test method [3] to learn which are most relevant under realistic FCCU conditions for different types of CO oxidation promoters.

Materials and Methods

Four CO oxidation promoters, Pt/Al_2O_3, Pd/Al_2O_3, $Pd/CeO_x/Al_2O_3$ and $Pd/CuO/CeO_x/Al_2O_3$ were prepared by wet impregnation of appropriate salt solutions on Al_2O_3 microspheres (95 $m^2 \cdot g^{-1}$, 0.50 ml g-1 water pore volume), followed by calcination 2 h at 650 °C. The loading of precious metal is 500 ppm. We have learned FCC catalyst has activity for HCN hydrolysis and can improve the selectivity of NH_3 oxidation to N_2. To avoid the interference of FCC catalyst and overheating of the CO promoters, an inert kaolin microsphere was used both as a control and as a diluent, and this material had been steamed at 816 °C for 4 hours in 100% steam. CO promoters were tested fresh by blending with this previously steamed material. The performance testing was done using the proprietary lambda sweep test method [3]. Down stream gas analysis was done by FTIR with N_2 yield determined by material balance. The dose of CO promoter was adjusted to match CO conversion activity, which is reported as an overall lean CO_2/CO by using the yields of CO_2 and CO obtained when the feed was $\lambda > 1$.

Results and Discussion

It has been found that HCN is the primary nitrogen-containing product formed from FCC coke combustion [3-4]. To understand how HCN and NH_3 are converted to NO_x/N_2, we fed HCN, NH_3, and NO_x individually as well as the various combinations with or without steam to probe the pathways of the oxidation of HCN, the hydrolysis of HCN to NH_3, the

selective oxidation of NH_3, and the reduction of NO to N_2 by NH_3, coke or CO and the effect of the catalysts. The concentration of co-fed gases CO_2, CO, SO_x, H_2O and O_2 varied cyclically and exponentially, but the total flow rate of these mixtures was held constant to maintain fluidization and mass transfer constant. We have found that HCN oxidation is faster than its hydrolysis to NH_3 so not all HCN is hydrolyzed to NH_3, but can be directly oxidized to NO_x. In the lean region, NO cannot be reduced by either CO or coke but it can be reduced by NH_3; Addition of CuO reduces NO_x yield by improving selectivity of HCN oxidation to N_2. Addition of CeO_2 lowers NO_x yield by improving selectivity of NH_3 oxidation to N_2 and enhancing NO_x reduction by NH_3.
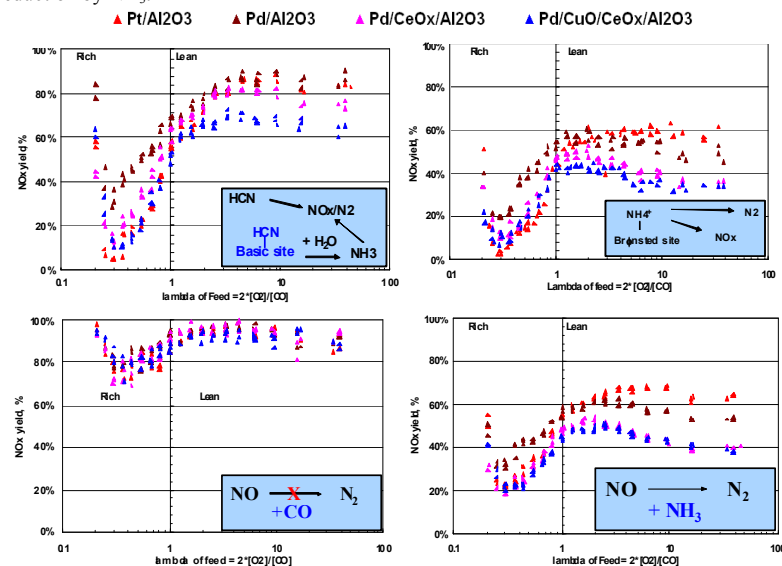

Figure 1 **NO_x** selectivity with various N-species in the feed a) HCN only; b) **NH_3** only; c) NO only; d) **NH_3** and NO.

Significance

The often-proposed NO-CO and NO-coke pathways are seldom travelled by FCC NO_x. Instead, NO_x is reduced by reacting with NH_3 via SCR route. The preferred route is to hydrolyze HCN to NH_3 and/or selectively oxidize NH_3 to N_2.

References

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