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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) indicative of pore diffusion. Furthermore, the aged sample never reached 100% conversion indicating a loss in bulk mass transfer conversion.

Elemental characterization (microprobe) of samples of catalysts from inlet to outlet segments revealed interesting but un-expected results. There was a significant amount of S, P and Si on the inlet segment which decreased axially towards the outlet segments. Other contaminants such as Na, Cl, and Ca, present on the catalyst also decreased from the inlet to the outlet segments. The level of contaminants increased with flight time. Surface area from BET and N_2 pore size measurements indicated a large loss of porosity and lower surface area with a decrease in small pores. A small decrease in CO chemisorption from 10,000 to 25,000 h of flight time was observed but likely due to masking of the Pd. Metal sintering is not expected at such low operating temperatures (<200 °C). Characterization and regeneration data confirmed masking as a major source of deactivation as discussed below.

The question that needed to be answered was where did these contaminates come from given they are not expected to be in the upper atmosphere where the catalyst is functioning. The data was shared with the airline company who provided some explanations based on their periodic inspection of other aircraft equipment.

The Si content was correlated with silicon containing O–ring fittings in the turbine that erode during operation and are periodically replaced [3]. The Na and Cl can be explained by salt water mist that enters the air intake when the aircraft functions at airports near salt water bodies. The P and Ca and traces of Zn result from traces of oil vapor used to lubricate equipment in the air conduits within the turbine. The sulfur collected on the catalyst is due to the emission from other aircrafts as you wait to take off. The use of deicing solutions at the airport before takeoff also can contribute to contaminating the air intake system.

Air sampling during flights within the cabin can meet the regulations using a six segment design. Each airline company replaced the catalyst during routine maintenance based on flight routes and flight hours. Typically, this is after approximately 25,000 flight hours.

2.4. Regeneration of deactivated catalysts

The contamination observed in ozone abatement catalysts was similar to that commonly experienced in stationary source applications where regeneration methods are already in place. Deactivated ozone abatement catalysts can be regenerated using wash solutions composed of either weak acids, bases or chelating solutions. A major conclusion from this work is that the P deposits as an aerosol on the surface of the washcoat, determined by electron microprobe analysis, masking the surface and blocking pores and active sites. The proper regeneration method effectively removes this from the surface restoring activity. This procedure provides an economic cycle where deactivated catalysts are essentially completely regenerated and re-used and is now common in the airline industry [3]. Long waits on the runaway behind other aircraft lead to engine exhaust odors entering the aircraft. This has been addressed by adding small amounts of Pt to the catalyst which oxidizes the odor bearing hydrocarbons eliminating the smell in the cabin.

3. Testing catalysts under real feedstock compositions

3.1. Combined heat and power fuel cells in Japan: start/stop operation

The low temperature water gas shift catalyst (WGS) (reaction 2) has received renewed attention since the introduction of natural gas reforming for low temperature residential fuel cell applications. Given the existing infrastructure of natural gas and the need for H_2, the Japanese, in cooperation with their government (Ene-Farm program) installed in more than 50,000 homes in Japan alone (at the end of 2013) with PEM fuel cells with H_2 generated in the home itself from reformed natural gas. The number of installed units is growing daily. (http://worthingtonsawtelle.com/fuel-cells-japanese-home/). Because the natural gas is converted to H_2 in the home, the reformer unit must be small and function according to the Japanese duty cycle as determined by their daily use of energy. The criteria for this market is daily start and stop which reflects their use of hot water and electricity. The reformer and fuel cell is shut down daily (DSS) during the sleeping hours from about 11 PM until about 6 AM. This adds a different requirement for the entire reformer, unlike that used in large chemical and petroleum operations that more or less operate at steady state 24/7 [4].

3.2. Water gas shift catalysts evaluated in the DSS mode

The reformer generates H_2/CO and CO_2 and requires a WGS catalyst to further enhance the H_2 content, required for the operating temperature (~75 °C) while decreasing the CO. A PROX catalyst (preferential oxidation catalyst) is used to further decrease the CO to less 10 ppm to avoid poisoning the Pt anode [4].

$$CO + H_2O \overset{Cu/Cu^{+1}}{\leftrightarrow} H_2 + CO_2 \tag{2}$$

During the shut-down mode of the DSS duty cycle water in the reformate will condense exposing the catalyst to liquid water which puts stress on the reactor internals, especially the catalysts. The catalyst most sensitive to exposure to condensed water at low temperature is the traditional CuZnAl particulate water gas shift catalyst. Water slowly oxidizes the active Cu surface (which is believed to be a mixture of Cu/Cu^{+1} to a catalytically inactive +2 state). Additionally, the vaporization/condensation of water, within the pore structure, can lead to mechanical failure. Thus we explored the use of a washcoated monolith catalysts containing Pt as water resistant catalyst. Evaluating this new formulation required a testing protocol consistent with the duty cycle of the DSS operation.

3.2.1. Pt containing WGS catalyst in accordance to start and stop (DSS) operation

Our early studies found that Pt/CeO_x was an active and stable when used as a low temperature WGS. Our feed gas composition (Vol%) consisted of 3% CO, 15% CO_2, 48% H2, balance steam reflecting the reformate product generated from desulfurized natural gas and the high temperature WGS catalyst. The catalyst was first evaluated as a powder (for ease of characterization by FTIR, DRIFT and HRTEM) and then washcoated on a monolith.

The powder and monolith catalyst showed stable performance under steady state conditions at 250 °C and above [5], When the DSS cycle was introduced, we allowed the gas temperature to decrease to 60 °C where steam would condense to liquid water. Upon return to 250 °C, some deactivation was noted. After multiple start and start cycles, the performance fell to an unacceptable value. Purging the system with N_2 only up to 450 °C followed by retesting showed no regeneration of activity thus eliminating water trapped in the pores as the cause of deactivation. These same studies were performed with the powdered catalyst with the same deactivation noted. Samples were then subjected to characterization tests to establish the deactivation mode(s). The most fruitful results were obtained from FTIR and DRIFT studies which showed that carbonate had formed primarily on the CeO_x during shut down. The catalyst could be completely regenerated with air at 450 °C leading us to speculate the Ce^{+3} (generated from the reducing environment) was responsible for the formation of carbonate when contacted with low temperature CO_2. Based on the test protocol that included the duty cycle of DSS, we concluded that alternative catalyst formulations would be required.

3.3. Addition of steam to feeds

Steam methane reforming, SMR, reaction 3, is a commercial technology that has been operating in large plants, world-wide for many decades. The syngas produced is often used to synthesize methanol,

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (3)$$

ammonia, Fischer-Tropsch products, or refinery hydrogen used for hydro-treating. SMR is certainly a mature technology [6] with seemingly numerous process hurdles (such as an endothermic operation, extremely high temperatures, high pressures, low and high pressure steam recovery, corrosion of the steel by CO, high nickel loaded catalyst, etc.). One can see a number of avenues for significant process improvement. Over decades of research and development, many of these shortcomings have been engineered to minimize energy demand, maximize yield, and reduce costs as one moved to commercialization. Substantial stepwise improvements have been realized, but other gaps remain that have not been solved, but because this remains a cost effective way to make H_2 for a large number of operating refineries, NH_3, or syngas (for methanol synthesis), it continues to be the syngas process approach of choice (although ATR, auto-thermal reforming, and CPO, catalytic partial oxidation, are alternative approaches).

Not all these hurdles will be discussed here, but rather some of the important process issues that they create. Additionally, there is the need for solutions to problems that often do not appear until one tests the catalysts under simulated process conditions [7]. These include high temperatures (>800 °C), CO driven corrosion of process unit components, costly high nickel loaded catalysts, a need to add steam to the feed [8], the need for high pressure, and the lack of a characterization technique to monitor the activity of a catalyst or accurately estimate its end-of-life. Aspects about the limited performance have been published in multiple, insightful articles by Rostrup-Nielsen and others in the past [6,9].

3.3.1. Addition of steam during methane reforming

During SMR, excess steam is added to the hydrocarbon feed to provide very high steam/methane levels in order to reduce carbon deposition on the catalyst and in the pores and metal dusting of the reactor walls [10]. This impacts performance and makes today's hydrogen plants mini steam plants where high temperature steam must be recycled to reduce operating costs. The generation of steam from liquid water has a high heat of vaporization which adds a large energy penalty, thus a lower steam level is also desired. All this added steam (typically 2 to 3/1 steam/CH_4) dilutes the H_2 and CO products, and its energy value must be recovered and recycled such that refinery hydrogen plants become steam plants, but the addition of steam extends catalyst life from weeks to years. Steam addition does contribute hydrogen atoms towards some of the H_2 formed, but more importantly it provides the critical extension of catalyst life—often the difference between commercial success or failure. Elegant efforts to eliminate steam co-feeds (dry reforming (see Section 3.4 below), addition of low levels of O_2, catalyzed hardware [11], etc.) have not proven commercially acceptable to achieve large volume (low CO) H_2 production for most of the industry with respect to ultra-low carbon formation over years of operation [12]. Whisker carbon formation can be seen using high vacuum electron microscopes, but it is difficult to extend these studies to real operating conditions to maintain, in situ, the desired H_2/CO levels for syngas generation. Lots of elegant work from those at Haldor Topsoe A/S and others have shown carbon growth under laboratory conditions often far away from operating conditions. What is needed is some means to monitor carbon formation and/or catalyst life on these catalysts under processing conditions and over extended periods of operation.

For land fill gas, typically CH_4 is about 55 Vol% and 45 Vol% CO_2. Thus coking is expected and will therefore require a method for regeneration. Dry (no added steam) reforming of methane is sometimes touted to be an attractive laboratory approach to producing H_2, but most commercial demand for H_2 requires catalysts which operate for years without decay. Most dry reforming reports in the literature only show performance data for months at best; this does not mean that carbon formation is not occurring- just delayed or reduced. One must make such dry reforming catalysts perform for years without substantial carbon formation and resultant decay which always seems to require some steam for a H_2 rich product. How can this be accelerated in the lab and accurately applied to field operations?

It is important to appreciate that touting a solution to an age-old problem requires addressing the problem under conditions which simulate critical operating conditions. Exhaust streams from combustion reactions contain substantial levels of water vapor, and this water vapor can reduce catalyst activity and/or drive new reaction pathways (not only for SMR cited above). Treating power plant exhaust streams is a major, global problem, but all these streams are wet and hot. Proposing catalysts that only operate in dry feeds and/or cooler temperatures is not going to solve most emissions problems. It is important to offer catalyst solutions under realistic testing protocols- in this case with added steam and other typical components of exhaust streams without loss in activity, yield or selectivity. There is no simple solution, and the need for steam should be considered as a major hurdle beyond discovery and on to commercial success.

3.3.2. Wet NO_x steams

Another case of using wet test streams applies to the removal of NO_x. Whether one is using saturated hydrocarbons or simple decomposition to removal the NO_x, it is important to test for catalyst performance in the presence of the typical levels of water vapor in the process stream [13]. Any viable catalyst must be tested in the presence of all the components of the exhaust feed which includes steam and CO_2. Adding additional treatment steps to remove water, CO_2, and/or O_2 or to cool or heat the process feeds to higher or lower temperatures can often push a process into commercially unacceptable territory. For example, combustion exhaust streams are rich in water vapor (10–16%). Removing water from a process stream operating at very high SV (>30,000 GHSV) adds considerable cost and imposes new demands on equipment space and treatment parameters, at the typically low levels of NOx (50 ppm to <2%) in most process streams. It is difficult to find a catalyst whose active sites for NOx removal are not also blocked by much higher levels of water vapor. For these same reasons, it is unwise to assume these much higher levels of NOx employed during catalyst testing (such as 500 ppm to percentage levels of NO) are going to be acceptable test conditions to remove real-world levels of NO_x (sub 50 ppm levels of NO).

3.4. Need to run under pressure

Unfortunately, many papers describe catalyst testing under atmospheric pressure because of facility limitations, cost, or genuine concerns about safe operations. However, there are times when one must test a catalyst at elevated pressures, especially when pressure can impact rates or secondary reactions. Dry reforming of methane (DRM), reaction 4, is a widely studied reaction [14], but usually studied at atmospheric pressure. DRM is a popular approach for making syngas or H_2, but one must remember that most of the world's syngas or H_2 needs require a

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{4}$$

pressurized product to mate with the downstream conversion/use of the syngas or H_2 [8]. [It costs too much in energy and capital to pressurize the desired syngas or H_2 prior to synthesis of methanol, ammonia, or for Fischer-Tropsch.]

A recent publication by Oyama, et al. [15] reports the dramatic difference in reaction pathways by running under modest pressure versus atmospheric pressure. They report that the DRM concept suffers an Achilles' heel: when run at elevated pressure, the H_2 produced during SMR (from reaction 3), reacts with the CO_2 in the feed to drive the reverse water gas shift (reaction (5)), thus producing more water and consuming the valuable H_2 product.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{5}$$

This does not occur in SMR (reaction 3) because the water gas shift reaction (the reverse of reaction 5), actually produces more H_2. When the DRM reaction is run at atmospheric pressure, the amount of water produced is small, but as soon as the pressure during DRM is raised to >5 atm, reaction 5 begins to dominate over reaction 3 such that one makes less H_2 (due to the higher reactivity of H_2 with CO_2 (reaction 5) than of CO_2 with methane (reaction 4)).

4. Scale up of the physical form of the catalyst to a process structure- powder to particulate

So often one optimizes a catalyst at the lab scale but then runs into problems in fabricating the commercial form of the catalyst. During any scale-up, catalysts must be modified for maximum effectiveness in a process stream at high space velocities. This may entail fabricating a membrane or making extrudates. Any membrane needs to be defect free; one can't have gas escaping through large voids in the membrane, otherwise the membrane ceases to separate anything. Alternatively, dense membranes must be made repairable- that is one must be able to repair defects/voids in a membrane in the module to avoid loss of permselectivity [16].

On the other hand, compacting catalyst powders into extrudates, monoliths, etc. requires the addition of binders and other additives. Years ago we (at Air Products & Chemicals) developed a novel zeolite catalyst which was excellent for the synthesis of a high value organic amine, but we had a great deal of difficulty in finding a binder which would produce durable extrudates wherein the binder itself did not lead to an undesirable secondary product. Binders often comprise surface active groups needed to compact the catalyst particles but those same surface active groups can catalyze other reactions. We learned that scaling up from a powdered zeolite to a pelleted zeolite having good attrition resistance was not an easy matter which others have recently pointed out in the literature [17]. How one focuses on optimizing the binder composition is not widely published nor understood and often is an art. We really need to better understand what the use of a particular binder (alumina, clay, silica, carbon, etc.) will do to catalyst performance. Binders can impart additional properties to a catalyst, sometimes undesirable, in return for the desired performance of the host material. Another article by Akhtar, et al. [18] discusses a host of properties and effects from the addition of a binder to a catalyst or an adsorbent.

5. Gasoline automotive catalysts—replacing platinum group metals (PGM) with base metal oxides catalysts

5.1. Current TWC converter operation

One of the most sought after challenges in the catalysis community is the replacement of expensive precious metals, used in the modern three- way gasoline emission control catalytic converter, with abundant and less expensive base metal oxides. In order to address this formidable challenge, it is necessary to understand the catalyst duty cycle to meet the emission standards as required from different countries. In the US the catalyst must simultaneously reduce more than 95% of the CO, HC (hydrocarbon) and NO_x emitted for 150,000 miles. Enhanced sensors and electronic controls, the use of rare earth metal oxides and cleaner fuels (free of Pb and reduced levels of S) have all contributed to this specification. The TWC functions in vehicles operated by consumers, unlike chemical and petroleum processes that operate under the supervision of trained engineers, scientists and skilled technicians.

The modern three- way catalyst is composed of Pd, Rh dispersed on a stabilized gamma Al_2O_3 to which is added CeO_x in solid solution with ZrO_2 and other rare earths [2]. This is deposited as a washcoat onto the walls of ceramic and metal monoliths of varying cell densities. Palladium is the component that catalyzes the oxidation of CO and HC to CO_2 and H_2O. Rh enables the conversion of NO_x to N_2 with H_2, generated under slightly rich conditions by Rh catalyzed steam and dry reforming reactions and to some extent water gas shift. The successful operation of the TWC system is enabled by solid state oxygen sensors in the exhaust coupled to a feedback control system maintaining the engine operating in a narrow air to fuel ratio oscillating around the stoichiometric point. The oxygen storage component (OSC) in the catalyst provides a redox buffering action to maintain the air to fuel ratio close to stoichiometric. High intrinsically activity precious metals can be supported on Al_2O_3 which in turn is deposited on high geometric surface area to volume monolith structure. Monoliths are exclusively used as supports because of their high geometric surface area to volume ratio (enhancing bulk mass transfer), thin washcoats decreasing pore diffusion resistance, large open frontal areas (~80–90%) for low pressure drop at high volumetric flows, excellent mechanical strength, resistance to thermal shock (rapid transients in temperature) and rapid response to changes in exhaust temperatures as the vehicle operates at varying speeds. The catalyzed monolith is housed in metal highly engineered housing in the exhaust 7–10 feet from the engine. An upstream close-couple catalyst is often placed about a foot from the engine to allow rapid heating of the catalyst (kinetic control) during the "cold start" portion of the Federal Test Procedure (FTP). This mandated test is composed of several modes of operation, including cold and hot start and stabilized driving where the catalyst must function in the kinetic regime during cold portions of the test followed by mass transfer when the exhaust and catalyst is hot [2].

5.2. The "duty cycle" for gasoline emission control catalysts

The exhaust delivered to the TWC, at the stoichiometric air to fuel ratio, is approximately <1% CO, 500 ppm HC (assumed to be C_3, $C_3^=$) and 600–800 ppm NO_x, with 10% H_2O, 14% CO_2, <1% O_2 and H_2, plus N_2 and traces of SO_x and lubricating oil detergent compounds of P, Zn, and Ca. The flow rate varies with the driving mode creating Gas Hourly Space Velocities (GHSV based on the physical dimensions of the monolith) from close to zero at idle up to 75,000 h^{-1} for high speed highway driving. This variation in flow rate often occurs within seconds.

Additional duty cycle requirements have been introduced for enhancing fuel economy. This is a mode called fuel cut. When a vehicle is coasting and no acceleration is required the fuel is shut off and air only purges thought the engine and into the catalyst. Often, prior to fuel cut, the vehicle is consuming a large quantity of fuel as the vehicle moves up a hill increasing the temperature within the monolith. When fuel cut occurs the hot air flows through the hot catalyst oxidizing the OSC from Ce_2O_3 to CeO_2 and oxidizing any fuel components adsorbed on the catalyst surface further raising the catalyst surface temperature. Fuel cut conditions exist where the temperature can be as high as 1050 °C causing extensive sintering of the materials. The Rh component is oxidized and reacts with the Al_2O_3 carrier forming an inactive $Rh(AlO_x)$ species. Upon return to normal driving, the $Rh(AlO_x)$ is reduced to Rh by H_2 generated by steam and dry reforming reactions with the air to fuel ratio slightly rich of stoichiometric. This regenerates the Rh to the metallic state where it is catalytically active for NO_x reduction [2].

5.3. Duty cycles in test protocols

First and fore-most the catalyst must have sufficient intrinsic activity to be deposited onto the walls of a monolith and have the low temperature (kinetic regime) activity required. The washcoat loading and the size of the monolith must be consistent with the available space in the exhaust system. Typically for platinum group metal (PGM) catalysts the volume of the monolith is approximately equal to the engine displacement. For less expensive base metal catalysts this is very challenging since metals and their oxides (i.e. Cu, Mn, Co, Ni, Cr, Fe, etc.) have much lower intrinsic activities than PGMs requiring large loadings and large monolith volumes. It is this attribute that allows small amounts of PGMs to be deposited on high surface area carriers and washcoated onto the walls of a monolith that allow them to be effective at acceptable monolith volumes. Packed beds would not be used due to the catalyst attrition (observed in the late 1970 and early 1980s) that eliminated them as carriers for the PGM for the converters.

For laboratory tests powdered catalysts can be used for primarily initial screening using model pollutant compounds. This allows the identification of potential candidates for advanced monolith testing. These materials should be aged at elevated temperatures (>800 °C) in the presence of steam to determine their resistance to sintering via conversion-temperature profiles. Characterization of their structure (XRD) and BET surface area after aging is to be correlated with aged activity to establish the mode of deactivation. Candidates that meet reasonable performance and structural stability are then to be washcoated onto monoliths for more advanced laboratory testing. The conversion test protocol should be conducted close to stoichiometric air to fuel ratios with the feed gas containing the proper amount of CO, HC and NO_x as well as about 10% H_2O (steam), 15% CO_2 and eventually ppm levels of SO_x. This allows establishment of activity profiles in both the kinetic and mass transfer regimes on both sides of the stoichiometric point at varying space velocities and temperatures. Characterization by physical and chemical methods are included as part of the test protocol. Adsorbed SO_x is observed by XPS. Aging tests must be evaluated for conversion of pollutants over extensive periods of time with start-up and shut down conditions.

Any new candidate materials must survive the extreme duty cycle of the internal combustion engine. This means retention of high activity at low temperatures (light off), comparable to Pd and Rh, after experiencing temperatures associated with high speed driving (~900 °C) and operating modes such as fuel cut. The catalyst must also resist permanent deactivation due to traces of sulfur compounds and/or lubricating oils.

Once viable monolith candidates have been identified during this discovery and optimization, they are ready for evaluation in real engine exhausts. These are conducted in an engine lab with engine dynameters. This is an expensive but necessary step in order to move to fleet tests and ultimately commercial production.

6. Other successful examples

6.1. Unanticipated hurdles after the invention—other published examples

There are also hurdles in other processes that emerge long after the investigators have made and demonstrated the initial discovery. Moving from the discovery phase to the development stage, and eventually to scale-up, pilot operations, and commercialization often generates unexpected hurdles that can derail the best inventions. We will give a few examples in the following paragraphs; unfortunately, there is no magic formula or process which allows one to successfully anticipate where these challenges can come from or how to address/avoid them, rather only by moving the discovery along into testing that more closely resembles the actual operating conditions can one prepare for a successful commercial run and the very large financial expenditure that goes into such a commitment. Understanding the eventual market/customer [19] and building critical processing hurdles into early catalyst testing improves eventual success in the marketplace.

A few articles already in the literature describe some of the details, the need for simulated process variables at the lab scale, and hurdles that one addresses in moving technology from discovery to demo units to production. A recent article by Peng Tian, et al. describes the fundamental and applications research efforts by the Dalian Institute of Chemical Physics [20] towards the commercialization of SAPO-34 for conversion of methanol to olefins. They spent a great deal of effort understanding and limiting catalyst deactivation at the bench level and fundamental research at low temperatures allowed them develop an optimized regeneration procedure. Ultimately, enhanced understanding of the entire process under simulated process conditions allowed them to run the commercial unit with better selectivity than those observed in the pilot and demo-scaled units.

David Brown, et al. [21] describe British Petroleum's efforts to commercialize a novel, non-iron catalyst (ruthenium/alkali metal/carbon) for NH_3 synthesis detailing the fundamental science and how that was used to optimize the catalyst and a process for NH_3 synthesis. They point out that a key part of the catalyst development was changing the H_2/N_2 feed ratio and the pressure at which NH_3 synthesis reactor would operate. This required clever engineering and significant overall process design to implement (at a 15 gm test scale) prior to eventual commercial application to multiple world-scale plants.

A fascinating article by Tom Degnan, et al. [22] follows the development by the Mobil Technology Company for the applications of ZSM-5 for FCC cracking from its discovery through to commercialization with focus on lessons learned along the way. Much of the early Mobil work focused on zeolite Y for cracking of petroleum, but by varying the boiling point of the FCC gasoline cut, they found that the portion boiling over 82 °C (355 °K) could be upgraded over ZSM-5 with increased octane number. Further by understanding steaming of ZSM-5 they were able to improve gasoline octane number; ZSM-5 had to be steamed more severely than zeolite Y under laboratory simulations to provide commercial performance estimates. Later they found that ZSM-5 had a much higher tolerance for vanadium levels than ultra-stable zeolite Y. Longer term testing at the lab bench established that ZSM-5 was less impacted than Y zeolite under coke forming conditions. Later they discovered that phosphorous additives to ZSM-5 improved the effectiveness of ZSM-5.

Implicit in any effort to move from discovery to the marketplace is an understanding of both the value of the discovery and how does one move the technology to the marketplace. Remarks are offered in a previous publication [19] in an effort to describe how one gathers resources for making such a transition. Jim Roth in his 1994 article describes the [23] need for partnerships between universities, industry, and government in order to identify the limits of existing technology and establishing the areas and approaches for improvements.

7. Other needs in current steam reforming operations

7.1. Ultra high temperature reactors

During steam reforming of methane, here are a number of competing reactions that occur along the long, adiabatic reactor tubes which require unusually demanding operating temperatures. In other processes, a limited amount of O_2 is added to combust a small amount of the reactant to generate sufficient heat to drive the endothermic reaction. In SMR, operating at such high temperatures which vary as the reactants proceed down the reactor tube and the necessary high pressures of ~30–50 atm. demands the use of expensive, high nickel alloy reactor tubes. These are susceptible to catastrophic failure under such extreme operating conditions. The presence of high levels of CO in syngas can provide conditions that lead to carbon formation which can fowl the catalyst and powder the extrudates High CO levels can lead to carburization and weakening of the alloy reactors [24]. Excessive carbon laydown can lead to catastrophic reactor tube failures. Alternative process designs (membrane reactors, auto-thermal reforming, catalyst modification, addition of inhibitors, CO_2 reforming, steam reforming of alcohols or extended alkanes) have not offered acceptable performance for most market demands. Instead, operators try to build in design features which ensure safe operation and continued performance (over years of operations in the plants). Catalyst adjustments (Ni alloys, alternative supports, lower levels of Ni, promoters, carbon burn-off, addition of precious metals [9,25], use of more exotic metals (gold)) have not widely displaced the traditional, very high nickel (>40%) supported catalyst nor lowered the operating temperatures. Nonetheless, being able to examine, at the lab scale, alternative approaches to driving SMR to higher syngas yields and with longer life (duty-cycle) is an important need. Some specifics follow.

7.1.1. Evaluating adiabatic processes in lab operations

Moving from the typical plugged flow tube lab reactors eventually involves having to test the catalyst in an adiabatic reactor. It is not easy to simulate a 50 ft. natural gas fired adiabatic tube reactor in the laboratory. Some have tried to devise 10–20 ft. high staged temperature zone reactors, but reducing this to a lab scale level that gives meaningful performance data is not easy to achieve. The commercial reactor tubes can be 50 ft. long and 5 inches inside diameter and often heated to 800 + °C using natural gas-fired burners mounted outside of the tubes in the furnace box. Building a large test furnace with different heat zones is a costly operation and developing a reactor that mimics this operational reactor is a real challenge short of making a giant leap in scale up. These issues need added inventions to demonstrate a commercial process that usually cannot be defined/understood with a fixed bed, plugged flow reactor. In addition, across the ~5 in (inside diam.) bed of pellets in a commercial reactor, with the gas fired burners driving heat through the thick nickel alloy tube walls to promote this endothermic reaction there is a non-uniform temperature [9] across the catalyst bed. Such a temperature profile is hard to monitor, duplicate or simulate in a lab or in a developmental scale reactor. The complexity and scale of the alternative designs above means that one often has to jump to adiabatic reactors run at a much larger scale than is possible in most laboratories before all the operating conditions are understood. Again, it would be desirable to be able to follow reaction intermediates and products along the working catalyst bed at some reasonable lab scale in an effort to control product yield and selectivity. These are ideas/areas for future study

7.2. Difficulty in monitoring Ni catalyst activity

The extreme operating conditions for SMR also make monitoring catalyst life and qualifying a catalyst very difficult. In situ studies would be great, but carrying out in situ characterization at such extreme temperatures, pressures, and reactor conditions is very challenging. What is needed is a means to equate catalyst performance during reaction with some physical catalyst property that one can monitor and equate to performance. Ideally, one would like a parameter such as copper metal surface area used for methanol synthesis catalysts, metal surface area used for hydrogenation catalysts, or polymer productivity/gm-catalyst used in olefin polymerization catalysts, but this has not proven possible with nickel SMR catalysts. Thus, we find it hard to accurately certify or even express catalyst activity of SMR catalysts. Reduced nickel on the catalyst surface is crucial to good performance, but it is hard to monitor reduced Ni levels on catalyst extrudates down the long process tubes in the high steam, CO, H_2 levels. For decades, groups have monitored nickel surface area, but measurements of Ni surface area must be made outside the reactor, sampled under inert atmospheres, and thus outside reactor conditions. Monitoring Ni levels in a working catalyst at such high reaction pressures is very difficult and characterizing the catalyst at low pressures is probably deceptive. Even some of the best Ni SMR catalysts yield relatively low numbers (~8 m^2/gm) for Ni surface area which drop quickly in operation to very low numbers (~1 m^2/gm) after only a few hours under reaction conditions, yet these catalysts will run for >5 years. So it is still unclear just what the working Ni surface of the active catalyst looks like and how to quantify this. If we could characterize the origin of activity of working Ni reforming catalysts, we might be able to devise ways to improve Ni catalyst life and/or reduce the very high loadings of Ni currently required.

8. Conclusion

This article is intended to give researchers insight into the importance of simulated test protocols associated with duty cycles ultimately required for development of commercial catalysts and systems. Stable performance of catalysts subjected to the duty cycle will add significant value and confidence to their possible commercial fate. Laboratory results allow effective decisions to be made regarding viability for success or rapid failure. The duty cycle must ultimately include the simulated feed gas composition delivered to catalysts in the laboratory. Success will then justify the extensive life in the expected commercial environment. Upsets are difficult to simulate and are only observed in field tests, however they can also be part of more advanced duty cycles gleaned from actual field tests. It is important for investigators to seek out all the critical components of the targeted process stream and to evaluate the impact of the obvious components that will impede performance. Investigators are urged to find those in the industry experienced in the commercial operation of a catalyst for a particular process, review the applied literature, or learn from retired industrial consultants.

The first example (Section 2 above) describes the test protocols for the successful development of ozone abatement monolith supported catalysts in high altitude aircraft. The combination of laboratory tests adhering to the expected duty cycle, subsequent flight testing with post characterization led to successful commercialization in 1980. The installation of catalytic ozone abatement converters in wide body aircraft continues today to improve the quality and health of air travelers world-wide.

Another example is given for a water gas shift catalyst under consideration for H_2 generation in a hydrocarbon reformer integrated to low temperature PEM fuel cell. By adhering to the daily stop and stop (DSS) duty cycle used in the Japanese residential, combined heat and power fuel cell market,we were able to eliminate CeO_x as a carrier for Pt. Catalytic performance testing, including the DSS mode, was performed with a simulated gas composition containing 12% CO_2 led to the deactivation of the catalyst by irreversible carbonate formation on the CeO_x during the shutdown mode. Therefore, we rapidly determined that new formulations were needed.

Another example is that of replacing precious metal with less expensive base metal oxides (BMO) from the gasoline automobile three-way catalytic converter. The challenge becomes obvious when one considers the extreme conditions experienced in everyday driving and its impact on the catalyst. The duty cycle requires high activity in the kinetic regime (low temperature) performance during cold start up, and high mass transfer conversion during high speed driving over varying space velocities and temperatures. The advanced laboratory testing protocol must include the expected feed gas composition, containing catalyst poisons such as sulfur compounds, before and after extreme high temperatures (>900 °C) in both stoichiometric gas mixtures and ultra-lean modes experienced during fuel cut. The volume of monolith required for a less expensive BMO washcoated to be effective to replace precious metals used in TWC for gasoline passenger car exhaust is very challenging given their relative low intrinsic activity verses precious metals.

Other examples of unanticipated hurdles have also been described above around the traditional steam methane reforming (impact of higher temperatures, steam levels, reactor regime, and quantifying Ni catalyst activity), the importance of running at pressure in DRM, the importance of understanding the impact of binders and other additives upon scale-up of catalysts, and the impact of wet process streams on catalyst performance.

A complete understanding of the duty cycle is essential in developing testing protocols for developing a new catalyst. Understanding the failure modes in real life by performance coupled with characterization provides direction for further improvements in materials while providing added focus during the testing phase of any new catalyst system. This all makes eventual practice of any catalyst innovation much more acceptable. We are not saying that fundamental studies should incorporate commercial processing conditions, but rather if experimentalists want to relate their work to an existing process, they should use conditions that ultimately reflect major performance hurdles for the intended application. As one of us pointed out over 20 years ago, “the discovery of model catalysts does add fundamental knowledge, but only (is of real commercial value) if that knowledge is pointed to the correct target.” [13].

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