KNOW BEFORE YOU LOAD

Wendy Yu, Christy Catalytics, USA, emphasises the importance of checking quality control, logistics, packaging and job site storage before loading a process vessel.

Once the proper type and size of inert catalyst support and hold down media have been selected for an ammonia plant application, selecting the right catalyst support manufacturer for the product, alongside ensuring smooth and on-time delivery to the plant site, are the next important steps.

Four key factors can impact a turnaround: quality of the inert media, logistics, material packaging, and job site storage. While the importance of quality control and logistics is well recognised, material packaging and job site storage are often overlooked, which could lead to issues that delay turnaround.

Quality control

When it comes to inert media manufacturing, there are several physical characteristics that should be evaluated. While these characteristics are much dependent on one another, the intricacies of their relationships may not be easily recognised by the untrained eye. One of the most crucial tasks for engineers is to understand the correlations between these characteristics and how each step of the process can affect them. Therefore, from crafting the right formulation of the support media to firing the materials at the proper temperature, every step of the process must be handled with great care.

For example, Christy Catalytic's T-38 and T-86 PROX-SVERS® support media are manufactured using a ceramic bonding system. Pure ceramic materials are blended into a plastic body, formed into spheres, and kiln-fired to activate the ceramic bonding system. Both media have low permeability, porosity, and water absorption with abrasion resistance due to their hardness. The T-38 media also utilises crack inhibitors to provide enhanced resistance to pressure and thermal shock.

Furthermore, high alumina support media, such as T-99 and T-99.5 PROX-SVERS are ultra-pure, with >99% alumina for applications where silica leaching (high temperature and water partial pressure) is a concern, such as in secondary reformers or high-temperature shift converters. The ultra-low metal oxide impurity levels and low catalytic activity make these media beneficial for reactive monomer purifiers in polyolefin plants. T-46 is another high alumina support media that is chemically bonded and is suitable for rapid depressurisation and thermal shock applications.

Figure 1. Examples of lamination.

Figure 2. High alumina secondary reformers support dome.

Porosity

Porosity is a significant parameter to monitor for quality control. Having low porosity support balls greatly increases inertness, which means they are less likely to interact with other chemicals. However, in a situation where the porosity is too high, impurities can creep in during operation, eventually poisoning the catalyst and leading to failure. High porosity also allows for moisture absorption, which can be a poison to some catalysts and applications and is also detrimental to physical properties such as strength and density.

During installation, the support balls can potentially be exposed to moisture if the package is left open. If the porosity is too high, the water molecules can enter the interior of the support media. If the vessel is rapidly heated, the moisture can rapidly convert to steam and be trapped inside the media causing it to fail catastrophically due to the large volumetric expansion of water to steam.

High porosity could also lower the cold crush strength and reduce impact resistance. This means that the media are more likely to be broken into pieces, which eventually will lead to degradation and bed blockage. Therefore, it is important to select the right inert support for each application.

Laminations in both ceramic and alumina materials

Lamination can occur in both ceramic and alumina supports. This is a significant problem as it can lead to low impact resistance and can reduce the thermal shock resistance and lower crush strength. During start-up or unplanned interruptions, alumina balls or ceramic balls can undergo thermal shock or depressurisation. Inferior balls can delaminate and/or break, resulting in higher pressure drop across the bed and/or bed blockage, which ultimately results in a premature shutdown (Figure 1).

Recycled balls

Some fertilizer plants reuse used or 'spent' catalyst bed support media. Some purchase used support media from ex-situ catalyst recovery companies or metals reclaimers. These suppliers are often not versed in the technology of the ceramic materials they are offering and might not appreciate the demands of the proposed use. Although reuse economics may be attractive, users of spent catalyst support media should understand the pitfalls, particularly if used media are to be acquired from an outside source.

Catalyst support media can exhibit scavenging capacity for contaminants. Some are installed specifically for trash collection, some may chemisorb sulfur or chlorine, and some may adsorb heavy metals. Support media rejuvenation is often limited to water-washing and screening for size, which is generally ineffective in removing true catalyst poisons. The surface trash collection or absorbed contaminants from the previous service can be reversed or kicked off when support media are reused in a different application.

Catalyst poisoning, equipment fouling, and costly downtime can be the result. Physical properties of used catalyst support media, such as the crush strength and impact resistance, which are key to catalyst bed support performance, can be severely degraded from the initial service. Reuse can result in excessive breakage, chips and fines, especially if care was not taken in the media's removal and storage. In turn, this can lead to pressure drop and flow distribution problems within the reactor and plugging problems downstream. Catalyst support media flushed from a unit or chemically washed following prior service may be contaminated with acid, caustic, or other potential catalyst poisons, such as detergents or surfactants. Unless thoroughly rinsed and dried, many of these poisons are leachable during subsequent reuse, resulting in a loss of catalyst activity.

The potential problems associated with reusing used catalyst support media tend to be exacerbated by how these products are accumulated. Used support media are frequently accumulated based only on size rather than composition, and accumulations can be mixtures of different media chemistries. Records on the prior use of re-analysis tend to be limited at best or completely absent. 'Lot analysis' from such accumulations may not represent or may totally mask the potential problems that previously used catalyst support media may cause.

The economic advantages of used media may represent a false economy. The cost of a new charge of 'truly inert' catalyst support media is very low relative to the cost of the catalyst which it is purchased to protect.

Recycled materials in support media manufacturing

All inert support media should be made with virgin materials intended for use in inert support media. Crushed or spent refractory, kiln furniture, off-specification or used support media should not be used as raw material. Similar to using recycled balls, while the cost savings may seem attractive at first, the potential issues it may cause can be expensive. When the raw material is obtained from an appropriate source, a chemistry report of a sample can generally predict its overall chemistry since the compositions are generally quite uniform. In general, raw materials for support media – both alumina and ceramic – are critical to their performance and compromises should not be made in this area.

Logistics

It is important to know the costs of downtime and to plan accordingly. However, it is possible that an unplanned situation may arise and the item needed has a long lead time. For example, some refractory products, such as hexagonal target tiles and support domes, may have a very long lead time. Hexagonal target tiles for a standard size vessel usually take 2 – 3 months to make, while the dome's lead time could be up to 6 months.

If the materials are needed right away and cannot be sourced locally, it may be useful to consider having the materials shipped via air freight, especially in an unplanned situation. Unplanned maintenance events are an unfortunate reality for plant operators, and the ability to react to emergency events effectively and quickly will save time and money.

Case study 1: secondary reformer dome swap

When a plant's secondary reformer dome collapsed and needed to be replaced right away (Figure 2), the operator contracted Christy Catalytics to remedy the situation. However, it transpired that a replacement dome would take several months to manufacture since the company's emergency stock dome had been recently sold to another customer.

The problem was overcome by rapid sharing of technical and quality control information, three-way conference calls with both customers, the waiving of disclosure information, and by setting up banking arrangements.

After several conference calls, a win-win solution was reached for both customers. As a result, a quick approval by all parties was made, and the dome and other specialty refractory materials were placed on a chartered plane within 8 days after the unplanned event began. Concurrently, an expedited manufacturing schedule was made to replace the original customer's material.

This situation could have been avoided. The end-user suspected that there was a problem 6 months before the dome collapse, but elected not to purchase and have on-site the materials needed should the dome collapse.

Figure 3. Proper packaging and loading of catalyst support media.

Figure 4. UV degradation to a flexible intermediate bulk container.

Case study 2: emergency air freight

A fertilizer plant had an urgent need for 44 m^3 of 13 mm T-99 PROX-SVERS alumina balls. Within 1 week, Christy Catalytics had 100 t of material qualified and sent to the customer. Similar to the previous study, financial and technical approvals had to be done expeditiously. The plant had changed ownership since the last commercial exchange, and so several obstacles had to be overcome rapidly. In addition, two products grades had to be combined, explained and subsequently approved for use, all while the material was being made and mobilised to an export airport.

Packaging

Common packaging issues include label damage and poor pallet design and quality. The label is frequently damaged due to weathering from dust, water, and wind. Therefore, the packages are usually prepared with plastic wrap on the outside to prevent damage to the label (Figure 3) and the packaged support balls should not be unwrapped until they are ready to be loaded into the vessel. Poor pallet quality could make the transit a challenge due to inadequate design or construction. The pallets could collapse, causing the entire stack to lean or even tumble to the ground, which would lead to safety and handling issues and potentially even contamination.

Job site storage

Media packaged in bulk sacks (also known as flexible intermediate bulk containers, or FIBC), 1 ft^3 or 0.5 ft^3 bags, or 1 ft^3 boxes should be kept in an environment which will keep the packages free from moisture and sunlight exposure. No matter how brief, exposure to sunlight will cause degradation of the bulk sacks and bag, due to attack on the polymeric fabric, strapping, and threads by ultraviolet light (UV). This will eventually occur, even if the polymer has been treated with a UV stabiliser since this is not permanently effective. Significant and permanent damage to polymeric bulk sacks or bags is possible in as little as 10 – 14 days of sunlight exposure. When the bulk sacks or bags are degraded, they will become brittle and will no longer be able to hold the same weight they were designed to.

Case study 3: UV degradation

In one case, a customer had their materials stored outside while waiting for a turnaround. The bulk bags were covered with protective materials on top; however, the bags' sides were exposed to UV light. The UV light was found to have significantly degraded the polypropylene bags during the inspection, and the bags had become brittle (Figure 4). This outcome is not uncommon, even in cold climates, and it is therefore advised that UV warning labels are adhered to bulk bags to ensure proper storage and prevent UV damage.

Summary

Quality control, logistics, packaging, and job site storage each play a vital role in ensuring that turnaround will take place safely and smoothly. Knowing what can go wrong prior to and during a catalyst loading can help plant operators to anticipate different scenarios and plan accordingly. WF