

Comparing Nickel and Vanadium Passivation with FCC Catalysts in Laboratory Microactivity Studies

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INTRODUCTION

Cracking residuum feeds in fluid catalytic cracking (FCC) units increases the level of contaminant Ni and V metals on cracking catalysts. This results in decreasing catalytic activity and increasing contaminant coke and hydrogen yields [1]. Over the years, a number of testing methods have been developed and used to rank catalyst performance. These include microactivity tests, either in fixed beds (MAT) or in fluidized beds, and pilot tests in circulating risers.

New catalysts being developed in laboratories will more often than not vary in their cracking activity from one another. Also, the propensity of these catalysts to trap and passivate nickel and vanadium will vary. Therefore it is imperative that one carries out evaluations while taking such differences in activity into account. To that end, we address in this paper a way for evaluating new catalysts for resid cracking.

EXPERIMENTAL

We prepared two catalysts, one containing 3 wt% REO and no metal-passivating component (Catalyst B) and second containing 1.2 wt% REO with a composite matrix containing a proprietary metal-passivating component (Catalyst C).

Both catalysts were deactivated by impregnating 3000/3000 ppm Ni and V using a modified Mitchell method [2]. The resulting materials were steam deactivated at 1061 K for 4 hr in a mixture of 90% steam and 10% air. We determined catalytic performance via a modified fixed-bed MAT unit. Conversion was varied by changing space time via the amount of active catalyst [3]. For second-order gas oil cracking in a fixed-bed reactor, the activity is defined as $x/(1-x)$, where x is the gas oil conversion. Contaminant coke, which is produced by Ni and V only, is obtained by subtracting the catalytic coke, in the absence of metals, from the overall coke, with metals, at the same conversion. In this study, we have used both hydrogen yields and contaminant coke yields as fingerprints of metal passivation. It is easier to use the former since hydrogen yields without metals are very small, and most of the hydrogen observed is due to Ni and V.

RESULTS AND DISCUSSION

Catalyst C was 65% lower in activity due to its lower zeolite and matrix surface areas and lower REO content as compared to Catalyst B. At 70% conversion (second order activity of 2.33), H_2 and coke yields are 1.14 wt% and 13.6 wt% for Catalyst B, and 1.36 wt% and 15.1 wt% for Catalyst C (see Figure 1a). Catalyst C which contains a metal passivating matrix, yields 19% higher hydrogen yield and 11% higher coke yield (not shown) compared to the catalyst which does not contain a metal passivating matrix. This is contradictory to the expected result where catalyst containing metal passivating matrix is expected to yield lower H_2 and coke yields.

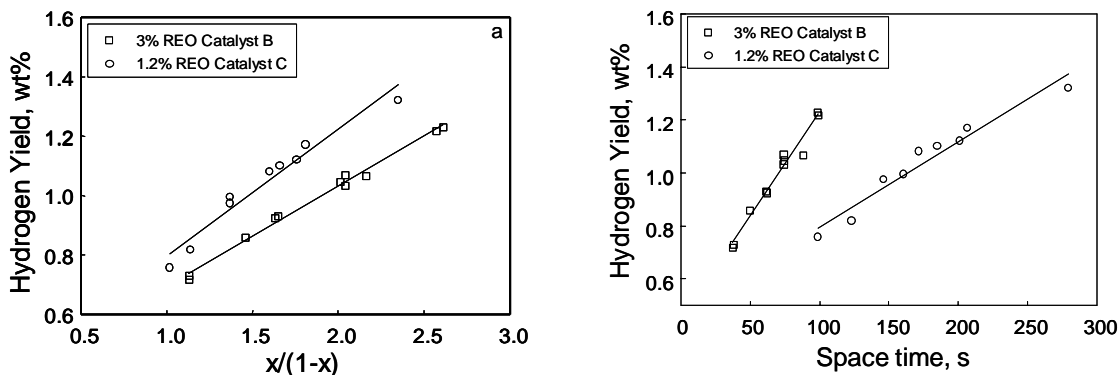


Figure 1a. Hydrogen yields versus second order activity function. **Figure 1b.** Hydrogen yields versus space time. Catalysts contain 3000 ppm Ni and 3000 ppm V.

Catalytic cracking over metal-contaminated Y-based catalysts is complex in that there are two sets of reaction pathways that result in the observed products (Figure 2). Catalytic cracking takes place over the Y-based catalyst via an acid catalyzed mechanism to yield hydrocarbon products including catalytic coke and some hydrogen. In a different set of reactions contaminant coke and hydrogen are formed by catalytic reactions on Ni and V species via a dehydrogenation pathway. Hydrogen formation via this route is comparatively more substantial.

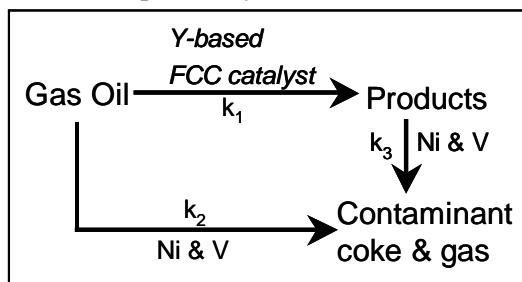


Figure 2: Schematic showing reaction paths in the presence of metal contaminated FCC catalysts. (k = overall rate constants)

When acidic Y-based catalysts have different intrinsic cracking activities, they will have very different space-time – cracking activity relationships with lower space times needed to obtain a required conversion with the more active catalysts. Since the catalysts for contaminant coke and hydrogen formation are Ni and V species supported on the Y-based FCC catalyst and not the Y-based catalyst itself, it is inherently incorrect to relate the formation of these contaminant products to the extent of gas oil conversion obtained via catalytic cracking over acidic Y-based catalysts.

For catalytic cracking, space time is the weight of the FCC Y-based catalyst divided by the reactant gas oil flow rate. For the formation of contaminant coke and hydrogen, space time is correctly defined as the weight of the Ni and V species divided by the reactant gas oil flow rate. However, since we keep the total concentration of Ni and V on the Y-based FCC catalysts constant during our comparative studies, we can use the cracking space time as defined by the weight of the FCC catalyst to analyze our results.

Figure 1b shows space time – hydrogen yield plots. Results as shown in this figure belied the fact that Catalyst C contained a metal passivating matrix; the earlier indication (Figure 1a) was that it gave higher hydrogen and coke yields than Catalyst B. The conclusions are now in line with expected behavior and orthogonal to the earlier indication. At 100 s space time, and an equivalent total metal weight of 0.024g, Catalyst C makes 35% less hydrogen and 58% less contaminant coke (not shown) than Catalyst B, indicating a better effectiveness of catalyst C for metal passivation due to its matrix.

CONCLUSION

Products obtained from catalytic cracking and contaminant coke and hydrogen due to Ni and V are obtained via different catalytic routes. One cannot directly relate the formation of contaminant hydrogen and coke to the extent of reaction for hydrocarbon cracking. Therefore, for FCC catalysts having different cracking activities and containing contaminant Ni and V, a comparison of coke and hydrogen yields at constant cracking conversion will lead to an incorrect assessment regarding metal passivation. To obtain the correct propensity for metal passivation, one needs to compare catalysts with different activities at a constant space time for flow reactors and at a constant catalyst to oil ratio for a circulating riser unit. Only if the catalysts being tested have identical cracking activities can one compare results at constant cracking conversion.

REFERENCES

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