Continuous Age Distribution Method for Catalytic Cracking

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Introduction
Continuous catalyst replacement during fluidized catalytic cracking (FCC) leads to an exponential distribution of catalyst ages in the working "equilibrium" catalyst mixture (E-cat). Fluid bed regeneration of coke-laden catalyst with air results in ~25 kPa of steam at ~975 K, which deactivates the zeolite Y-based catalyst by simultaneously hydrolyzing tetrahedral framework aluminum (dealumination, Al\textsubscript{T}) and tetrahedral framework silicon (Si\textsubscript{T}). Dealumination occurs rapidly [1], reaching a pseudo-equilibrium of ~80% Al\textsubscript{T} removal within a day or two, but Si\textsubscript{T} loss is much slower, with nominally 50% of Si\textsubscript{T} collapsing over 80 days. FCC catalysts also commonly contain a separate alumina or stabilized alumina matrix [2], and most of these are hydrothermally very stable. The selectivity characteristics of zeolite and matrix differ however. Clearly then, the activity and more importantly the selectivity of cracking catalyst can be expected to vary with age, the overall performance of the E-cat being due to both the discrete properties of a given age as well as its percentage within the mixture.

Despite the significance of the age distribution, this effect is typically neglected when simulating refinery catalyst deactivation in the laboratory. Empirical age distribution methods have been proposed before [3] but these are cumbersome and provide no guidance on conditions needed to match a specific refinery.

Materials and Methods
A Continuous Age Distribution Method (CADM) of steam-deactivation has been developed which reproduces the full distribution of zeolite micropore surface area found in refinery E-cat (Fig. 1), doing so in a single steaming. A screw feeder continuously adds fresh FCC catalyst to an initially empty steaming reactor, the temperature of which declines with time according to a logarithmic profile which depends on the kinetics of Si\textsubscript{T} decay in the lab and the refinery, and on the replacement rate of catalyst in the refinery. A literature correlation with unit cell dimension is used to separate the contributions of Al\textsubscript{T} and Si\textsubscript{T} to the overall micropore area. The method is based on fundamental kinetic and reactor models, and so has the potential to both reproduce and predict, a priori, refinery catalyst performance.

$$T(t) = \frac{E_R / R}{\ln[L(t)/L_{50}] + \ln[\alpha]} = \frac{E_o / R}{RT_{298} + \ln\left(\frac{L}{L_{298}}\right)} + \ln[\alpha]$$

Results and Discussion
Arrenhius plots of laboratory steaming data were initially found nonlinear and in poor agreement with rates derived from refinery E-cat. A new calibration algorithm and $E_o$ hypothesis testing then showed that $E_o=117$ kcal/mol made the properties of the catalyst in the steamer continually match the targeted E-cat for up to 7 days. Intermittent operation of the steamer allowed us to prepare discrete 10 wt% segments within the age distribution, and the results of Fig. 1 show that CADM-steamed catalyst segment properties were very similar to expectations based on density separations and 1st order Si\textsubscript{T} decay. We next varied the refinery catalyst replacement rate (1/t\textsubscript{50}), and while we obtained a directionally correct response for activity and micropore area, the results deviated systematically from 1st order decay.

After harshly pre-steaming FCC catalyst, Pine [4] found that Arrhenius plots were linear and that vanadium and sodium affected $k_o$, but not $E_o$. In ongoing work we find that fresh commercial zeolites contain 10-20% of metastable Si\textsubscript{T} which can be eliminated by a mild presteaming. Subsequent Arrhenius plots are straight and agree with refinery decay rates. This allows us to eliminate the dependence of the CADM ramp on $k_o$ since $k_o$ is the same in the lab as the refinery. The initial nonlinearity was thus due to the metastable Si\textsubscript{T}. After presteaming, all Y zeolites investigated so far by us give $E_o \approx 80$ kcal/mol, even with vanadium, in agreement with Pine [4]. Since $E_o = 80$ kcal/mol for all Y zeolites and $k_o$ has been eliminated, CADM requires no further calibration. If a base catalyst fails to match the E-cat target, adjustments can be made to the CADM temperature ramp via the regenerator temperature $T_R$ or steam pressure $P_{steam}$ to correct the offset. Once the reference catalyst is on target, other catalysts will also necessarily give their correct micropore areas for that FCC unit.

Separately, we find that by varying CADM addition time the selectivity of lab-deactivated samples can be made to match low metals E-cat in nearly every detail. The effects of V and Na are embedded in $k_o$, so if laboratory V and Na match the refinery, the CADM calibration will not change. But (1/t\textsubscript{50}) may need to increase to compensate for zeolite destruction, just as in the refinery. CADM is expected to reduce contaminant H\textsubscript{2} and coke.

Significance
CADM provides a fundamentally sound method to comprehensively reproduce E-cat in the laboratory. The ability to accurately reproduce and predict catalyst properties and performance should enable for the first time truly quantitative analysis of refinery operations.

References