Extending Catalyst Life: Laboratory Aging Tests as Tools to Enhance Catalyst Performance

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Introduction

Laboratory screening tests are essential tools in the evaluation of industrial heterogeneous catalysts. While the initial activity and selectivity of a catalyst can be easily and quickly determined in the laboratory, obtaining an estimate of catalyst life, especially in a short term laboratory test, is a much more challenging task. This is because under normal operating conditions, a commercial catalyst may perform for many months or even years. Despite this difficulty, a number of reliable accelerated aging tests, covering a wide range of applications, have been developed at Süd-Chemie. These aging tests reproduce the physical and chemical changes that occur during commercial operation, but over a much shorter time scale. Such tests have played a key role in the development of many important catalysts that are currently in use in industry today. Examples from two different applications will be discussed.

Materials and Methods

All catalyst screening experiments were conducted in isothermal test units. Selective hydrogenation experiments were carried out at "back end" conditions with a mixed acetylene/ethylene feedstock. Olefin oligomerization tests were performed with mixed propane/propylene feeds.

Results and Discussion

Selective Hydrogenation of Acetylene

Palladium catalysts are the most common catalysts used in industry for the selective hydrogenation of acetylene to ethylene. A key deactivation mechanism for these catalysts is the deposition of polymer on the surface and in the pores of the catalyst. The gradual build-up of this hydrogen-deficient oligomer leads to a decrease in both catalyst activity and selectivity. An accelerated aging test was developed that caused a significant amount of polymer deposition after only 100 hours on stream. While use of a Group IB metal as a promoter to reduce "green oil" formation is well known [1], aging tests showed that the promotional effect could be significantly enhanced by modifying the catalyst preparation procedure. After operation in a bench scale unit, the polymer was extracted and characterized by GCMS. Interestingly, the results show that the new catalyst not only produces less polymer, but the polymer is less olefinic in character (Figure 1). The new catalyst was successfully commercialized and has shown outstanding performance in two commercial units.

Olefin Oligomerization

Solid phosphoric acid catalysts have been used commercially for olefin oligomerization for many years. While this catalyst has often been referred to as "phosphoric acid supported on kieselguhr" [2], in reality the silica has reacted with the phosphoric acid to form at least two different phases of silicon phosphates [3,4]. The catalyst is therefore more properly viewed as phosphoric acid supported on a carrier composed of silicon phosphates. In commercial oligomerization units the end of catalyst life is often caused by an increase of pressure drop. Laboratory aging tests show that with some catalyst formulations, rapid pressure drop increase is caused by an increase in the actual size of the catalyst. This "swelling" of the catalyst is associated with a chemical change that occurs between the silicon phosphate phases of the catalyst. The driving force for this chemical change is a combination of water in the feed and heat from the polymerization reaction (Figure 2). Recognition of this failure mechanism was the key to developing an improved, more stable catalyst which was subsequently introduced to the market.

Significance

These two examples clearly illustrate how accelerated aging tests can be used to develop improved industrial heterogeneous catalysts. Such evaluation methods have played a key role in the development of many of the most successful catalysts on the market today.

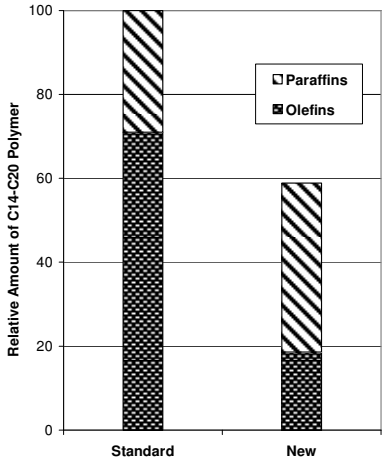

Figure 1. Composition of by-product polymer from two different promoted Pd catalysts.

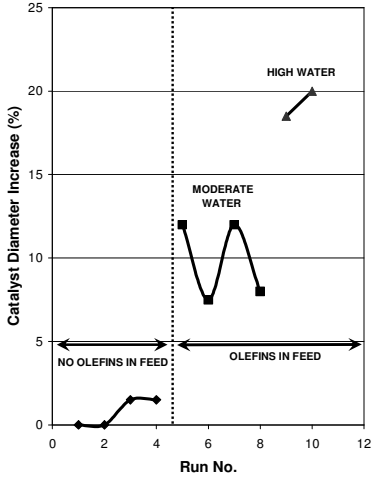

Figure 2. Physical changes in oligomerization catalyst as a function of reaction conditions.

References

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4. D.M. Poojary, R.B. Borade, F.L. Campbell III, and A. Clearfield, *Journal of Solid State Chemistry* 112, 106 (1994).