

# SAFETY CONSIDERATIONS FOR AMMONIA PLANT CATALYSTS

Operating conditions of the new plants subject catalyst to more severe service, and there is less margin for error in plant operation.

Duane W. Allen  
Girdler Catalysts  
Louisville, Ky.

The catalysts used for the production of ammonia present very few safety problems. Catalysts used are solid materials that normally present no toxicological problems. There are certain minor precautions that should be emphasized in handling and loading, and there are a few situations where reasonable judgement must be exercised during plant operation. Safety, as used in this paper, encompasses both plant and personnel protection.

## Desulfurization catalysts

Of all the catalysts that are used in ammonia production, the activated carbon used to desulfurize natural gas is the only one that is combustible. The ignition temperature in air can be as low as 430°F. for carbons impregnated with iron or copper, and this should be kept in mind when storing and handling activated carbons. When removing activated carbon from a reactor, it should first be regenerated. If for some reason activated carbon must be removed from a reactor without regeneration, a little additional care should be taken in handling and disposal. In many areas the natural gas being desulfurized contains appreciable quantities of heavy hydrocarbons. These are absorbed on the carbon and are normally removed during regeneration. In some instances the concentration of absorbed hydrocarbons is sufficiently high that ignition of the vent stack occurs during regeneration. Thus, used carbons removed without first being regenerated can contain appreciable concentrations of flammable hydrocarbons and could be easily ignited.

Zinc oxide used for desulfurization of reformer feed gas presents no real hazard in handling or during operation. Normal precautions should be taken during loading and unloading to insure that excessive dusting does not occur. Personnel handling the catalyst should be protected against possible ingestion of catalyst dust. This is normally a minor problem, but it should be emphasized here that ingestion of metals should be avoided. This precaution would apply to all the catalysts used in an ammonia plant. Dusting conditions could be most severe when handling used catalyst damaged by some operational upset.

## Reforming Procedures

For best operation of primary and secondary reformers certain procedures should be followed. The weight of catalyst loaded to each tube should be determined and recorded. Tubes should be vibrated to prevent bridging. If bridging does occur, hot spots will develop. At best, this results in a

shorter tube life and could result in tube failures. If furnace firing is controlled by one or two hot tubes, production losses will occur.

In some cases air is used in heating up the primary and secondary reformers. Some reforming catalysts contain several percent graphite. Graphite will react with air at temperatures above 750°F. This does not cause a problem in the primary reformer since the heat generated is readily dissipated through the tube walls. The secondary reformer, however, presents a slightly different situation. There it is possible for the heat formed from air and graphite reacting to build up, and temperatures can be reached that will damage the secondary reformer catalyst as well as the reformer itself.

Removal of used reforming catalyst presents no real safety problem. Normally, the reactor system is cooled with steam to temperatures below 400°F. The steamflow can then be discontinued and the reforming catalyst exposed to air and removed. I have seen reforming catalyst removed from a furnace where the furnace temperature was over 1,000°F. and there were no difficulties encountered. This procedure is not one that we recommend.

## Careful Control of Temperature

Occasionally, plants have passed natural gas over the reformer catalyst in order to bring temperatures up to a level that permits generation of steam. This can be done, but careful control of temperatures must be exercised to prevent the formation of carbon in the reformer tubes, and it is a procedure that we do not recommend. It is almost impossible to determine the exact temperature of the system since it is not possible to read tube wall temperatures, and thermo-couples are not normally located inside all the tubes. Temperature readings taken at the manifold can be misleading since flow rates are usually quite low. Because of heat losses, the gas temperature in the manifold can be several 100°F. below the temperature in the reformer tubes. Furnace wall temperatures, as determined by thermocouples, can also be misleading since all burners are not in operation and furnace wall temperatures are not uniform.

Carbon laydown will not only damage the catalyst but can also lead to damage to tubes and manifolds if proper care is not exercised in removing the catalyst. At this point it may be well to emphasize the obvious—that operation of a reformer without steam is an exercise in futility.

Extremely high temperatures can be obtained in both the primary and secondary reformers. Loss of either steam or hydrocarbon feed to the primary reformer can result in severe overheating since the heat of reaction constitutes the major

heat load. If furnace firing is not cut immediately, temperature levels will be reached that will result in damage to catalyst, tubes, and furnace. In secondary reformers excessive addition of air will result in extremely high temperatures. Instrumentation is designed to protect against these upsets, but they still occur occasionally.

## High Temperature CO Conversion

High temperature shift catalysts, like reformer catalysts, present only minor safety problems. There are no known hazards involved in handling the new catalyst during normal initial loading. When placing the conventional iron-chrome high temperature shift catalysts on stream, certain precautions should be taken. There have been instances where air is used during the initial heat-up of a new plant. The air flows through the primary and secondary reformers and the high temperature shift converter. When steam becomes available, steam flow is established and the air flow is discontinued. If air is in contact with high temperature CO conversion catalyst at temperatures above 550°F., it is possible for the oxygen to react with graphite in the catalyst. The resulting high temperature will damage the catalyst and can exceed the design limitation on the reactor.

Reduced iron-chrome catalysts are pyrophoric and will readily oxidize when exposed to air. When the used catalyst is to be discarded, it can be removed in the reduced state with no difficulty if certain precautions are taken. The catalyst bed should be purged with steam and then cooled to the minimum temperature possible with the available steam. The outlet manway can then be opened and the catalyst removed. As the catalyst leaves the reactor it should be sprayed with water, and it should be kept wet until it is removed from the plant area.

There have been occasions where high temperature catalyst beds were cooled with steam and then purged with nitrogen down to ambient temperature. The top and bottom manways were then opened for inspection purposes. It was felt that the nitrogen purge could be discontinued. After sitting for some time, temperatures in the reactor suddenly started to rise and eventually exceeded 1,300°F. With both the top and bottom manholes open, the reactor acted as a chimney and air was pulled in. Once the catalyst started to oxidize, the temperature started to rise, the air flow increased, and the reaction snowballed.

Iron-chrome CO conversion catalysts have been damaged while being purged with "inert gas". When using gas from an inert gas generator, analyses should be made to insure that the nitrogen is oxygen free. Oxygen concentrations of 2% to 3% in nitrogen can result in high temperatures arising from oxidation of the reduced iron in a used high temperature shift catalyst.

## Low Temperature CO Conversion

Low temperature CO conversion catalysts are more susceptible to poisoning and to damage from overheating than the other catalysts used in ammonia plants. The active ingredients of this type catalyst are copper and zinc, and there are no special precautions required in the handling of these catalysts during loading.

The reduction of LTS catalysts is highly exothermic, and if care is not taken during reduction, the catalyst can be easily overheated. Adequate reduction facilities must be available, and these should include meters for metering and controlling the flow of both the carrier gas and the hydrogen. Procedures used for removal of LTS catalyst can be similar to those used

for removal of HTS catalyst. If the catalyst is to be discarded, it can be removed in the reduced state. If the catalyst is to be reused, it must be very carefully oxidized out of service.

LTS catalysts are very sensitive to sulfur and chloride poisoning, and every precaution should be taken to minimize the possibility of sulfur compounds and halogen compounds from contacting the catalyst. Plants using LTS catalysts should use a conservative approach in designing the system for desulfurizing the feed gas to the plant. Process steam should also be sulfur-free. Linings for secondary reformers, transfer lines, etc. are also possible sources of sulfur. If these are changed, the LTS converter should be bypassed until the feed gas is free of sulfur. HTS catalysts can also contain sulfur and should be properly desulfurized prior to admitting gas to the LTS converter. One possible source of chlorides is the steam. Some lubricating oils used in air compressors contain chlorides, and they should not be used.

## Methanation Problems Unique

Methanators present safety problems that are somewhat unique in an ammonia plant. An upset in the CO<sub>2</sub> removal system or the inadvertent introduction of a high CO feed can result in excessive carbon oxides being fed to the reactor. The resulting high temperatures can easily exceed design temperatures of the methanator vessel. Protection against excessive temperatures is obtained by use of a high temperature alarm system that automatically bypasses the bed when a pre-set temperature is exceeded. In plants employing sulfonal for CO<sub>2</sub> removal, it is recommended that two thermocouples be tied into the alarm system since the methanation catalyst will be gradually poisoned by sulfur. After some time onstream, the catalyst in the upper portion of the methanator will become inactive, and a thermocouple located in this area would not give a high temperature reading.

It should also be emphasized that during an upset condition the flow of high CO<sub>2</sub> and/or CO methanator feed should not just be bypassed. It is also necessary to close the block valves to the methanator. At one plant, during an upset in the CO<sub>2</sub> removal system, high temperatures activated the alarm and automatically opened the bypass valve. The plant operators did not close the block valve in the methanator feed line. As a result a small flow of gas containing a high CO<sub>2</sub> concentration continued to flow through the methanator at full operating pressure for several hours. Temperatures in the methanator exceeded 1,300°F. during this period. Fortunately, the reactor did not rupture; although, some deformation did occur.

Formation of nickel carbonyl is also a possibility in a methanator. Nickel carbonyl is extremely toxic, and whenever men are going to enter or open a reactor, stringent precautions should be followed to insure that nickel carbonyl is not present. Even in a closed system, carbonyl formation should be prevented since nickel can be removed from the catalyst with a resulting loss in activity.

Conditions favoring nickel carbonyl formation are high pressures, high CO concentrations, temperatures in the range of 120°F to 350°F, and the presence of a catalytically active nickel. Of special interest to plants employing sulfonal systems is the fact that sulfur compounds have been cited as promoters for the carbonyl forming reactions. Nickel carbonyl formation is most likely to occur during startup and shutdown. Methanators should not be blocked-in under an atmosphere of process gas that contains CO. All carbon monoxide should be purged from the system before the reactor has a chance to cool below the normal operating temperature. Some thought should be given to startup of a cold reactor if it is necessary to use a gas-containing CO. With new catalyst, in the oxidized state, there

is no problem since the nickel is not catalytically active; and it does not become reduced until temperatures are reached that are above the maximum temperature at which nickel carbonyl can be formed.

If a cold, reduced methanation catalyst is to be placed back onstream with CO-containing feed gas, it must be assumed that some carbonyl will be formed. If the gas is to be heated to temperatures above 400°F. in some subsequent part of the process, the nickel carbonyl will be decomposed. If the gas is vented during startup, precautions need to be taken to insure that personnel are not exposed to the vented gas. Sending the gas to flare is one way of insuring that the carbonyl is decomposed.

### **Less Margin for Error**

In a general way, these are only some of the safety aspects

relating to catalysts used in an ammonia plant. The real cost of the catalysts used in an ammonia plant is ultimately determined by the tons of ammonia produced per dollar of catalyst installed and not by the initial catalyst cost. One way for the plant operator to obtain a better return on the dollars invested in catalysts is to follow the recommendations of the catalyst vendor. All catalyst suppliers will furnish detailed instructions for loading, start-up, operation, shut-down, and removal of catalysts. If proper procedures are used, catalyst removal can become a minor problem.

In closing, it should be emphasized that the proper handling of catalysts is most important in the new, large, single-train, high-pressure plants. Practices that could be tolerated in the older, lower-pressure plants cannot be tolerated in these newer units. Operating conditions of the new plants subject the catalyst to more severe service, and there is less margin for error in plant operation.