

CATALYST EXPERIENCES IN THE NEW, LARGE AMMONIA PLANTS

As is not uncommon with plants of new design, the higher pressure plants have created a new set of problems, some of which are brought on by changes in reforming, shift, and ammonia synthesis catalysts.

Eugene A. Comley
Catalysts and Chemicals Inc.
Louisville, Ky.

Over the past two years there have been numerous problems associated with the start-up and operation of the new large-tonnage ammonia plants, including some difficulties with the various catalytic units. These difficulties have not been confined to any particular process design, reactor unit, type of catalyst, or manufacturer.

The large-tonnage ammonia plants are the result of an advanced technology which uses several new design concepts. It was to be expected that some shake-out period would be required to iron out the design and operating techniques associated with the new designs.

The tremendous expansion of the ammonia industry over this period has greatly thinned the ranks of experienced operating and maintenance personnel, and undoubtedly some of the problems encountered in the start-up and operation of the new plants can be attributed to this factor.

The new technology introduced new equipment and imposed more severe operating conditions on the conventional mechanical and reactor units. This too has, no doubt, contributed to some of the difficulties encountered.

The new technology of ammonia production has demonstrated a like need for new technology in catalyst manufacture and operation. Some of the catalyst experiences which have been associated with the problems in the new ammonia plants and what is being done to improve the catalyst technology to meet the new plant technology, will be discussed here.

Basic manufacturing steps

The production of ammonia from natural gas involves six basic process steps which are as follows:

1. Removal of sulfur from the feed stock.
2. Reaction of the natural gas with steam and air to produce a raw synthesis gas of hydrogen, nitrogen and carbon monoxide.
3. Reaction of carbon monoxide with steam to produce hydrogen and carbon dioxide.
4. Bulk removal of carbon dioxide from the synthesis gas by liquid scrubbing.
5. Removal of residual trace quantities of carbon oxides by reaction with hydrogen to produce methane.
6. Reaction of hydrogen and nitrogen to produce ammonia.

Each of these steps, with the exception of Step 4, is a catalytic process and is discussed with particular emphasis on the problems encountered in the new large ammonia plants.

Desulfurization of natural gas

The feed stock used to produce ammonia in the United States is natural gas, consisting largely of methane and containing vary-

ing amounts of sulfur in the form of hydrogen sulfide or mercaptan. Since sulfur in any form is a poison to the nickel reforming catalysts, it must be removed from the natural gas before any further processing can be done.

The usual method for removing the sulfur is by adsorption on activated carbon in a cyclic process. The natural gas is passed through a bed of carbon on which the sulfur is adsorbed until the carbon is saturated. At that time the gas flow is stopped and the sulfur removed from the carbon by steaming.

Activated carbon has long been used for this service, and has proved very satisfactory for removing small quantities of hydrogen sulfide and larger quantities of mercaptans.

With the advent of the high pressure reforming plants, the capacity of untreated activated carbon became seriously limited due to the adsorption of heavier hydrocarbons from the natural gas. This interfered with the adsorption of sulfur and subsequent regeneration of the carbon.

In order to increase the capacity of the carbon and minimize the quantities required in the new large ammonia plants, chemically treated carbons were developed which satisfied the new capacity requirements. One of the newly developed carbons was an anionic-promoted carbon which had a sulfur capacity several times that of any carbons previously used.

The new carbon was acidic in nature and certain precautions had to be taken during the regeneration of the carbon to prevent the formation of a corrosive condensate from steam condensing on and leaching the anions from the carbon. The proper operating technique called for the addition of ammonia to the steam during regeneration. Purpose of the ammonia was to neutralize the acid character of any condensate formed.

This chemically treated carbon has been successfully used in numerous plants with no operating difficulties or problems. But there have been several instances where serious corrosion of the support screens, the carbon drums, and the downstream piping have occurred. In most such cases corrosion was shown to be the result of improper regeneration procedure. In one or two cases it appeared that corrosion occurred even when following the proper procedures.

In order to eliminate the potential corrosiveness of the carbon system, a new chemical treated carbon has been developed. It is non-anionic in character, has a sulfur capacity equal to or greater than the anion treated carbon, and does not require any special regeneration procedure. This new carbon is now in operation in several plants and is giving satisfactory trouble-free service.

Developments in the primary reformer

During the past two years there have been numerous problems associated with the primary reformer catalyst in the new large ammonia plants that are far in excess of what might be antic-

ipated from previous reforming experience.

The principal and most serious problem has been the excessive break-up of the reforming catalyst, with its attendant increase in pressure drop and the formation of hot spots in the reformer tubes. A secondary problem which has been allied to the reformer catalyst is the fouling of waste heat boilers downstream of the reformers.

Before getting into a discussion of the catalyst itself, it should be pointed out that the design of the new ammonia plants imposes much more severe operating conditions on the catalyst than was the case just a few years ago. Higher pressure and temperature operation, higher space velocities, higher differential pressure forces on the catalyst, smaller diameter and longer reforming tubes—resulting in greater expansion and contraction forces on the catalyst—all contribute to this more severe service. In addition to these factors, many of the new plants have experienced various mechanical difficulties and startup problems which have resulted in numerous crash shutdowns and imposed further demands on the catalyst.

Over the past several years reforming pressures have increased from near atmospheric to about 500 lb./sq.in. gauge; space velocities have gone from 1,000 to more than 7,500 vols./hr.; and heat transfer rates have risen from 10,000 to 28,000 BTU/hr./sq.ft.

These are substantial changes. It is not surprising that changes of such magnitude would have a significant effect on the catalyst. The surprising thing, however, is that the catalyst used in the first of the new large ammonia plants performed and held up very satisfactorily. It was not until a separate problem arose that any difficulty was experienced with the reforming catalyst.

Reforming catalyst problems

This new problem encountered by most new plants has been the fouling of the waste heat boiler downstream of the primary and secondary reformers. The principal cause of the fouling is silica, but the source of the silica is still a matter of conjecture.

Although the evidence is very strong that silica will not migrate from primary reformer catalyst under normal operating conditions, the waste heat boiler problem has been so severe that the industry has demanded that the reforming catalyst be virtually silica-free.

The removal of silica from the catalyst has resulted in a catalyst which shows a substantial loss of strength upon reduction and operation. The reduced catalyst also shows a greater susceptibility to break-up when contacted with water. Although the new silica-free catalyst is made with an initial crush strength that is much greater than the old silica-containing catalyst, the increased crush strength did not appear to alleviate the problem.

Silica previously incorporated into the catalyst acted as a bonding agent, particularly at high temperatures; there was little loss of strength upon reduction and with time of operation. The silica-free catalyst shows a marked and continued loss in physical strength with time of operation. This reduction in the physical strength, coupled with the more severe reforming service and numerous plant shut-downs, has resulted in severe catalyst break-up in several plants and has necessitated the replacement of the reformer catalyst one or more times.

The silica-free catalyst has given acceptable service in a large number of plants, especially when it was not subjected to numerous up-sets in operation. The catalyst, however, is susceptible to breakage as a result of frequent changes in operations, such as startup and shutdown. It also is more susceptible to damage when contacted with water after it is reduced.

An extensive development program has been carried out over the past year in an effort to find some other bonding agent that would minimize or eliminate this loss of strength in operation and, at the same time, would circumvent the silica problem. A modified catalyst has been developed which, hopefully, realizes these objectives. The modified catalyst is now operation in several plants. However, several months of plant operation will be necessary to demonstrate whether the modified catalyst technology fully satisfies the requirements of the new plant technology.

Secondary reforming developments

Although the catalyst used in the secondary reformers has not been the cause of any particular operating problems, removal of silica from the catalyst has resulted in a catalyst that is much weaker in the reduced state, and which is subject to excessive breakage, particularly if contacted with water. The secondary reforming catalyst has had to be replaced in two plants because of excessive catalyst breakage.

There is a much stronger argument for the elimination of silica from the secondary reformer catalyst, since this catalyst normally operates at a temperature of 300 to 400°F higher than the primary reformer. There is conflicting evidence that silica will migrate from the catalyst under the secondary reformer operating conditions. But again industry is insistent that silica be eliminated from the catalyst. The modified catalyst referred to above, under primary reforming, can also be used for secondary reforming, thereby eliminating this potential problem area.

Conversion of carbon monoxide

Virtually all of the new large ammonia plants employ a single stage CO conversion system, with one or more beds of conventional high temperature shift catalyst followed by a bed of low temperature shift catalyst.

The high temperature shift catalyst is essentially the same as that used in previous low pressure plants, and has been virtually trouble-free in the new high pressure operations. There have been several instances of fouling of the high temperature catalyst bed by solid deposition on the top of the bed, but these problems have been relatively minor. They have been corrected by removing the top portion of the catalyst and eliminating the source of the solid contamination.

The low temperature shift catalyst is much more susceptible to damage than the high temperature shift catalyst, both from poisons and from maloperation. Although sulfur has only a small effect on the activity and performance of the high temperature shift catalyst, even trace amounts of sulfur greatly affect the activity of the low temperature shift catalyst.

Temperature also has a very pronounced effect upon the activity of the low temperature shift catalyst. Those much in excess of the design temperature can greatly reduce or completely destroy the activity of the catalyst.

There have been a number of low temperature shift catalyst charges lost through maloperation during start-up or operations. Such maloperation usually is the result of subjecting the catalyst to too high a temperature. As plant operators have become better acquainted with the catalyst characteristics and its operating technology, damage has been greatly reduced.

Service life of the catalyst has been steadily increased to where, in most cases, it now exceeds 1-1/2 yr. and sometimes 2 yr. It is anticipated there will be continued improvements which will result in longer life of the catalyst. The low temperature shift catalyst has also been modified to give it a much higher degree of thermo stability, making it less susceptible to damage by exposure to high temperatures, particularly for short durations of time.

The catalyst is, however, still susceptible to damage by extremely high temperatures. Care should be exercised to prevent hot gases from the high temperature shift converter from contacting the low temperature catalyst before being cooled to the operating temperature of the low temperature shift catalyst. Some design systems use a direct water quench to effect this cooling. There is the danger that in the event of water failure, the hot gas may contact and severely damage this catalyst.

Methanation problems

There have been several instances of methanator problems wherein the catalyst was either severely overheated or was poisoned by solution carried over from the carbon dioxide removal system. The methanation reaction is a highly exothermic one, and the system is normally designed to handle carbon oxide concentrations in the neighborhood of 1 to 2%.

In the event of a pump failure in the carbon dioxide removal system, it is possible to contact the methanation catalyst with a gas containing large concentrations of carbon dioxide. The resulting extremely high temperatures in the methanator can seriously damage the catalyst and may even damage the reactor vessel. Most of the new plants have protective devices to guard against an extreme upset. But special care should be paid to these protective devices to make sure that they are properly set up and operable.

Another source of damage to the methanation systems has been the carry-over of carbon dioxide scrubber solution, some of which contains either arsenic or sulfur and both of which are poisonous to the catalyst. Several such instances have been encountered in the new ammonia plants. The best protection against upsets of this sort is the inclusion of water-wash trays in the top of the carbon dioxide scrubber, and/or the installation of a knock-out pot between the scrubber and the methanator.

Ammonia synthesis

The new ammonia plants utilize an ammonia synthesis cycle operating at a pressure between 2,000 and 3,000 lb./sq.in. gauge. Very few problems have been encountered in this section of the new plants; the catalyst, in all cases, has shown sufficient activity to meet the design requirements at the lower pressure.

One of the principal problems with ammonia synthesis catalyst

in the past has been the gradual buildup from pressure drop due to attrition of the catalyst during operation. One of the newest developments with this catalyst has been the removal of the edges and corners of the catalyst by polishing.

This gives a catalyst that is more uniform in shape and size, and which has a higher packing density in the reactor. The initial pressure drop for a given volume of catalyst is higher than that for a bed of irregular shaped particles. But it is anticipated that the attrition loss and pressure buildup will be much less and will result in a longer catalyst usage.

Conclusions

There is little doubt that the new ammonia plants, based on the production of ammonia synthesis gas at pressures approaching 500 lb./sq.in. gauge, are experiencing more troubles than the older plants which operate at a much lower pressure. This is not unusual in that many new designs pose certain design and operational problems that are gradually solved as the engineers, suppliers, and operators become more familiar with them.

The new designs have demonstrated they are workable and feasible, but that further agreements and technology are required for them to attain their maximum efficiency. Catalyst technology is one facet. The catalyst manufacturers have demonstrated, and are demonstrating, their ability to meet the challenges of the new technology.