A Review of Catalysts Used in Ammonia Production

Rapid progress is being made in improving the operation of catalysts used in large ammonia units. Here's a look at some recent developments.

J.S. Cromeans, and H.W. Fleming
Catalyst Consulting Services, Inc.
Louisville, Ky.

Many new types of catalyst loadings were charged in furnaces during 1970-71. In fact, more combinations of different types of catalyst were loaded in this one year than in the previous history of high pressure reforming. In a certain sense, we may say process designs have been ahead of catalyst, as well as metallurgical, developments. This has made it necessary for ammonia operators and contractors to seek better catalyst loadings. In many cases, it has been necessary for plant operators to do a certain amount of experimentation in their catalyst loadings. Catalyst vendors, also recognizing the operator's needs, have been making progress in developing and improving catalysts to meet the more severe process requirements of high pressure plants. Substantial progress was made during 1970-71 in eliminating hot bands and hot spots *(1)*.

Some of the typical new catalyst loadings for the high pressure plants are shown in Table 1. These new catalyst loadings show a trend to use a smaller particle size catalyst, especially in the upper half of the tube. There has also been a trend to use the new ceramic base catalyst. A variation of calcium aluminate base catalyst made in a small particle size is also now in commercial use.

During 1970-71, the ammonia industry generally paid more money per cubic foot for catalyst with the ultimate objective of achieving increased reliability and lower operating cost per ton of ammonia. Expenditures to reduce catalyst failures and to determine the cause of catalyst problems causing plant shutdowns are justified when one considers lost income on the order of $250,000 per week on a large tonnage plant *(2)*.

The quality of catalysts being loaded into reformers during 1970-71 has been better than in earlier years because of improved specifications and better inspection procedures.

The operating run lengths on high pressure primary reformers were extended by several plants. A few plants have now achieved run lengths of six to 13 months with their primary reformers without having process gas out of the furnace. With the longer runs and the elimination of crash shutdowns, a more accurate picture is beginning to

Table 1
Primary reformer catalyst loadings

Plant	**A**	**B**	**C**	**D**
Top Half of Tube				
Type of Catalyst				
Base	Ceramic	Ca-Al	Ceramic	Ceramic
Wt. % Nickel	12 - 14	24 - 26	12 - 14	18 - 20
Particle Size	5/8 in. x 1/4 in.	5/8 in. x 1/4 in.	5/8 in. x 1/4 in.	5/8 in. x 1/4 in.
Bottom Half of Tube				
Type of Catalyst				
Base	Ca-Al	Ca-Al	Ceramic	Ceramic
Wt. % Nickel	24 - 26	24 - 26	18 - 20	18 - 20
Particle Size	5/8 in. x 3/8 in.	5/8 in. x 3/8 in.	5/8 in. x 3/8 in.	5/8 in. x 3/8 in.

(All are rings with 1/4 in. dia. hole)

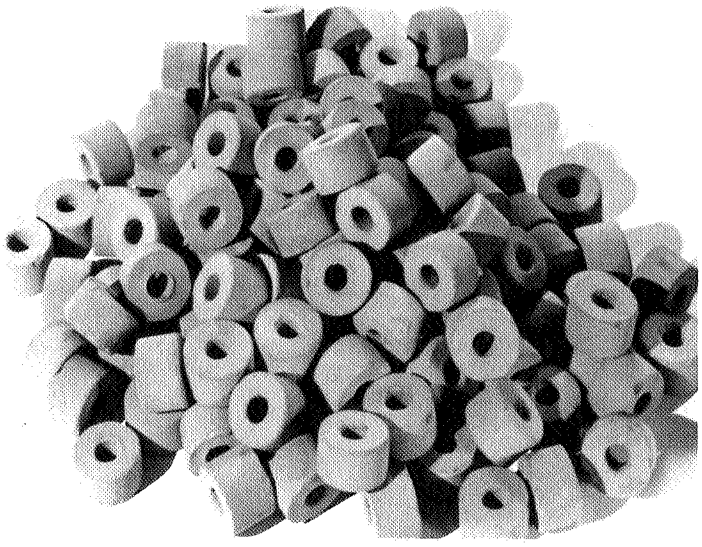


Figure 1. Primary reformer catalyst.

Figure 2. High temperature shift catalyst.

emerge on the aging of primary reforming catalysts.

In the new high pressure plants, there has been a significant aging of the catalysts used. This is in contrast to the low pressure, low space velocity operations of the older plants where little aging occurred for practical purposes. The aging of the catalysts appears to be caused by three principal factors: 1) the alumina in the bases losing surface area, 2) the nickel losing activity and 3) the nickel reacting with the catalyst base.

Effect of sulfur studied

It has also been observed the primary reforming catalyst performance in high pressure plants is more affected by sulfur than the catalyst performance in low pressure plants receiving the same feed.

The effect of sulfur on primary reforming catalysts, Figure 1, was studied in depth by several operators during 1970-71. Much work was done to improve the removal of hydrogen sulfide and mercaptans from plant feed streams. There was increasing use of zinc oxide in desulfurization service. Several plants began receiving process natural gas with substantial concentrations of carbonyl sulfide. For practical purposes, one may consider that carbonyl sulfide is not removed with the usual activated carbon desulfurization system. A catalytic conversion process or molecular sieve adsorption system is required for the removal of carbonyl sulfide. Since these systems require substantial capital outlays, efforts were made during 1970-71 to work with the gas supply companies to minimize the concentrations of carbonyl sulfide in the feed to the primary reformers.

The principal effect of carbonyl sulfide on primary reforming catalyst is to sulfide the catalyst and slow the rate of the steam-hydrocarbon reforming reaction over the catalyst. At the lower reaction rate, there is a greater tendency to deposit carbon on the catalyst and cause gradual coking of the steam methane reforming catalyst. The net results are that the tubes become hot, and hot spots begin to show up on the tubes. In the primary reformer, the nickel catalyst converts the carbonyl sulfide to hydrogen sulfide. The effect of 2 ppm by volume of carbonyl sulfide may be considered to be the same as 2 ppm by volume of hydrogen sulfide on the primary reformer catalyst and any down stream low temperature shift catalyst. Depending on the particular design loading, this concentration may reduce a primary reformer throughput by 20- to 25%. To maintain throughput with 2 ppm by volume of sulfur present means firing tubes to relatively high tube skin temperatures on the order of 30- to 100°F higher than normal, depending on the furnace load.

During 1970-71 we observed improved equipment inspection procedures being carried out by operators as part of routine operating practice. As a result of early detection of equipment failures, plants were shut down with a minimum of equipment and catalyst damage. Better operator training has minimized the number of crash shutdowns. Where primary reformer tube leaks have been encountered, several operators have found it practical to continue operating until a shutdown could be properly planned. With the proper catalyst selection, loading and operation, primary reformer tube leaks can be minimized.

In the immediate future, areas which warrant further study and action by primary reformer operators to improve their on-stream reliability and safety of operation are as follows:

1. Selection of optimum catalyst and loading
2. Improving startup and shutdown procedures.
3. Further training of operators
4. Optimization of operations
5. Planning for operation with gas curtailment
6. Planning for turnarounds

High temperature shift catalyst

High temperature shift catalysts, Figure 2, are used commercially to catalyze the water gas reaction, $CO + H_2O \rightarrow CO_2 + H_2$ at temperatures in the range of 650- to 850°F. The terms "high temperature" or "primary shift" are used to distinguish between the shift catalyst operating in the 600- to 900°F range, from the shift catalyst operating in the 400- to 550°F range, which is referred to as the "low temperature" or "secondary shift" catalyst. The high temperature shift is often called the iron-chrome catalyst, and the low temperature shift, the copper-zinc catalyst.

The use of the iron-chrome catalyst dates back many years and the composition has not changed appreciably. The major constituents are from 7- to 11 wt. % Cr_2O_3 and 80- to 90 wt. % Fe_2O_3. However, the minor elements vary even today and must be controlled to give the best high temperature shift catalyst.

In contrast to the chemical composition, the physical properties and form have changed drastically over the years and must be clearly specified to obtain the best catalyst. High temperature shift catalyst were initially used in the form of lumps. These were obtained by sizing the dried filter cake to large particles of a low bulk density. A later development was to make powder from the lumps and form them into tablets with tabletting presses. The size was 3/8 in. x 3/8 in. or 1/4 in. x 1/4 in. tablets. This gave a material with a density of about 90- to 100 lb./cu. ft. Further study of the manufacturing techniques reduced the density to about 60 lb./cu. ft. Currently, high temperature shift catalysts are sold in the range of 60- to 80 lb./cu. ft. in a tabletted form of these sizes: 3/8 in. x 3/8 in.; 3/8 in. x 3/16 in.; 3/8 in. x 1/4 in. 1/4 x 1/4 in., and 1/4 in. x 1/8 in.

The high temperature shift catalyst in the tabletted form which has high activity has been noted for its low crush strength after reduction and during use in the converter. This property has not been detrimental to the use of the catalyst as long as solids did not accumulate in the top part of the bed to cause a pressure drop. If one were faced with the problem of removing solids accumulated upon the top of the bed, the low crush strength of the catalyst would present a problem. In many instances, any problem in the high temperature shift converter which requires a movement of the catalyst, usually ends up in the purchase of a new charge.

The best catalyst of any type has the highest activity and strongest crush strength. At one point, industry was faced with choosing between high crush, or sacrificing crush strength for higher activity. Industry elected to use a high activity catalyst with low crush. Now, however, there are signs that crush strength is being improved without imparing the activity. All the physical characteristics of surface area, pore volume, attrition, and crystal structure are important in determining the activity and crush strength of the catalyst.

In the commercial use of the catalyst, the choice of the design conditions largely determine the exit CO concentration. The water gas shift equilibrium and the kinetics of the reaction are fixed by the design. There is a much confusion in the industry about the life and the activity of the high temperature shift catalyst, especially when the exit CO climbs above the design value. The confusion results from a lack of understanding of the interplay of the kinetics and the equilibrium of the water gas shift reaction, the volume of catalyst loaded, the operating pressure and the many different reactor designs. The different reactor designs are:

1. Single bed
2. Two beds without interbed cooling
3. Parallel beds
4. Multi-bed with interbed cooling
5. Gas Quench
6. Guard beds and HTS units.

Table 2
Typical operating process conditions and cubic feet of catalyst/ton NH_3

Plant	**A**	**B***	**C***	**D**	**E**	**F**	**G**	**H**	**I**	**J**
Capacity, ton/day	100	100	300	300	600	600	1,000	1,000	1,500	1,500
CO, mol %										
In	10.5	12.4	11.8	9.7	12.8	12.7	13.0	11.5	11.0	12.7
Out	1.8	1.0	3.0	1.85	4.0	3.1	3.0	3.4	2.4	2.6
S/G, Exit	1.0	0.9	0.8	0.66	0.5	0.4	0.44	0.40	0.6	0.7
Temperature, °F										
In	720	720	760	725	715	700	710	720	725	740
Out	840	670-710	880	815	790	815	820	820	830	840
Pressure Out	263	230	35	278	410	398	423	440	433	425
Space Velocity										
Wet Gas, V/V/H	4,720	1,200	1,200	3,460	6,400	4,800	4,050	6,300	5,250	6,700
Cu.ft. Catalyst/ton NH_3	2.1	8.2	6.7	2.4	1.27	1.44	1.78	1.25	1.52	1.24

*No low temperature shift

It is apparent that one is comparing apples with oranges if he tries to equate the performance of one shift converter with another one in a different plant unless they are identical in all respects. Table 2 lists the typical operating conditions and catalyst volumes per daily ton of ammonia for ten different plants. The inlet CO varies from 9.7 to 12.7, and exit CO from 1.8 to 4.0. The range of inlet temperatures are from 700- to 760°F, and the outlet from 710- to 880°F.

The outlet pressure is from near atmospheric to 440 lb./sq. in. gauge. The wet gas space velocity covers a range of 1,200 to 6,700. The cubic feet of catalyst per daily ton of ammonia goes from a low value of 1.24, to a high value of 8.2. Obviously, the life of the high temperature shift catalyst may be quite different depending upon the plant design. A detailed analysis of the catalyst performance compared to the design parameters is required to determine the normal life for a high temperature shift catalyst in a particular plant. Using 1.5 cu. ft. of catalyst/daily ton of ammonia as an average value for the 600 to 1,500 ton/day plants with a life of 2 yr. gives a cost of 4.6¢/ton of ammonia for the high temperature shift catalyst.

During the normal life span of the catalyst, the exit carbon monoxide slowly increases towards the design value. The inlet temperature initially usually is lower than design, and is slowly increased to maintain a low CO value until the end of run conditions are reached. Then the catalyst should be changed for a new charge. However, other factors from operations may enter the picture, interrupt the orderly operation, and cause a catalyst change out prematurely. These factors cause high pressure drop, channeling, or abnormal temperatures.

Causes of process interruptions

A high pressure drop during operation is most frequently caused by solids build-up in the top portion of the bed. These solids come from the refractory lining of the secondary, volatile impurities in the primary and/or secondary catalyst, catalyst fines, solids in the process stream, and solids from a leaking waste heat boiler. These solids filter out in the top 1- to 3 ft. of the bed, coat the catalyst causing loss of activity and in the end, create a pressure drop high enough to cause a plant shutdown. The best cure for this problem is to remove the source. However, if the source cannot readily be removed, the judicial selection of catalyst particle size arranged properly in the top part of the bed will help one live with the problem. If the source of the solids cannot be removed, the best long range solution is a guard vessel ahead of the high temperature shift convertor which may be by-passed to replace the catalyst when the pressure drop becomes too high.

The backblowing of a high temperature shift convertor to maintain operation is an expedient measure that can be used at times to extend the life of a charge of high temperature shift catalyst. This is usually applicable where solids are entering the bed with the process feed. Where action of this type is used, a more serious problem is present which should be corrected.

Occasionally, high CO leakage is caused by channeling, resulting from poor gas distribution in the top of the converter. The entering gas blows the catalyst around reducing it to fines and piles it up in the middle of the bed or on one side leaving a shorter path for the gas to travel to the exit. In some cases, where the dust or fines are distributed evenly across the top of the catalyst bed, a high pressure drop may shut down the plant before channeling becomes too severe.

The improper operation of waste heat boilers frequently cause the collection of solids in the high temperature shift converter. *(3)* The process gas temperature can be affected to an extent that it causes high CO leakage. If the waste heat boiler becomes fouled to an extent that the inlet temperature to the high temperature shift is too high, the exit CO may go above the design value because of the water gas shift equilibrium. If the waste heat boiler is too efficient and lowers the process gas temperature below design, the exit CO may go above the design value because of the kinetics of the reaction. The same phenomenon may occur if the waste heat boiler leaks liquid water. This may lower the inlet process gas temperature below design as well as deposit solids and poisons upon the catalyst.

In many of the 600 to 1,500 ton/day plants, the volumes of high and low temperature shift catalysts are approximately equal, but the book price per cubic foot for the low temperature shift catalyst is two to three times the price of the high temperature shift catalyst. The performance of the high temperature shift catalyst can, in effect, control the performance of the low temperature shift catalyst if it evolves poisons, or allows a higher than design quantity of CO to be fed to the low temperature shift convertor.

A new charge of high temperature shift catalyst contains sulfur which is evolved during operation. If the sulfur is not removed during startup with the by-passing of the low temperature shift catalyst, the total sulfur quantity will be transferred to the low temperature shift catalyst, inactivating a portion of it. Effective desulfurization of the high temperature shift catalyst is required to achieve optimum life with the low temperature shift catalyst.

Even though the high temperature shift catalyst has been used commercially for 40 yr., mediocre or poor performance will be obtained unless the design engineer pays close attention to the inlet gas distributor, the preparation of the top of the bed, the solids in the process gas, the reduction procedure, the manner of desulfurization, the outlet temperature, the space velocity, the pressure, the S/G ratio, the particle size of the catalyst, the support apparatus, the dimensions and configuration of the vessel, and the chemical and physical characteristics of the catalyst. Excellent performance is obtained when these parameters are carefully studied and adopted according to the requirements of a particular plant.

Low temperature shift catalysts

Most ammonia producers are now using low temperature shift catalysts which, in their manufactured form, consist of copper oxide, zinc oxide, and alumina. These are high activity catalysts. The initial activity of these catalysts presently accounts for four- to sevenfold of the activity required by most designs. This has permitted operation of these catalysts at inlet temperatures of about 400- to 425^{o}F.

It is well know that many of the operating plants were designed when it was believed the low temperature shift catalyst would be operated with inlet temperatures of 430- to 470^{o}F. This has required many plants to operate their low temperature shift catalyst at these elevated inlet temperatures to properly balance out the heat exchange in the plant. Also, some plants have found it ncessary to by-pass a portion of the process gas around the low temperature shift catalyst to maintain sufficient temperature for operation of the methanator.

In a typical 1,000 ton/day ammonia unit, the design, or end of run carbon monoxide leakage may be as high as 0.5 mol % in the exit dry gas. In such a plant with new catalyst, the carbon monoxide leakage may be 0.20 mol % or less. To take full advantage of the high activity of the new low temperature shift catalysts, it is necessary to operate the catalyst at low temperatures. Typical equilibrium carbon monoxide concentrations which may be achieved with high activity catalysts, are listed in Table 3.

It is desirable to achieve as low a CO leakage as is practical. Usually, 0.1 mol % carbon monoxide leakage is equivalent to the loss of 10- to 14 tons/day of ammonia on a 1,000 ton/day unit.

Table 3
Equilibrium CO concentrations
vs temperature and S/G ratio

Equilibrium Temperature of	Equilibrium CO, mol % S/G	
	0.40	0.60
400	0.14	0.09
425	0.17	0.11
450	0.24	0.16
500	0.39	0.26
550	0.59	0.39
600	0.85	0.59

Methanation catalyst

Methanation catalysts, Figure 3, are in general use in the production of ammonia synthesis gas. Almost all recently designed ammonia plants include a methanator in their processing scheme. *(4)*. Usually, some type of nickel catalyst is used to promote the methanation reactions. These reactions are $CO + 3H_2 \rightarrow CH_4 + H_2O$, and $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. In a few instances, noble metal catalysts have been employed; however, their cost has limited their applications.

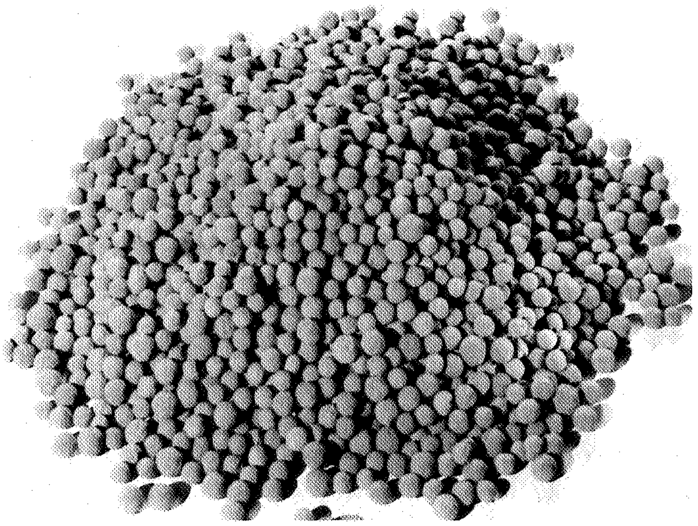


Figure 3. Methanation catalyst.

Nickel methanation catalysts supplied during 1970-71 have been in the form of spheres and tablets. The particle sizes have been in the range of 1/8 in. The average physical strength of the methanation catalyst particles has usually been greater than 20 lb. dead weight load. The bulk density of these catalysts on recent shipments has varied from a low of about 45 lb., to a high of near 80 lb./cu. ft.

The methanation catalysts have varied in nickel content from 15- to 35 wt. % in the latest commercial offerings. Catalysts containing 35- to 60 wt. % nickel exhibit greater activity and resistance to poisons, but the higher cost has limited their applications. More than 95% of the catalysts sold have been in the oxidized form requiring reduction for activation. The nickel oxides have usually been supported on an alumina or an oxide support containing calcium, aluminum, and silicon oxides. There has been a trend to lower silicon oxides in the supports. The surface area of the catalysts has been in the range of 50- to 100 M^2/gm with the lower silicon oxide content bases.

When methanation catalyst were first introduced, they were used in plants employing mono-ethanol amine for removal of carbon dioxide ahead of the methanator. There was concern during the early years of using methanators that the MEA carry-over would fould the catalyst. It was soon learned the MEA was hydro-cracked to methane, water, and ammonia with some degradation of the ammonia to nitrogen. The catalyst remained active under normal operating conditions following MEA carbon dioxide removal systems for run lengths in excess of 5 yr.

With the development of each new carbon dioxide removal system, such as hot potassium carbonate, catacarb, sulfolane, Benson and Fields, Vetrocoke, Econamine, Fluor Solvent Process, Purisol and others, the characteristics of the feed stream to the methanator has had to be restudied. With the proper design considerations, methanation catalysts have now demonstrated a good life after a number of these newer carbon dioxide removal systems. The operation of catalysts with higher carbon dioxide inlet loadings associated with many of the newer CO_2 removal processes has led to a greater appreciation of the differences in the rates of hydrogenation of carbon monoxide and carbon dioxide.

With the several new carbon dioxide removal systems and the design parameters available to the contractors, one may find that the methanator in his new plant is the first of its kind. In such cases, a careful review needs to be made of the principal variables affecting methanation to insure successful performance.

Variables to be considered should include; the type of catalyst (chemical and physical properties), the particle size of catalyst, the design temperatures (start of run and end of run,) the operating pressure, the space velocity, the effluent specifications, the normal feed gas compositions, the upset feed gas compositions, the trace contaminants in feed, and the methods of monitoring performance, as well as as the reactor and overall plant design. And finally, safety in high pressure methanator operations requires adequate trip out, depressuring, and venting provisions in case of runaway temperature conditions.

Ammonia synthesis catalyst

The successful production of anhydrous ammonia depends on reacting hydrogen and nitrogen over a catalyst under pressure at elevated temperatures. The catalysts used to promote the reactions ($N_2 + 3H_2 \rightarrow 2NH_3$) are fused iron oxide catalyst promoted with potassium, calcium, and aluminum oxides. The catalysts require reduction for activation. The catalysts are rugged and withstand repeated abuse. They are usually operated at pressures in the rage of 100 to 1,000 atmospheres. The catalysts gradually age with use, but have now demonstrated a life in excess of 5 yr. in the low pressure large tonnage plants.

To achieve the optimum production of ammonia with a given charge of catalyst in a synthesis loop, perhaps the most significant variable within the operator's control is his operating temperature. Table 4 lists several typical equilibrium concentrations of ammonia at two different pressures with several temperatures. These are shown to emphasize the large variation of ammonia concentration with temperature.

As with the high temperature shift catalyst, there is confusion among

Table 4
Equilibrium concentrations of NH_3, mol %

Temperature, °F	Pressure, lb./sq. in. gauge 2,000	4,000
800	23.4	35.4
850	18.2	29.5
900	14.2	24.4
950	11.3	20.1
1,000	8.9	16.6

As with the high temperature shift catalyst, there is confusion among plant operators due to a lack of understanding of the interplay of the kinetics and the equilibrium of the synthetic ammonia reaction. If the exit bed temperature is too high, the concentration of ammonia will be below the design value because of equilibrium. If the exit bed temperature is too low, the concentration of ammonia also will be below the design value because of the kinetics even though the equilibrium is more favorable. To optomize the production from a given converter, the operating temperatures must be carefully reviewed and the temperatures adjusted as the catalyst ages.

In conclusion

Rapid progress has been made in improving the operation of catalyst in the large tonnage ammonia units. The catalysts are being subjected to fewer upsets and less abuse. Longer run lengths should contribute to the achievement of better plant safety records.

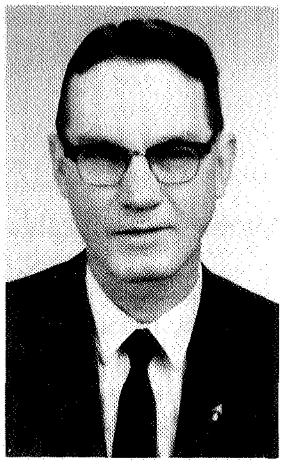
Acknowledgment

Our thanks to Dr. R. M. Reed, chemical engineering consultant, for his critical review and comments. #

Literature cited

1. Fleming, H.W., and J.S. Cromeans, "Primary Reforming Catalyst," paper presented at Ammonia Plant Safety Symposium (September 2, 1970).
2. McCallister, Robert A., *Chem. Eng. News,* 30 **49** (May 17, 1971).
3. Attebery, J.R., "Failure of a Primary Waste Heat Boiler," in CEP Technical Manual "Ammonia Plant Safety," **12,** 34 (1970).
4. Habermehl, Robert, "Recent Economics in the Productions of Ammonia Synthesis Gas," paper presented at Symposium on Recent Advancements in Nitrogen Fertilizer Processes, AIChE 57th Annual Meeting, Boston (December 1964).

FLEMING, Harold W.



CROMEANS, John S.

DISCUSSION

ANDERS NIELSEN, Haldor Topsoe, Denmark: I would like to make a comment to the discussion on primary reformer catalyst problems. It is true that in high pressure high severity reformers, the catalyst has a different job, and I agree that if there is an excessive amount of sulfur passing through the purification system, this is certainly one possible cause of problems. Another explanation which has been mentioned to account for reformer problems is the presence of higher contents of higher hydrocarbons in the feed resulting in a greater tendency to carbon lay-down.

We do believe that while the sulfur poisoning and presence of higher hydrocarbons in the feed are certainly important factors and may be the cause of the problems in many cases, they alone are not responsible for all of the problems you described with large numbers of hot spots or hot bands as sometimes found in reformers. We believe such problems may occur simply if the catalyst activity is too low to cope with the demands to it set by the heat flux into the tube. We believe that at such conditions higher hydrocarbons and also methane can crack in the gas film at the inner tube surface resulting in a carbon deposition on the inner tube surface.

You mentioned that there has been increasing use of different catalysts and that small-size particles have been used successfully in the upper part of the tubes. It would be reasonable to expect that small catalyst particle size would improve the problem because as we know, the reforming reaction is to a large extent diffusion limited so when you pack small catalyst particles you also pack more activity which would then help the situation. Small particles also mean higher pressure drop and we believe what is called for is a catalyst of extremely high activity in the upper half or two thirds of the tubes.

I should like to make also a small comment on what you said about the methanation, and particularly the question of reaction rate of carbon monoxide versus that of carbon dioxide. I believe John Cromeans said yesterday that roughly the rate of methanation of carbon monoxide is approximately twice that of carbon dioxide. I think we have an additional effect here being that when both compounds are being methanated simultaneously the carbon monoxide is more strongly chemisorbed by the catalyst and so preferably converted. Therefore, although this is a crude over-simplication, the catalyst tends to convert the carbon monoxide before it really starts converting the carbon dioxide.

Q. Will you please describe the variation in activity of calcium aluminate catalyst that have been used in the past with time in service?

FLEMING: Yes, the calcium aluminate base catalyst is probably the most active catalyst initially on the market today. They have a high surface area which at the operating temperatures in a reformer slowly changes, transforming gamma to alpha alumina that has a low surface area. This affects activity adversely. The high area alumina reacts readily with nickel oxide when it has an opportunity and anytime the catalyst is exposed to steam without the presence of hydrogen or natural gas, there is the opportunity of converting some nickel to nickel oxide and reacting it with the calcium aluminate base to make an inactive form of nickel aluminate.

Then in addition to the deterioration of the alumina surface area and the formation of nickel aluminate, the calcium aluminate base catalyst lose physical strength rapidly the first day the catalyst is placed on stream and continue to lose it as it is used. Now, in spite of these reactions, if one starts a plant up and operates it, a calcium aluminate base catalyst does wonderful. But the more upsets, the more one overheats the catalyst, the more severe is the catalyst activity loss, until finally in the upper part of the reformer furnace where the low temperature activity is needed most, there is little activity left. If the plant operates without upsets and the catalyst is not overheated, this activity loss occurs very slowly and a run length of one to two years has been obtained.

However, what we find in the top ten feet of the tube with a calcium aluminate base that has been overheated several times is a fairly inactive catalyst which causes high tube wall temperatures. Initially, the tube well temperature is about 1575 to 1600°F and during the first three months the calcium aluminate base catalyst gives good performance. But if there have been some upsets or emergency shutdowns in six to nine months there will be a real hot furnace with skin temperatures approaching 1700°F.

The condition of the furnace really depends upon the temperature of operation for the catalyst. If the catalyst has been operated gently, this loss - this aging that we talk about, occurs rather slowly and a good run results. But, if the second day you are on stream, a natural gas feed is suddenly interrupted and the catalyst is heated to 1600 to 1700°F, then one may have aged the catalyst rapidly. So the picture you should have is that calcium aluminate works well in the hot part of the tube if its physical strength will stay with you. In the colder part, it works well if you treat it kindly, but if you mistreat it with heat, then you will have a problem rather quickly. Does this answer your question?

HAYS MAYO, Cooperative Farm Chemicals Assn.: Not entirely. There are many cases where the top fired reformer has not been abused, sulfur in the feed gas is low and the operating conditions have been rigidly adhered to and yet the catalyst loses activity to the extent that tube wall temperatures reach 1750° after three to six months operation. I was attempting to explore the curve showing decrease of activity with time under normal conditions, not upset conditions.

FLEMING: Well, you again get into the problem here, your type of furnace. With a down fired furnace, you put a lot more requirement in the top part of your tube than in an upfired furnace. I can't say really that a downfired furnace – that there has been one that has operated too well on calcium aluminate, although you will find occasionally a furnace that has done well. They'll go two or three years, but in most of the downfired furnaces, they've gotten into problems rather quickly, in six to nine months. And if you measure the activity of that catalyst, it has fallen way off.

Now in upfired furnaces where the firing in the upper ten feet is not severe, the calcium aluminate base operates satisfactory, and the furnace – overall furnace will run very properly. But what we have in calcium aluminate is an unstable catalyst and you could draw different curves with temperature, but in every case it will be losing activity. So when Hays wants me to draw a curve, I'd have to draw one based on temperatures, and I don't think there are any two reformers that average out the same temperatures.

But the point you should get is that calcium aluminate is unstable to heat, and if you can operate it gently, which you can in an upfired furnace, you can get real good service. Now the downfired furnace where it gets hotter quicker, then there is where I think you will find the big differences.

MAYO: I agree on the points.

DAVE WHITE, Borden Chemical: Some of the people I've discussed this problem with plus direct experience indicates that as the gas transmission lines and their LPG extraction services become overloaded, the heavy ends and even their circulating wash oils carry over and through their headers. If we are not alert to catch these spill overs on our OSR units, they become saturated, since you cannot regenerate out these heavy ends from the OSR carbons. The result is carbon build-up on the inlet reformer catalyst.

MAYO: The history of the top fired reformer using calcium aluminate catalyst is that a large percentage develop hot areas generally between eight and twelve feet from the top of the heated area in a period of 3 to 9 months after being put into service. This is not to say that calcium aluminate catalyst are not suitable for the service. It is to say that such catalyst used in the past have not been able to cope with the operating conditions imposed upon them in the top of the top fired reformer.

WHITE: Right, I know what you refer to. Another idea that has helped where you have these poor temperature profiles, hot bands, etc. At our meeting in Portland two years ago, our friends from Australia suggested using air with steam to oxidize this carbon build up during cooling and heating cycles. I asked John Cromeans to work up a safe procedure to do this since you could burn up your secondary reformer catalyst.

After 18 months and four cycles I can report that from one of the worst temperature profiles on the Chemico Reformer, we now have one of the best I've seen. This catalyst is five years old with many cycles and no catalyst change except on replaced tubes due to exit tee leaks.

I might add that on the first two cycles we found many pounds of both sulfur and carbon in our stripping steam effluent. Now we find less than a pound when we check. The real test is a good temperature profile.

FLEMING: Now this oil will definitely cause you a problem. However, this hot banding problem where you have gotten away from it with a smaller size, especially ceramic base, if you are getting this carryover, it's taking it. You know, Hays, again on calcium aluminate, the reason I am a little stubborn is that most of the hydrogen plants in contrast to ammonia plants have upfired or sidefired reformers and practically all of them are still on calcium aluminate and they will get two to three years service.

Now, it is only with the downfired reformer as used in the modern large tonnage ammonia plant that the calcium aluminate base operates about the way Hays says; you have a problem with it, and it is because of its inherent instability with temperature, and then in the upper parts you are requiring activity out of it which it will not keep with use.

G.P. ESCHENBRENNER, M.W. Kellogg Co.: I would like to question the last statements concerning hydrogen plants. I believe most hydrogen plants operate at considerably lower pressure levels than modern, large tonnage ammonia plants and, for these plants, any hot band problem or its absence is not related to the direction of the firing. We have constructed several downfired hydrogen plant reformer furnaces that have shown no signs of hot bands. The pressure level is a very significant variable and hot bands occurred first with high pressure reformers and changes to catalyst compositions. Recently there has been promising results with proper selection of catalyst in the high pressure downfired furnaces. In general, in order to minimize the catalyst volume and make maximum use of the available catalyst, it is desirable to heat the process fluid as rapidly as possible to the proper reaction temperature levels in the catalyst tubes. Downfired furnaces will achieve this objective best; and with the selection of suitable catalyst and optimum equipment sizes, catalyst volume and operating flexibilities are achieved. Joint developments between the furnace designers and catalyst suppliers are the best route to reliability in this particular area.

CECILIA KANG, Consultant, Princeton, N.J.: I would come back to the discussion on the calcium aluminate base catalyst. As we know, there are a large variety of calcium aluminate catalysts, and I don't think you can expect the same kind of performance on different types of calcium aluminate catalysts. As for the ceramic base catalyst you are right that it is more stable but also you start with a lower activity than the calcium aluminate type. May I ask, how does the aging curve of certain calcium aluminate catalysts compare with the ceramic base catalyst under normal conditions? Do you have this kind of information?

FLEMING: First, let's take the different varieties of calcium aluminate bases. Some plants have had in them at the same time all the varieties that they could buy. And by the end of six months, they could not tell any difference. Now there undoubtedly are some differences to begin with, but these differences aren't important. The first two or three months any catalyst works fine. But it's from the six months on that it's of importance. And we really haven't found much difference in the different calcium aluminate bases in the downfired reformer after a six months period.

Now the aging curves of calcium aluminate versus ceramic, let's say this, that the aging curve is much better for the ceramic based catalyst than the calcium aluminate. Originally you may find a little bit more activity on a high nickel calcium aluminate base, but with time the ceramic base, the activity of the ceramic base will not decay as rapidly and with time it will be at a higher level than the calcium aluminate base and basically the reason why is that the ceramic base has been fired and stabilized before use.

Its surface area is low. It's a stable material. It does not lose surface area to any extent. There may be small loss during use. Also, the reaction of nickel oxide with alpha alumina is much, much slower than with the higher area gamma alumina. So we don't get this taking the nickel out of service, so to speak, by forming nickel aluminate.

That doesn't happen nearly as readily. So that in the end, from six months on, the activity of the ceramic based will be higher than that of the varieties of calcium aluminate bases that I am acquainted with.

KANG: I disagree with some statement you just made here, there are some information about the calcium aluminate type base catalysts with service for two years, and you hardly find any nickel aluminate at most part of the tube, especially six feet and down. And also there are some bench scale information showing that even though you have some nickel aluminate, but when you have the temperature at something like 1100 degree F. and higher and with some hydrogen there or with the gas composition like the process gas, the nickel aluminate is reversible. You find instead of the nickel aluminate staying there, it reverses to nickel. So this is one point of difference in the aging.

I admit that the ceramic type base is more stable. My question is, under normal operating conditions, how long does the ceramic type base take to have higher activity than the calcium aluminate type: one year or two year or anything like that?

As for the six months statement there, I think I raise some question too. I have seen operating data for a year or two years without apparent appearance of hot band with the calcium aluminate type of base. It is not only limited to one unit; there are a few units like that.

FLEMING: is this a downfired furnace?

KANG: Yes, I'm referring to downfired furnace. And the reason I think you cannot say there are a lot of these is because, there are certain type of calcium aluminate base catalysts which are not widely in use. So you can't point your finger to this unit and that unit and you cannot make a definite conclusion about how fast the catalyst ages.

FLEMING: Well, let me state that during this past year, last year about this time people in some plants had just started replacing whole reformers with ceramic based catalyst, and up till that time they've tried all the calcium aluminate bases that were available on the market, and they had all kinds of experiences. Some of them change out at six months, some in nine months. I do not know of any that really were working satisfactorily for a year.

Now these units that I'm acquainted with, many of them have changed to the ceramic base, and to date they are happy with it. Now that is about a year on stream. And no one can say at this stage whether they will go two years. We will know this time next year. But the ones that were unhappy with the calcium alumihate base and have changed to ceramic have largely cured their problem.

JOHN LIVINGSTON, ICI, Billingham, England: I would first, Dr. Fleming, like to endorse some of the statements made by yourself and Hays about abuse of catalyst. We certainly found at Billingham that it's not so much the abuse of catalyst as the design of catalyst that I think is the all important factor. We have seen plants on long runs deteriorating steadily due to a loss of activity in the primary reformer catalyst. This was particularly, in fact almost entirely, the case with naptha feedstock.

Having turned the plants over to natural gas we have found that after running for something like 15 months in one plant and ten months on another one that there's been no drop in activity whatsoever. There in fact has been something like one, one and a half degree shift away from approach, and in fact some two months ago we opened up one that was down for other reasons and the reformer on the one that had run for 15 months and pressure drop measurements across catalyst in those tubes showed an increase after 15 months of only one pound.

I would now like to ask, a question. What possible parameters would you in fact change if I came to you asking for a methanator design giving you compositions which showed in fact a factor of two difference in the water inlet gas composition?

FLEMING: I believe you could take care of this with the activity of the catalyst. You have two ways to go. One is to increase the nickel content, and the other is to reduce the particle size. One may use a combination of both parameters if the desired results cannot be accomplished with one alone. Now, also temperature is a real good tool, but once a plant is designed you usually don't have any liberties in raising inlet temperature.

In the best designed plants, one takes the inlet temperature up to 600°F. Actually these methanation catalysts will run at an outlet up to 750 to 800°F and do a good job. So that there is really no technical problem here in coping with these parameters. It is generally the design of the plant that has already been fixed. If the parameters haven't been taken into proper consideration, then one is caught and the only solution is to change the activity of the catalyst with increased nickel content or smaller particle, or both.

PHILIP A. RUZISKA: Esso Research & Engineering Co.: I'd like to report on three high pressure reformers that we have using calcium aluminate catalyst. We have long-term experience with two different brands of calcium aluminate catalyst. In each plant we've had in excess of two years life. Two of our charges are still in operation after about two and a half years, while the third was recently replaced. These are all upfired units, and we have not experienced the catalyst difficulties reported with other furnace designs. We are very pleased with the upfired designs.