

Advances in the Development and Evaluation of Low-NO_x CO Combustion Promoters for FCC Regenerator Applications

Darrell Rainer, Lin Luo and Jorge A. Gonzalez*

Albemarle Catalysts LLC, FCC R&D, 13000 Bay Park Road., Pasadena, Texas 77507 (U.S.A.)

*Jorge.Gonzalez@albemarle.com

Introduction

NO_x emissions from the regenerator of a fluid catalytic cracking (FCC) unit account for up to 50% of the total NO_x emissions in a modern integrated refinery, which is about 2000 tons/year [1]. One contributor to such high NO_x emission is the wide application of conventional Pt-based CO combustion promoters. The function of CO combustion promoters is to enhance CO oxidation in the dense bed of FCCU regenerators where the catalyst can act as a heat sink, while reducing the exothermic CO oxidation in the dilute bed and, therefore, prevent the afterburn damage to the regenerator overhead hardware. The significant increase in NO_x formation induced by Pt-based promoters is partly caused by the resulting lack of CO to reduce NO_x. In addition, it has been suggested that Pt promotes NO_x formation from N-containing intermediates [2]. Thus, it becomes environmentally attractive to develop non-Pt based low NO_x CO combustion promoters which provide sufficient CO oxidation while markedly reducing NO_x formation.

To develop such additives, realistic lab deactivation testing is important for the prediction of additive performance in commercial applications. Thus, the deactivation of additives under simulated FCC conditions has been investigated here. Cyclic deactivation (CD), which deactivates FCC catalyst through cracking, stripping and regeneration cycles, provides a close simulation of the FCC operation and is one of the best deactivation approaches to address additive deactivation [3-4]. By combining CD with a Coke Combustion Test [5-7], a realistic rank of CO combustion promoters can be obtained. Albemarle has developed a specific testing unit for performing such evaluations [8].

Materials and Methods

A commercial spent catalyst was used as the coke source in the Coke Combustion Test. This coked catalyst contains 0.91 wt% carbon, 470 ppm S, and 220 ppm N. 0.2-1 wt% of the CO Combustion Promoter was blended with 50 grams of the spent catalyst and the blend was pretreated in a fluidized bed reactor under N₂ at 700°C for 1 hour. After the pretreatment, 2% O₂ in N₂ was introduced into the reactor and the emission gases were monitored by an FTIR Multi-gas analyzer (MKS).

Deactivation of the CO Combustion Promoter was conducted by cyclic deactivation of an additive/FCC catalyst blend with a high Sulfur containing (3 wt% S) Kuwait VGO. The additive level in the blend was 5 wt% and the FCC catalyst (Conquest 87) was pre-steamed at 788°C for 20 hours before CD (PST FCC Base). After deactivation, a calculated amount of the additive/FCC catalyst blend was mixed with 50 grams of the spent catalyst, to reach the targeted additive level. The mixture was then evaluated by the Coke Combustion Test.

Results and Discussion

Figures 1a and 1b show the lab-scale testing results of several different CO combustion promoters in which both CO and NO levels were monitored. The number printed above each bar is the ratio of the CO decrease (relative to the baseline from the spent catalyst alone) over the NO fraction (on the same basis). This is defined here as the CONO effectiveness factor. A higher CONO effectiveness factor indicates lower NO_x yields at constant CO oxidation rates (or, conversely, higher CO oxidation rates at constant NO_x yields), and, hence, a more selective promoter.

In every case, the fresh developmental samples exhibit superior NO selectivity (lower NO yields and higher CONO effectiveness factors) at comparable CO oxidation activities relative to both commercial counterparts. This trend is also observed for the analogous deactivated samples, except in the case of Additive “D”, for which the CO oxidation activity is essentially lost after deactivation. This particular example demonstrates the importance of incorporating a realistic deactivation step into any comparative assessment of additives performance.

These lab-results suggest the potential of these new additives for reducing NO_x yields in commercial FCCU's. Early industrial trial results have supported this conclusion. Figure 2 shows the impact of one of these low-NO_x CO combustion promoters on the CO and NO_x levels measured in an unidentified commercial unit relative to a baseline established with a Pt promoter. The 5-day rolling averaged NO_x value drops by over 30%, while the CO level fluctuates around the original baseline for the Pt promoter. This significant drop in NO_x emissions achieved at the comparable CO combustion level effectively demonstrates the commercial effectiveness of this new additive.

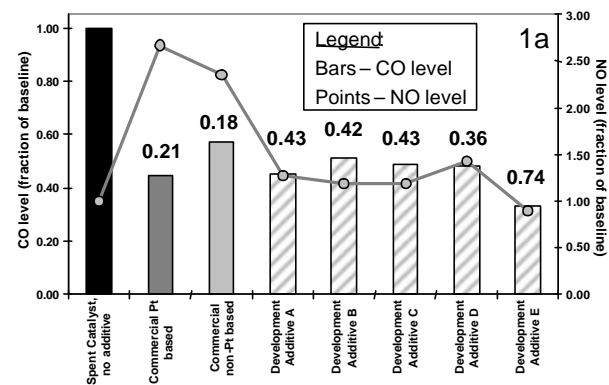


Figure 1a. Lab-scale testing results for fresh CO combustion promoter additives blended in with a commercial spent catalyst at 1%. The numerical value above each bar is the CONO effectiveness factor.

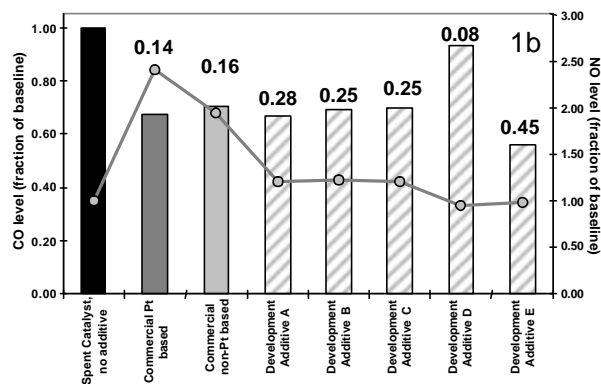


Figure 1b. Lab-scale testing results for the same set of promoter additives as in 1a after cyclic deactivation of each additive. The numerical value above each bar is the CONO effectiveness factor.

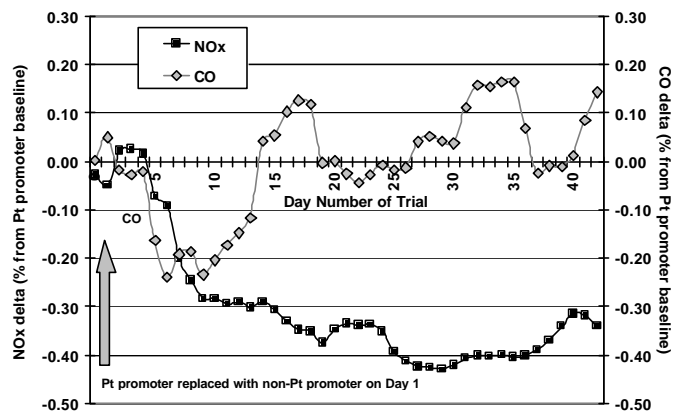


Figure 2. Commercial data from an unidentified FCCU after replacement of a Pt CO combustion promoter with a newly developed low-NO_x non-Pt CO combustion promoter.

Though there is some variation in the CO level in the trial depicted in Figure 2, over the course of the entire trial the average CO value is comparable to the baseline established with the Pt promoter. The NO_x level, however, shows a clear and consistent reduction with the new additive, achieving NO_x decreases of 30-40% relative to the levels observed with the Pt additive.

Significance

Both on a fresh and deactivated basis, lab-scale performance testing of certain developmental low-NO_x CO combustion additives has shown more than a three-fold increase in the CONO factor compared to a standard commercial Pt-based CO combustion promoter. Of this set, the rankings did not appreciably change after deactivation using a method designed to roughly simulate an exposure in the FCCU of one day, except in the case of one sample that lost essentially all CO oxidation activity after such exposure, illustrating the need to test samples under realistic deactivation conditions. Commercial data corroborates the value of this approach for the development of novel FCC combustion additives.

References

1. Barth, J. O., Jentys, A., Lercher, J. A., *Ind. Eng. Chem. Res.*, 43, 3097-3104, (2004).
2. Davey, S. W., Environmental catalytic cracking technology, Petroleum Technology Quarterly <http://eptq.com> – *The Refining, Gas and Petrochemical Processing Website*, (2000).
3. Gerritsen, L. A., Wijngaards, H. N. J., Verwoert, J., O'Connor, P. *Catal. Today* 11, 61-72, (1991).
4. Rainer, D. R., Rautiainen, E. and Imhof, P. *Applied Catalysis A: General* 249 69-80 (2003).
5. Yaluris, G., Zhao, X., and Peters, A. W., *Proceedings of the 212th ACS National Meeting*, Orlando, Florida, 901-905, (1996).
6. Efthimiadis, E. A., Iliopoulou, E. F., Lappas, A. A., Iatridis, D. K., and Vasalos I. A. *Ind. Eng. Chem. Res.* 41(22), 5401 – 5409, (2002).
7. Dishman, K. L., Doolin, P. K., and Tullock, L. D., *Ind. Eng. Chem. Res.*, 37, 4631-4636, (1998).
8. Luo, L., Rainer, D. and Gonzalez, J. A., *App. Catal. B: Environmental*, in press.