

## Towards a new generation of NO<sub>x</sub> additives

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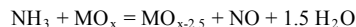
### Introduction

Environmental regulations are pressuring petroleum refiners to reduce NO<sub>x</sub> emissions from the regenerator of the fluidized catalytic cracking (FCC) unit. Frequently, CO concentration in the regenerator flue gas must be controlled, and this is easily accomplished using precious metal CO oxidation catalysts. However, HCN, formed by the pyrolysis of the nitrogen in coke, is also present and the precious metal (PM) CO oxidation catalysts (CO promoters) inadvertently convert at least a portion of the HCN to NO<sub>x</sub>.

### Materials and Methods

Conventional base metal water-gas shift catalysts were prepared at 0.5 -10 wt% loading. The proprietary Lambda Sweep test method [1] for FCC regenerator simulation was employed in the reaction studies.

*Selective oxidation hypothesis.* NO<sub>x</sub> formation may be avoided by selective partial oxidation of HCN or NH<sub>3</sub> solely to N<sub>2</sub>. Useful catalysts normally employ mixed metal oxides and operate by the Mars-van Krevelen mechanism<sup>2</sup>. We propose to rank catalytic activity and selectivity for the selective oxidation of ammonia using  $\Delta G^\circ$  for the stoichiometric reaction



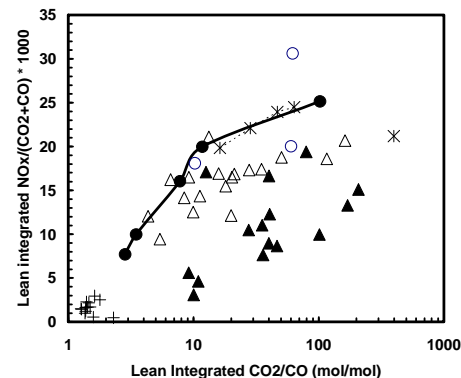
Metal oxides with  $\Delta G^\circ < 0$  are hypothetically active for NO<sub>x</sub> formation. Pt is predicted active to form NO<sub>x</sub> while certain base metal oxides might make N<sub>2</sub> but be unable to make NO<sub>x</sub>.

*Water-gas shift.* Adding the water-gas shift (WGS) and hydrogen oxidation reactions gives CO oxidation, suggesting such catalysts may function as CO promoters. The free energy hypothesis suggests that the base metal WGS catalysts might have lower selectivity to NO<sub>x</sub>.

*Hypothesis on promoter overheating.* PM CO promoter typically is dosed at ca. 0.2 wt% of inventory but only a fraction of it remains active in the E-cat. It was therefore our hypothesis that CO promoters may be overheated with respect to bulk of the catalyst in the regenerator. The  $\Delta G^\circ$  theory suggests overheating will increase the likelihood of NO<sub>x</sub> being formed.

### Results and Discussion

WGS catalysts prepared with 10 wt% base metal oxide (BMO<sub>x</sub>) loading on alumina were tested using 1% fresh, 1% steamed promoter. Results plotted in Figure 1 show that CO<sub>2</sub>/CO ratios higher than for fully promoted E-cat (10-20) were routinely obtained. The 10 wt% loading BMO<sub>x</sub> selectivities for NO<sub>x</sub> were only somewhat improved over PM however.



**Figure 1.** Lambda sweep NO<sub>x</sub> yields obtained as a function of integrated lean CO<sub>2</sub>/CO for 10% BMO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (Δ) or 0.5-10% loading BMO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> (▲), 500 ppm Pt (○) or Pd (\*) on Al<sub>2</sub>O<sub>3</sub>, 8 ppm Pt/Al<sub>2</sub>O<sub>3</sub> (●), or control runs without additives (+). BMO<sub>x</sub> promoters gave high CO conversion but NO<sub>x</sub> was not dramatically improved until the BMO<sub>x</sub> loading was reduced.

WGS catalyst performance data for 0.5-10 wt% loading are also plotted in Figure 1, without regard to the MO<sub>x</sub> loading, and some of these results are further improved. Those samples with low loading gave the most dramatic improvement in NO<sub>x</sub> selectivity. Loading is thus responsible for the selectivity improvement, consistent with overheating and the  $\Delta G^\circ$  theory.

### Significance

If the BMO<sub>x</sub> promoters were to show sufficient activity maintenance during use in the actual FCC unit, refiners may be able to reduce NO<sub>x</sub> while controlling CO emissions, eliminate the use of conventional precious metal CO oxidation catalysts, and avoid the capital expense and operating issues of SCR.

### References

- (1) Stockwell, D. M. Prepr. Amer. Chem. Soc. Prepr. Pap.-Am. Chem. Soc., Div. Petr. Chem. **2006**, 51 (2), 405.
- (2) Grasselli, R. K., in *Handbook of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, Vol. 4 (1997) 2302.