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Feature article

Moving from discovery to real applications for your catalyst

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ABSTRACT

We discuss the importance of operating conditions and feed gas composition in evaluating any catalyst. Test conditions are often simplified in early catalyst evaluations, but ultimately catalysts need to be evaluated close to the anticipated process conditions if one wants to make generalizations about performance with regard to an anticipated product in the marketplace; the sooner the better. This will allow others to focus on the crucial steps that one has to take to apply a new discovery to a new or existing product. We examine several different test parameters that can significantly impact a number of different reactions. One focus is on testing catalysts early during the discovery/optimization stage under conditions which anticipate major operational hurdles down the road to eventual development and onto commercialization. In particular we discuss the importance of realistic feed-gas compositions, extreme operating conditions, understanding duty cycles, in test protocols, carbon formation, catalyst attrition, wet process feeds, transient exposure to contaminants in the feed, the need to understand the impact of pressure, and catalyst morphology. These catalyst features are applied to a variety of reactions including FCC, water gas shift, steam methane reforming, auto exhaust cleanup, ozone removal in aircraft, and refinery hydrogen production. A few extended examples are also provided using prior references that describe the conversion of lab discoveries to established commercial processes.

1. Introduction

1.1. Objectives: consider all expected operating conditions in the test protocol

Successfully commercializing catalysts is an important goal of catalyst companies. It requires a multi-disciplined team composed of personnel from R&D, marketing and sales, manufacturing and technical service. One of the most important technical factors for success in the catalyst business is having a complete understanding of the expected performance goals, life and the probable conditions the catalyst may experience during its' life. This is referred to as the "duty cycle."

Catalyst companies must develop testing protocols to consider variable feedstock compositions, flow rates, temperature and pressure variations, start up and shut down procedures, and of course pressure drop, life and costs among the most notable. Naturally this requires close communication with the customer, the data of which is often protected by secrecy agreements. An awareness of the expected operating conditions needs to be factored into the test protocol to qualify the catalyst.

Some processes are operated in a coking regime and therefore catalyst regeneration must be integrated into the process. Fluid bed catalytic cracking of crude oil fractions to gasoline and olefins incorporates a regenerator to remove coke from the zeolite based catalyst. The heat of combustion is integrated into the feed preheat. The catalytic dehydrogenation of propane to propylene, using an oxide of chromium (i.e. chromia) or a precious metal catalyst, generates appreciable amounts of coke which requires regeneration. In the Houdry Process for dehydrogenation of alkanes, multiple catalyst beds cycle through various process gases during which the accumulated coke is burnt off the catalyst in a separate regeneration stage (which provides the heat for the endothermic dehydrogenation), followed by evacuation, and repeating the dehydrogenation step [1]. The test protocol for both these commercial processes, therefore, must include a number of regeneration conditions as an important factor in the design and qualification of a suitable catalyst. Besides carbon formation, preventing catalyst attrition in slurry or fluidized processes is another catalyst design feature. Thus, an important factor in qualifying an acceptable catalyst

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for processes where the catalyst is continuously moving is its mechanical strength. Examples of such important requirements are presented throughout this article.

In this manuscript, while discussing the importance of evaluating catalysts under conditions close to actual processing conditions, we will also point out several gaps/needs in specific catalyst testing technology and methodology which are driven by the varying process conditions. Within the industry, such gaps/needs might not be pursued due to staffing, equipment and limited demands on time, while in the academic community such skills and focused characterization techniques are looking for new problems to solve. In industry fundamental research is needed, but pointed closer to the commercial target conditions. A few examples are also given of processes as they moved from discovery to commercial and the challenges that were addressed, often around the duty cycle. The authors will share some of their experiences that, following discovery, are typically factored into research and development of new commercial catalytic materials. Examples will be given for ozone abatement catalysts, water gas shift, FCC, deNO$_x$, catalytic reforming of hydrocarbons for H_2 generation for low temperature fuel cells and for refinery hydrogen, syngas generation and the challenges in replacing precious metals with base metal oxides in gasoline three-way automobile exhaust catalysts.

1.2. Upset conditions

Duty cycle conditions are predictable while upsets are not and must be addressed after extensive field or in process life testing. Some examples of such transients follow. Lack of adequate temperature control, due to a failed upstream heat exchanger, will generate abnormally high inlet temperatures that will likely cause extensive catalyst/support sintering. Leaking from the failed heat exchanger will introduce oils to the feed causing selective or non-selective poisoning requiring regeneration to return the catalyst to acceptable performance. Deposition of corrosion products or sublimation of catalyst components, from upstream process equipment, will shorten catalyst life by masking reactant access to catalytic sites within the porous network of the support and may also increase pressure drop. Such is the case for many stationary pollution abatement applications. Unexpected deactivation modes are addressed in the duty cycle and are revealed by extensive field testing. Catalyst characterization, coupled with performance data is essential in determining the deactivation mode responsible for loss of life. These occurrences lead to new regeneration inventions and recommendations to the plant manager for changes in the process such as adding upstream filters or sorbents. In summary, a catalyst may work perfectly well at the optimum set conditions but upsets (due to variations in process feed conditions, delivery, weather, etc.) must be considered as possibilities before moving to a development stage or when qualifying it for commercial use. This involves looking at the expected feed conditions, temperature, pressure, etc. Anticipating these possibilities can give one commercial supplier a major operating advantage over another. Experience and a close working relationship with the customers is critical for predetermining the most probable issues to be addressed during both the development stage as well as the during implementation of any process.

2. Ozone (O_3) abatement catalysts in commercial aircraft

2.1. FAA implements O_3 standards

The Federal Aviation Administration (FAA) passed legislation in the late 1970's to decrease ozone (>85% conversion) which enters the cabin of high flying aircraft through the heating and air conditioning system (HVAC) (Federal Registry 1980). After receiving numerous complaints from the crew and passengers of discomfort when flying from the US to Asia or Europe over polar routes, analysis of the cabin air quality revealed that 1–4 ppm of O_3 was present. Ozone is a lung irritant and was present in make-up air when flying at altitudes above 35,000 feet especially when flying over the polar region. This altitude was typically used since air resistance was decreased thereby reducing fuel consumption.

2.2. Laboratory duty cycle tests and initial catalyst and system design

After many different technologies were considered, the most viable was catalytic decomposition of ozone. Catalyst screening was conducted taking into account the expected O_3 concentration in the air in the upper atmosphere, the extent of conversion (catalytic decomposition of O_3 to O_2, reaction 1) required, inlet temperature, variation in flow rates, pressure and pressure drop, vibration resistance, space required in the HVAC, weight and expected life. The good news was the upper atmosphere does not contain any catalyst poisons such as oxides of sulfur, chlorides, or metal oxides. This was a valid assumption but a bit naïve as will be discussed later.

$$2O_3 \rightarrow 3O_2 \qquad (1)$$

After extensive short and long term laboratory testing using feed gases closely simulating the air intake in the upper atmosphere, the most promising catalyst was found to be Pd/ϒ-Al_2O_3 provided the inlet temperature exceeded 120 °C [2]. The in-flight operation and landing the airplane would introduce variable high gaseous flows, pressure drop, vibration and mechanical shock. Therefore, a ceramic monolith (later the ceramic was replaced with a metallic monolith) was selected as the support of choice for the catalyst. This was a good choice given the success of the monolith for automobile exhaust emission control. The Pd/ϒ-Al_2O_3 slurry would be wash-coated and fixed onto the walls of the monolith. This provided low pressure drop, mechanical and vibrational stability and acceptable weight. The only problem was the conversion was lower than required. It was apparent that such a low concentration of O_3 would lead to a reaction controlled by bulk mass transfer. Thus a segmented design of several slices of cylindrical monoliths of varying diameters (each with 1 inch thickness spaced 1 inch apart) in series would be required to prevent the establishment of the boundary layer at the catalyst surface [2]. The enhanced turbulence did introduce a small increase in pressure drop but did meet the conversion requirements and was acceptable for flight tests.

2.3. In flight tests and post catalyst characterization

The first flight tests were conducted with three reactor systems containing the ozone abatement catalyst in the different aircraft locations in the HVAC with the air intake extracted from the stage of compression that delivered at least 150 °C inlet temperature. After 10,000 and 25,000 flight hours the catalysts were returned and cores were cut from various radial and axial segments of the monoliths. Laboratory reactor and characterization tests were conducted. Conversions were measured and found to be deactivated most seriously in the first segment with lesser deactivation for downstream segments. The conversion vs increasing temperature profile was measured and compared to a retained sample of fresh catalyst. The flight aged catalyst showed serious deactivation relative to the fresh sample. The profile showed an increase of about 55 °C in the temperature required for 50% conversion (T_{50}) of the 4 ppm ozone fed indicative of a loss of kinetic activity. More instructive was the large decrease in slope of the aged catalyst relative to the fresh sample (Aged T_{90} = 170 °C vs. fresh T_{90} = 100 °C) indica-