Development of High-Accessibility, Sinter-Resistant Fluid Cracking Catalysts

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Introduction

The term "sintering" when applied to FCC catalysts operating under commercial FCCU conditions typically refers to the generation of catalyst particle liquid phases and surface melts of the type common in the preparation and production of certain ceramics. In FCC, these phenomena can result in catalyst surface glazing and accessibility losses with attendant degradation in performance, particularly with regard to bottoms cracking. Certain contaminant metals, such as iron, calcium, sodium, and vanadium, can exacerbate these problems by serving as metal "fluxes" which promote sintering (or "glazing") of the alumina and silica containing components in the catalyst [1-3].

This paper describes an investigative approach for identifying and quantifying the degree of sintering experienced by a particular catalyst under deactivation conditions prescribed to enhance and identify these effects, as well as the results acquired for a set of three developmental catalysts designed to exhibit varying degrees of sinter resistance.

Materials and Methods

The primary indicator used here for determining the relative degree of resistance to sintering by a catalyst is the Albemarle Accessibility Index (AAI), an asphaltene penetration test developed as a basic measurement to quantify the accessibility of the catalyst for penetration by the larger molecules composing the heavier FCC feed fractions [4, 5]. The deactivation protocol under which the AAI responses are measured has been described in the literature previously under the name CD-ALFA (cyclic deactivation with accessibility loss via Fe addition) [6, 7]. This method employs mild steaming conditions (comparable to actual steam levels experienced by the catalyst in the FCCU), high iron additions, and long exposure times to induce catalyst accessibility losses comparable to those observed in unit operation.

Results and Discussion

The graph in Figure 1 shows the AAI plotted vs. the added iron level over the course of a CD-ALFA deactivation for three catalysts in a related set, two of which are proprietary formulations which have been designed to exhibit enhanced resistance to iron-induced sintering. Increased resistance to sintering can be achieved both by elevating the fresh AAI and also by retarding the relative rate of AAI loss as a function of fluxing metal addition and exposure time, each of which contribute to a higher final AAI after deactivation.

The two sinter-resistant catalysts exhibit significantly higher fresh AAI values relative to the benchmark (27.5 and 19.8 for the sinter-resistant samples, respectively, versus 10.8 for the benchmark), with this advantage persisting throughout the course of the deactivation. In the final deactivated state, the two sinter-resistant catalysts exhibit AAI values of 33.6 and 15.2, respectively, while the non-sinter-resistant benchmark features an AAI that has dropped to 1.3. Based on copious commercial experience [5, 6, 8-10], these AAI benefits clearly observed for the two sinter-resistant developmental catalysts would be expected to provide significantly enhanced bottoms cracking activity, especially in a unit environment with moderate to high levels of the aforementioned fluxing contaminant metals (particularly iron and/or calcium).

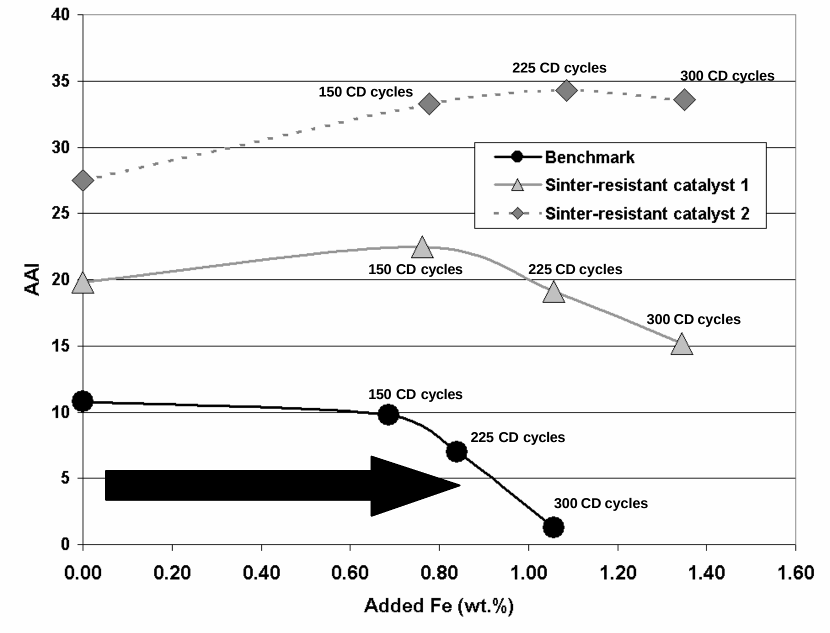

Figure 1. Absolute AAI as a function of Fe addition during the CD-ALFA deactivation process for three catalysts.

The graph in Figure 2 shows the percentage AAI retention for the same set, again plotted vs. the added iron level throughout the CD-ALFA deactivation process. This plot is particularly illustrative of the enhanced sinter-resistance of the two developmental catalysts; not only do they both exhibit higher absolute accessibility indices at the deactivation conclusion (Figure 1), but they also demonstrate a markedly increased resistance to AAI loss, independent of the starting AAI. In fact, for Sinter-resistant Catalyst 2, the final deactivated AAI is actually higher than the fresh value. This can be explained by the common observation that steam exposure increases AAI. For most catalysts in commercial operation this steam-induced increase is quickly offset by the effects of the contaminant metals driving the sintering process forward and the AAI down. In the case of Catalyst 2, however, under these conditions, the sinter-resistant nature of the sample is such that the steam induced AAI increase persists, the heavy addition of iron in the deactivation method being insufficient to reverse it.

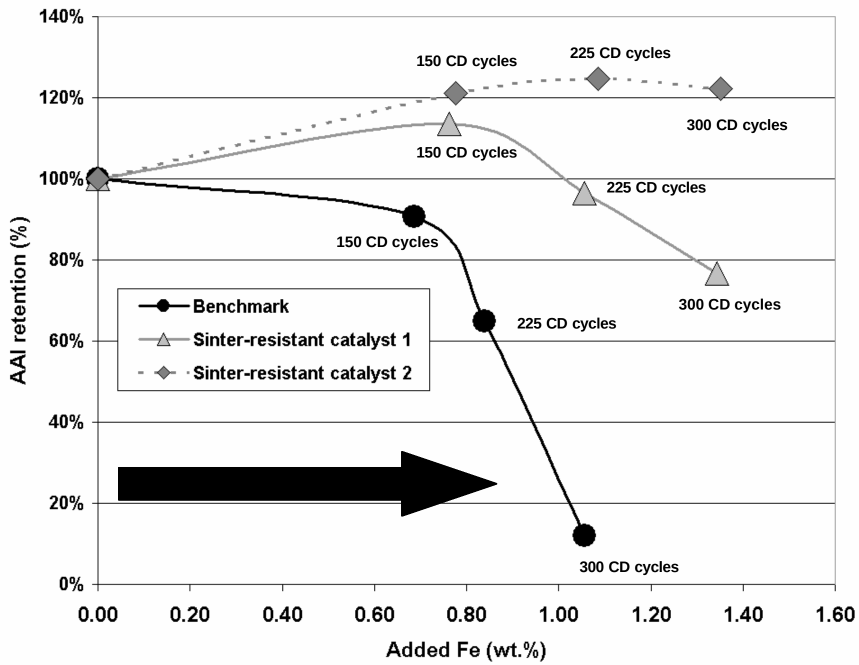

Figure 2. Percent AAI retention as a function of Fe addition during the CD-ALFA deactivation process.

Significance

Contaminant metals present in the FCC process drive sintering reactions in the catalyst that result in loss of accessibility for the larger molecules in the heavy feed fraction to reach the internal reaction sites. Resistance to these sintering reactions is an important element in the effectiveness of an FCC catalyst in resid operations. This particular study details a method for measuring the sintering-resistance of a catalyst, and highlights the dramatic improvements in this area featured by the developmental technology investigated.

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