

# CATALYST SAFETY IN LARGE AMMONIA PLANTS

Hazards exist in handling of catalyst as well as from exposure to dust and nickel carbonyl poisoning; proper procedures are important.

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The first problem in dealing with any catalyst in an ammonia plant is that of loading and unloading drums. In most cases catalyst suppliers now deliver catalysts in drums containing between 200 and 400 pounds weight of catalyst. It is fairly safe to say that these are too heavy for the average person to handle and it is, therefore, essential for efficient drum handling techniques to be developed to minimize the risk of strains, bruises, etc., to the personnel involved in the loading. It is the duty of the foreman or superintendent in charge of loading operations to insure that in all cases suitable block and tackle systems are available.

In the D. W. Allen paper, the general problem of ingestion of catalyst dust was raised. The importance of this point varies from catalyst to catalyst but can nowhere be considered more important than in the case of one of the most common catalysts used. This is high temperature shift catalyst which is an iron/chrome oxide catalyst. The ingestion of chrome into the lungs is particularly dangerous and it should always be standard practice that when anyone is handling this catalyst, either loading or unloading, the persons involved should wear dust masks.

## Two Main Categories

The normal catalysts used in sulfur removal systems in ammonia plants can be divided into two main categories. Category 1 is the activated carbon system with the carbon usually impregnated with metal oxides, such as iron oxide or copper oxide or both, to improve the sulfur absorption of the bed. General details of this type of system have already been described. The second system is the cobalt molybdate and zinc oxide desulfurization system and with this combination of catalysts there are certain points requiring attention.

During startup the zinc oxide catalyst is not reduced, but the cobalt molybdate catalyst has been known to cause a dangerous situation. This can arise when heavy feed stocks are being reformed and it is considered necessary for the primary reforming catalyst to be reduced prior to startup of the plant proper. When this operation is to be carried out, the normal technique is to recycle a process gas stream containing hydrogen, some CO and some CO<sub>2</sub> through the desulfurization system and then into the primary reforming catalyst. When this is done at reasonably high pressures, the cobalt molybdate catalyzes methanation of CO and CO<sub>2</sub> in the gas stream. I know of one plant in Germany where a desulfurizer reactor was severely damaged due to a runaway reaction taking place during startup of a plant.

As a general rule, it is advisable to limit the CO plus CO<sub>2</sub> content of any gas stream passing through a cobalt molybdate bed to not more than 5% during the reduction. By this means,

if conditions are suitable for the methanation reaction to take place, the total temperature rise through the bed will not be sufficient to cause damage to either the catalyst or to the reactor. Discharge of desulfurizer catalysts does not normally present a serious problem but it is important to remember that carbon laydown or hydrocarbon laydown on zinc oxide and/or cobalt molybdate is always possible. With certain types of feed stocks trace metals can be laid down on these materials also and are likely to be pyrophoric on exposure to air. It is important, therefore, always to have available water hosing facilities when catalyst are to be discharged.

## Overheating of Tubes

One of the main problems in satisfactory operation of reforming catalysts is that of overheating of catalyst tubes. The cause of the overheating can be one or more of several occurrences and there is little need to expand on what has already been said on the subject. However, the situation is a potential hazard and is one of the hazards most frequently encountered in ammonia plants where the ammonia plant superintendent has to balance the risk of operating with dangerously hot tubes against shutting the plant down with the resultant loss in ammonia production. In hydrogen plants attached to refineries, the economic consequences of a shutdown can be even more serious. Imperial Chemical Industries have developed a technique for sealing off reformer tubes in operation and this technique was described briefly some years ago at the AIChE Safety Symposium.

One of the problems I have recently encountered in several plants in the U.S.A. is that of cooling an overheated catalyst bed. In the case of high temperature shift catalyst, the most suitable medium is undoubtedly steam. As this is usually available in large quantities, and does not seriously affect the catalysts, no great problem lies here. Steam, however, is distinctly unsuitable for cooling low temperature shift catalysts because it has a deactivating effect. In the case of this catalyst and methanation catalyst, an inert gas such as nitrogen is undoubtedly the most suitable cooling medium and should be used whenever possible. A very serious problem arises in the case of methanation catalysts when the only purge gas available is natural gas. I know of several plants where the staff have discovered to their dismay that methane cracking is an exothermic reaction and takes place with unpleasant ease at temperatures of approximately 1,000°F. and above. Thus, if a purge system is to be used and the only gas available is natural gas, it is essential that the temperature alarms are set at a low enough temperature for the purge gas to be introduced safely into a catalyst bed which has not yet reached a temperature of, let us say, 900°F.

## Two Types of Catalysts

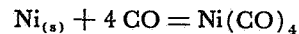
Ammonia synthesis catalysts can be divided into two general types. The conventional catalyst is supplied as magnetite  $\text{Fe}_3\text{O}_4$  which has been treated with various promoters. The second type is a pre-reduced catalyst which is supplied as metallic iron with a stabilizing surface covering of  $\text{Fe}_3\text{O}_4$ . The latter catalyst has the advantage of needing little reduction, but there have been occasions where drums of pre-reduced catalysts which have inadvertently been over-heated in the presence of air, have reoxidized completely with development of a considerable increase in temperature. Generally, these drums of catalyst have sealed lids, but it is very important that pre-reduced catalyst should be handled carefully.

Reduction of conventional catalysts is a fairly lengthy procedure, but cannot normally be considered a hazardous operation. It is probably more to be considered a problem of avoiding the de-activation of the catalyst, than of any particular hazard being developed.

One potential hazard does exist in ammonia synthesis loops and this has been drawn to my attention by several people. During loading of ammonia synthesis catalysts, it is almost inevitable that a certain amount of fine dust will be produced. This is particularly true of pre-reduced catalyst, which is slightly more friable than the conventional type. When the synthesis reactor is brought on line, the dust is forced downwards through the reactor and can be blown through the lines until it collects in some low point or near some restriction point in the synthesis loop. If this finely divided material is discharged into the air, it presents a very serious fire hazard because the material will be iron metal and this, in finely divided form can be spontaneously combustible when exposed to air.

## Nickel Carbonyl Formation

A brief examination of the equilibrium data on formation of nickel carbonyl may be worthwhile at this stage. For the reaction



the equilibrium constant  $K_p = \frac{p_{\text{CO}}^4}{p_{\text{Ni}(\text{CO})_4}}$  and is expressed by the following equation

$$\log_{10} K_p = \frac{-7330}{T} + 21$$

Where T is the temperature in degrees K. It can be seen that the equilibrium is in favor of nickel carbonyl formation for (a) low temperature (b) increasing pressure and (c) increasing carbon monoxide concentration.

Apart from the mechanical solutions that have to be devised for this type of problem, there are certain other recommendations that should be made. The first is that when a methanator is isolated, it should always be maintained above the system pressure with nitrogen to prevent ingress of carbon monoxide. Secondly, when the methanator is being blown toxic concentrations of nickel carbonyl may be present in the vented gas. If the gas is vented well above ground level, any nickel carbonyl should be rapidly diluted, but it is obviously safer to destroy the nickel.

Nickel carbonyl is an extremely toxic substance affecting the chest giving rise to acute pneumonia. There is a delayed effect of at least two days before this is normally seen.

In the U.S.A., for normal operation over a prolonged period of time the maximum level is set at 0.001 ppm. This is because there is considered to be a risk of formation of lung tumors and cancer of the nasal sinuses.