

High Resolution Electron Microscopy Study of Nano Structure in CO Emission Control Additives

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For a safe operation of the Fluid Catalytic Cracking (FCC) unit, afterburn control is essential. Afterburn occurs when uncontrolled CO leaves the fluid catalyst bed in the regenerator and combusts in the gas phase above the bed. Afterburn can lead to severe temperature excursions exceeding metallurgical limits of the regenerator. Secondly, as regulations on the CO emissions become more stringent, refiners must consider better ways to promote the oxidation of CO by using combustion promoter additives (COP) [1]. A CO emission control additive can be applied for the catalytic oxidation of CO to CO₂. Several hundred ppm levels of precious metal are used as catalytic active sites. The CO conversion efficiency depends on the amount, size and location of metal clusters. It is important to understand the deactivation behavior under industrial conditions in order to improve the microstructure and performance of CO control additives. It is known that the deactivation of COP in the regenerator is due to one of or combined factors as follows: (1) Hydrothermal sintering which will lead the size and distribution changes under high temperature with the addition of steam. (2) Poisoning due to other components such as SO₂ in the unit is also the possible reason for noble metal degradation [2]. (3) Pore collapse, loss of surface area and changes in metal oxidation state / changes in the metal support interaction are considered to be the main deactivation mechanisms for combustion promoters. In this study, both probe corrected scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) are employed to investigate the size, distribution and structure evolution of precious metal in COP before and after industrial deactivation.

STEM and SEM investigations were conducted on the fresh and deactivated COP samples. The fresh sample was ground into small powders and put on the carbon film of copper grid for TEM examination. The deactivated industrial sample was from an US refinery where COP-550 effectively controls afterburn, and has spent a residence time of 4 weeks in the unit. In FIG. 1, the High-resolution STEM image shows a detailed structure of the fresh CO emission control additive. Single atomic scale Pt is dispersed on the matrix of γ -Al₂O₃. The γ -Al₂O₃ lattice of the matrix can be easily distinguished. Only small Pt clusters and monoatomic Pt are present in the fresh sample. In FIG. 2, YAG electron backscattering image indicates the nano Pt particles in deactivated samples from the FCC unit. The size analysis showed that the Pt nano particles have an average size of about 13 nm which indicates a significant sintering. Increased Pt particle size means decreased metal surface area and effective sites of Pt, which certainly will cause the degradation of the COP additives. After being exposed for weeks to high temperatures (up to 750°C) in an alternative oxidative/reductive environment containing 10% H₂O, migration and agglomeration of Pt atoms (Ostwald ripening) and /or small clusters are expected to happen in the unit for COP additives. The visual inspection on the industrial sample retrieved from a commercial unit confirms that the sintering behavior of Pt nano particles is indeed one of the most likely mechanisms for the deactivation of the COP additives in the FCC units.

References:

- [1] A.A. Bhattacharyya, and J.S. Yoo, in "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf Sci.* Elsevier Science Publishers B. V., Amsterdam, Vol. 76 1993, Cutul., 531
- [2] L. Luo, D. Rainer, and J.A. Gonzalez, in "Laboratory deactivation testing for the stability of FCC CO combustion promoters", *Appl. Catal. B: Environ.* 72, 2007, 212.

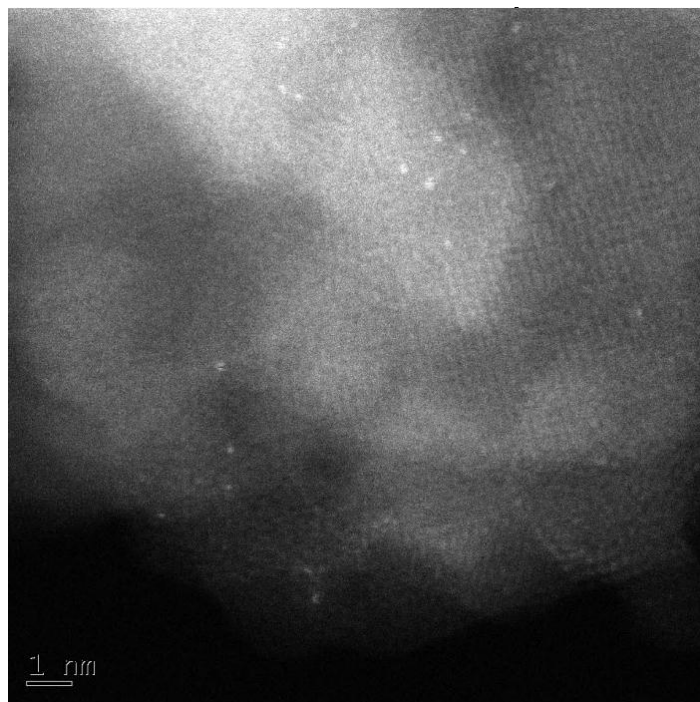


FIG. 1. High-resolution STEM image of fresh CO emission control additive. Single atomic scale Pt is dispersed in the matrix of $\gamma\text{-Al}_2\text{O}_3$. There are places where there are a few more atoms close together with a trend to form small clusters.

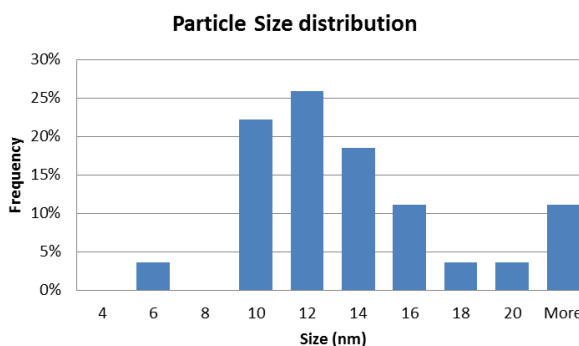


FIG. 2. YAG electron backscattering image and size distribution data from the deactivation sample in FCC unit after at least a thousand cycles. The average particle size is 13 nm which indicates a significant sintering which certainly will cause the degradation of the COP additives.