

Understanding of FCC Catalyst Deactivation: Cyclic Thermostress Sintering Mechanism

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FCC catalysts in commercial units are exposed to hydrothermal deactivation, mechanical degradation, metal contamination and poisoning that cause them to lose activity. In order to maintain the desired level of productivity in the FCC unit, an equilibrium catalyst is continuously purged from the inventory and replenished with a fresh one. Accurate prediction of catalyst deactivation rate in commercial units under real operating conditions is essential not only to the catalyst management strategy but also to the evaluation process and selection of catalysts to satisfy customers' objectives. There are numerous laboratory deactivation methods for fresh catalysts to simulate commercial Ecats, ranging from simple hydrothermal deactivation to very complex age distribution schemes. No deactivation method is fully capable of matching commercial FCC Ecats physical and chemical properties yet.

A typical FCC catalyst consists of zeolite crystals dispersed in alumina or silica porous matrix. Catalyst activity depends, among others, on the surface area of zeolite and matrix, and the ratio between them. The equilibrium catalyst from a commercial FCC unit was separated into four equal fractions using the density fractionation method. All fractions were characterized in terms of physical and chemical properties. Using the population balance equation for the circulating catalyst in the FCC unit, the densities of individual fractions were mapped onto a time scale (the average residence time) to analyze the time evolution of its properties. It was noticed that the ratio between zeolite and matrix surface area was much higher for Ecats than lab deactivated catalysts.

As the catalyst circulates in the FCC unit, it is exposed to hydrothermal deactivation. It is well recognized that under such conditions, the catalyst's matrix sinters and the zeolite framework loses aluminum atoms. In both cases, surface area loss is observed. Simulation of the catalyst deactivation in the lab shows that zeolite is usually less stable than the matrix and deactivates faster. Using heat and steam, under lab controlled environment, it is impossible to obtain a zeolite-to-matrix surface area ratio that is similar to the ratio observed in the field. This paper focuses on a new mechanism that is proposed to explain this peculiar catalyst behavior.

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In the FCC unit, catalyst constantly circulates between riser, stripper and regenerator. In the regenerator, the coke on the catalyst is burned causing an increase in the catalyst particle temperature. Next, the hot catalyst is transferred to the riser where it is mixed with a mist of colder feed. The boiling feed droplets and the endothermic cracking reactions rapidly lower catalyst particle temperature. As a result of temperature quench, thermal stresses arise that compress the catalyst particle. Depending on the operating conditions, the temperature difference between regenerator and riser can reach few hundred degrees centigrade over a fraction of a second that corresponds to thermostresses of several thousand atmospheres. The cold catalyst from the riser eventually goes back to the regenerator where it is heated up again by exchanging energy externally with the surroundings and internally by absorbing heat of the exothermic reaction of coke burning. As the particle temperature goes up now, the tensile thermostresses stretch the particle. Even though the catalyst particle temperature returns to its initial value in the regenerator at the end of such a circulation cycle, the catalyst properties such as density and surface area are irreversibly changed. It happens because porous catalyst particles exhibit complex non-elastic response to thermal loads.

A mathematical model has been formulated to describe evolution of catalyst properties as it cycles through the FCC unit. The model takes into account catalyst age distribution by solving population balance for the FCC unit. The complex material response to the thermal loads has been built into the model through visco-elasto-plastic constitutive equation. Very good agreement has been achieved between experimental data and model predictions as illustrated in the Figure.

