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CYANIC ACID SYNTHESIS IN A FLUIDIZED BED REACTOR

Kagaku Kogyo
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It is only fairly recently that cyanic acid, along with acetylene, ethylene, carbon monoxide, and other chemicals, has become an important raw material in the organic synthetic chemical industry. This has been due mainly to the increase in demand for cyanic acid resulting from the creation of polyacrylnitril type synthetic fibers known under such names as orlon, vinion-N, and chemstrand.

Cyanic acid was hitherto made by the Castner method where sodium cyanide, made from metallic sodium, charcoal, and ammonia, was decomposed by sulfuric acid. Since this is a relativelty costly method, an effort was made in a number of countries to discover a less expensive means of manufacturing cyanic acid. In response to the development of a polyacrylnitril synthetic fiber industry in Japan, research on cyanic acid production, not dependent on sodium cyanide, has been undertaken in various laboratories, and some of the results are known to have been already put into industrial practice.

1. Direct Method of Cyanic Acid Synthesis

The study of cyanic acid synthesis is not new and a number of patents can be found on the subject. The methods of cyanic acid synthesis can be generally classified into those which directly synthesize the acid from raw materials and those which indirectly involve a cyanide in their process. From the standpoint of economic large scale production, the former direct process should be our goal. Among the direct methods of cyanic acid synthesis sofar proposed are (1) the Andrussow method, (2) the formamide method, and (3) the methane-ammonia method. Andrussow's method uses methane, ammonia, and oxygen or air with a Pt or Pt-Rh screen catalyst, and it depends on the following exothermal reaction:[1]

$$2NH_3 + 2CH_4 + 3O_2 = 2HCN + 6H_2O + 23kcal$$

 [redacted]

Since this reaction is similar to that for synthesizing nitric acid by the oxidation of ammonia, its industrial application would seem feasible, and actually this process has been industrialized in the USA although details are not known.[2] Catalysts composed of platinum type metals are known to wear excessively at high temperatures in a carbon-containing atmosphere, and much research is going on in order to improve this situation, including the use of alumina-based Pt catalysts.[3] In Japan, the Koei Kogyo KK (Koei Industrial Co., Ltd.) constructed a sodium cyanide plant at Yaizu in Shizuoka Prefecture in 1944 based on this reaction, but the plant never went into operation. Recently, Prof. Sasaki of the Yamagata College made detailed studies of this process, and he reports fairly successful results with experimentation on a pilot plant scale.[4]

The formamide method is a method which was originally studied by W. Reppe and others, and it consists first of synthesizing methyl formate from methanol and carbon monoxide under pressure, using sodium methylate or similar catalysts, then reacting this methyl formate with ammonia to form formamide and methanol, this methanol being recovered and the formamide dehydrated to yield cyanic acid.(5)

$$CH_3OH + CO \longrightarrow HCOOCH_3$$

$$HCOOCH_3 + NH_3 \longrightarrow HCONH_2 + CH_3OH$$

$$HCONH_2 \longrightarrow HCN + H_2O$$

Although this reaction must take place under pressure and although the process has several steps, it has a great advantage over the other methods in that HCN of fairly high concentration can be obtained in the final stage of the process. On the other hand, since formamide decomposes relatively easily into carbon monoxide and ammonia, the dehydration process must be undertaken under rigidly controlled conditions and with a properly selected catalyst.[6]

$$HCONH_2 \longrightarrow CO + NH_3$$

If pure carbon monoxide becomes more easily available with the popularization of the carbide closed furnace or through some other development, this method of cyanic acid synthesis could become much more important industrially. At present, the Yokohama Plant of the Nitto Chemical Company uses this method in Japan.

The third methane-ammonia method has also been investigated for many years (7) and it is based on the following endothermic reaction,

$$CH_4 + NH_3 = HCN + 3H_2 - 64 \text{ kcal}$$

where the reaction products are HCN and hydrogen gas. The merits of this method are that the concentrations of HCN and hydrogen in the reaction product gas are fairly high, and since there are no water-soluble gases such as carbon dioxide in the product gas, the separation of HCN is fairly simple. Recently a method has been reported in which oxygen, sufficient to maintain self-combustion, is added to the methane-ammonia mixture, and in which the heat from this combustion is utilized in the endothermic HCN synthesis reaction so that no catalyst is required.(8) This process seems quite interesting, and it can be considered to be a method intermediate between the first and third processes.

2. Study of Cyanic Acid Synthesis with a Fluidized Red Reactor

Although the methane-ammonia process has the advantages mentioned above, it also has its problems such as that of proper materials for the reaction tube and thermal economy, resulting from the high reaction temperature involved. There is also the problem of thermal decomposition of methane and ammonia at the wall of the reaction chamber or at the surface of the catalyst due to the high temperatures involved, or of decomposition by catalytic cracking, that is,

$$CH_4 \rightarrow C + 2H_2$$

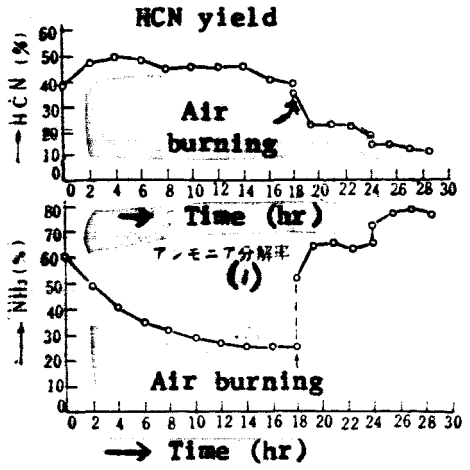
$$2NH_3 \rightarrow N_2 + 3H_2$$

and the adsorption of carbon, resulting from the decomposition of the methane, on the surface of the catalyst is known to significantly reduce the activity of the latter. Many of the patents taken out on this process generally allow a high rate of gas flow and the use of a catalyst with reduced activity in order to minimize methane decomposition, an example of such a catalyst being sintered alumina particles. Under such circumstances, temperatures as high as 1000° to 1300°C are required to obtain a reasonable yield of HCN. With these problems in mind, the author and his collaborators investigated catalysts suitable for this reaction with the purposes of (i) reducing the reaction temperature without sacrificing cyanic acid yield, (ii) avoiding side reactions by means of improving catalytic efficiency, and (iii) finding a catalyst with low attrition.

We first conducted experiments with a fixed catalyst bed reactor, and investigated the characteristics of catalysts by measuring the time variation of cyanic acid yield and the rate of decomposition of ammonia.(9) Experimental conditions were: reaction temperature 1050°C, methane gas flow 200 cc/min, ammonia flow 100 cc/min, the methane gas being crude methane (natural gas) from the town of Mohara in Chiba Prefecture.

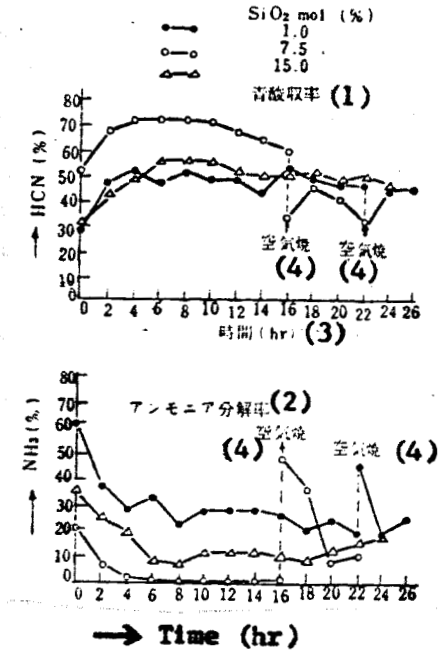
The catalysts tested were alumina and alumina-silica, and the results showed that neither was suitable because of severe loss of catalytic activity and also lack of durability. In Figures 1 and 2 are

shown typical experimental results with alumina and alumina-silica used respectively. The term "air-burning" in the diagrams signifies the pumping of air through the reaction chamber in order to burn out the carbon deposit. It should be noted in these results that the decrease in HCN yield is usually accompanied by a rapid increase in the rate of ammonia decomposition. For the alumina-silica catalyst (silica 7.5 - 10 mol%), the activity is very high for an hour or more, but it gradually declines with prolonged reaction time. Since it was discovered that this loss of activity was due to a solid phase reaction between the alumina and the silica occurring at high temperatures, we next turned our attention to an alumina-thoria type of catalyst which was expected not to have any objectionable solid phase reaction. The results of HCN synthesis with an alumina-thoria catalyst are shown in Figure 3, and they are quite satisfactory from the standpoint of catalytic activity and durability.



(1) Ammonia decomposition rate

Figure 1. Alumina catalyst



Legend:

(1) HCN yield
(2) Ammonia decomposition rate
(3) Time
(4) Air burning

Figure 2. Alumina-silica catalyst

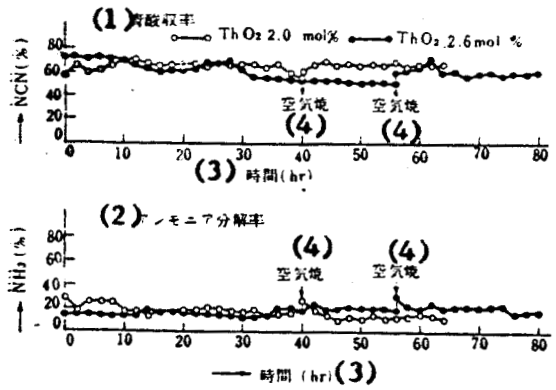


Figure 3. Alumina-thoria catalyst

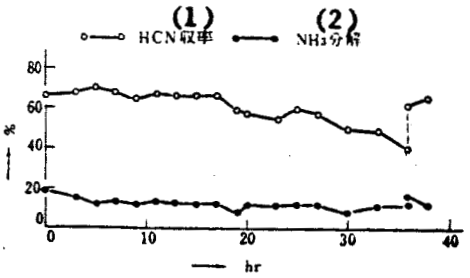


Figure 4.

As already mentioned, the reaction for synthesis of cyanic acid from methane and ammonia is strongly endothermic with 64 kcal required per mol, and one is confronted with the serious problem of how a large amount of heat is to be supplied to the reaction in the case of a physically large plant. We therefore turned our attention to a fluidized catalyst bed type reactor since in such a type of reactor, the temperature distribution in the reaction chamber is known to be fairly uniform and heat conduction is also good.

Now in a fluidized bed reactor, the catalyst particles collide with each other and the walls of the reaction chamber so that unless the particles can withstand abrasion, there will be scattering loss of the particles as well as other types of trouble. Also, depending on the linear velocity of the gas in the reaction tube, the catalyst particles must be of a certain range of sizes in order to maintain the fluidized state in the reactor bed. It is therefore necessary that the catalyst particles do not break up into finer particles when heated up to the reaction temperature.

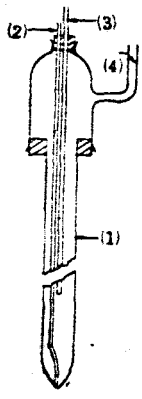
Considering industrial application as well as the satisfaction of the above mentioned requirements, the authors investigated the techniques for manufacturing alumina-thoria catalyst.[10] Our raw material was hydrated alumina ($Al_2O_3 \cdot 3H_2O$), an intermediate product in aluminum refining, and this was processed in the following manner:

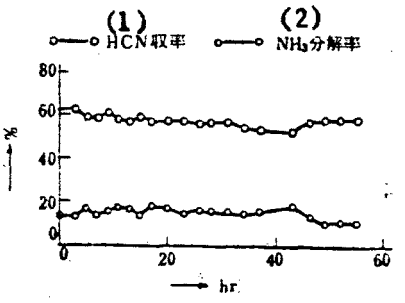
Dissolve → filter → sodium aluminate → hydroxide
↓
filter → gel → hot air dry → sinter
↓
wash → dry → final product

In other words, alumina hydrate is dissolved in caustic soda, the solids are filtered out, and the filtrate containing pure sodium aluminate is hydrolized with a dilute HCl solution containing thorium nitrate. The hydroxides of aluminum and thorium are both precipitated, filtered, and hot air dried. With the proper conditions for precipitation and drying, a very dense semi-transparent cake of the hydroxides is obtained. By sintering this for one hour at 300°C in a muffle furnace, the precipitate loses its gelling property, and it can then be easily washed. Upon washing, the catalyst generally breaks up into fine sand-like grains, but the particles opportunely turns out to be 30 to 100 mesh size in general which is exactly the grain size suited to the present purpose. Also since this disintegration in size occurred through natural fracturing during washing, these small particles now have the least strain, and are durable to impact and abrasion.

The efficiency of this catalyst was first tested by means of the fixed catalyst bed method, and it was found that at a reaction temperature of 1050°C, the thermal decomposition of methane was severe and the cyanic acid yield was simultaneously reduced considerably. By lowering

the reaction temperature to 950°C, the results shown in Figure 4 were obtained, the results stating that catalytic efficiency was not lost at this lower temperature. We therefore ran an experiment with the reaction tube (fused quartz) shown in Figure 5 with the experimental conditions being as follows: alumina-thoria catalyst (thoria 2 mol%) 60-80 mesh size, 30 cc; reaction temperature 900°C; methane flow 400 cc/min; and ammonia 200 cc/min. As shown in Figure 6, the average yield was about 58%.





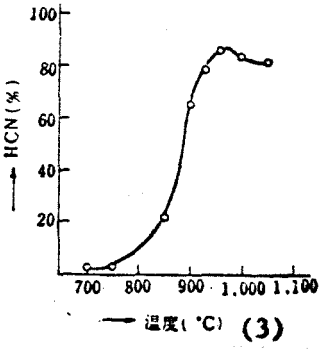


Figure 5. Figure 6. Figure 7.

Legend: (1) HCN yield
(2) NH_3 rate of decomposition
(3) Temperature

Since we now knew that an alumina-thoria catalyst which was specifically prepared for use in a fluidized bed reactor retained its high activity at lower reaction temperatures, we next turned to an investigation of a simple alumina catalyst, not containing thoria, which would have been of more advantage in industrial application. The alumina catalyst was prepared in the same manner in which the alumina-thoria catalyst was prepared, that is by the HCl-hydrolysis of sodium aluminate. Taking 50 cc of 30-100 mesh size alumina catalyst prepared in this manner with a methane flow of 400 cc/min and ammonia flow of 200 cc/min, the cyanic acid yield as a function of reaction temperature was as shown in Figure 7, where it can be seen that there was maximum yield at 950-980°C. At a reaction temperature of 930°C, the HCN yield as a function of time was as shown in Table 1 and Figure 8.

o — o HCN yield • — • NH_3 rate of decomposition

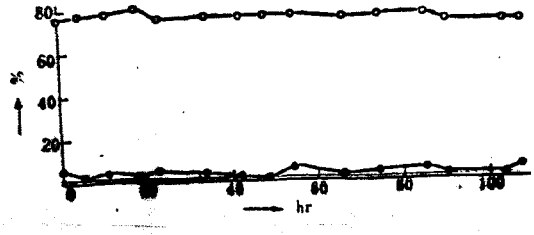


Figure 8.

Table 1

Time (hrs)	HCN yield (%)	NH_3 rate of decomposition (%)	Exhaust gas
1	77.0	5.4	50.8
5	78.0	3.2	50.7
11	78.2	4.6	50.2
18	80.8	2.7	49.5
23	75.8	5.4	48.5
34	76.7	3.8	49.6
42	76.3	2.5	49.1
48	77.0	1.9	50.2
54	76.6	6.7	49.8
66	77.7	3.0	49.8
74	76.6	4.4	49.5
85	77.7	5.3	50.3
90	74.5	3.0	48.9
103	74.2	3.1	49.2
107	74.2	5.6	49.2

It can be readily seen that the yield hardly changes even after 100 hours of reaction time, and that the rate of decomposition of ammonia is also very small. In this particular experiment, the average HCN yield per ammonia consumed was 77%. The quantity and composition of the exhaust gas were also found to be fairly constant, that is, 50 liters/hr with a composition of 27% methane and 65% hydrogen. This proves that there is very little methane decomposition at the catalyst surface, and that this catalyst is characteristically efficient in promoting the HCN-synthesis reaction.

Based on the basic experiments just described, a small scale pilot test was carried out. The apparatus for making the catalyst consisted of a large wooden vat lined with paraffin and also a porcelain container. The water used for preparing the catalyst consisted of ordinary city tap water treated by the addition of aluminum sulfate and sodium aluminate solution with the upper clear part being drawn off for use. A sketch of the reaction apparatus is shown in Figure 9 where A, B, and C are the rotameters for ammonia, methane, and nitrogen respectively. The nitrogen was used to replace air in the reaction tube. D is a tubular electric furnace with silicon carbide heating elements, R is a transformer and thermostat control, T_1 and T_2 are thermocouples with the former actuating the thermostat, G is the HCN absorption tower, H is a gasometer for measuring the volume of the exhaust gas, I is a cooler for the water used for HCN absorption, and J is a water rotameter. The sheath for T_1 and the tube L introducing the gases into the reaction chamber were of opaque quartz, both of these tubes making an air-tight seal through the cast iron cap M. The materials and the dimensions of the main components of the apparatus are indicated in Table 2. The electric furnace and the upper section of the reaction tube can be seen in Photograph #1.

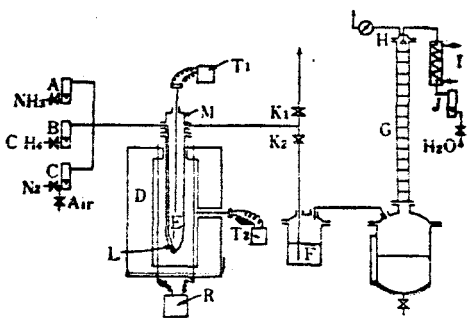
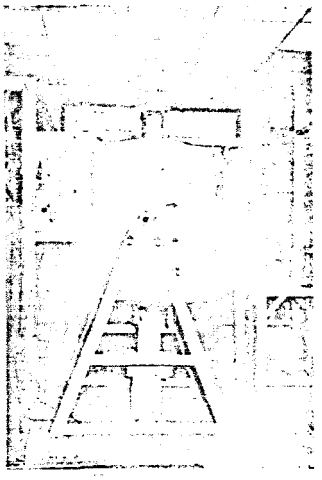


Figure 9.

Table 2

	Material	Dimensions	Remarks
Reaction tube	Transparent quartz tube	I.D. 70 mm Wall 5 mm Length 1000 mm	Hot section 480 mm long
Cyanic acid absorption tower	Copper	I.D. 115 mm 48 stages 100 mm apart	Single cap "bubble bell" type; iron HCN water tank, 200 liters



Photograph No. 1

The catalyst used in the pilot experiment was prepared in the same manner as for the basic experiment, and its properties were tested with the basic experiment apparatus. For both alumina-thoria and alumina catalysts, the results obtained in the pilot plant experiment were almost identical with those of the basic experiments as can be seen from the curves in Figures 10 and 11 for the two cases respectively.

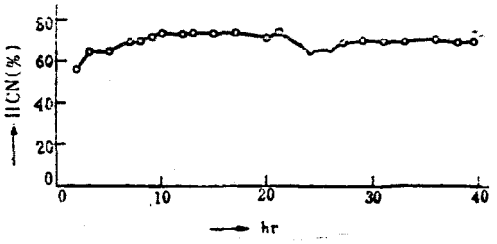


Figure 10. Alumina-thoria catalyst

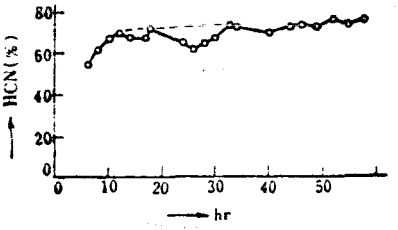


Figure 11. Alumina catalyst

For the case of the alumina catalyst, the slight drop in yield noted at 25 to 30 hours is due to a leak in the system, and the average yield was computed from the data for later than 33 hours of reaction time. The results of the pilot experiments are tabulated in Table 3.

Table 3

Type of catalyst	Alumina-thoria (thoria 2 mol%)	Alumina
mesh size	32-100 mesh	32-100 mesh
quantity	1250 cc (1100 g)	1250 cc (1140 g)
Flow velocity		
ammonia	5 liter/min	5 liter/min
methane	10 liter/min	10 liter/min
Reaction temperature	930 ± 10°C	930 ± 10°C
S. V.	720 hr^{-1}	720 hr^{-1}
Furnace temperature	1070-1100°C	1070-1100°C
HCN yield	72%	74%
NH_3 rate of decomposition	7.5%	6%
HCN yield/NH_3 consumed	90.5%	92.5%
S.T.Y.	208 g/hr/liter	214 g/hr/liter
HCN concentration	Ca 15 vol%	Ca 15 vol%

In the method of directly synthesizing cyanic acid from the raw materials methane and ammonia, the difficulties included are the high reaction temperature, the resulting thermal decomposition of methane and rapid loss of catalyst activity, and the problem of supplying adequate heat to the zone of endothermic reaction. The fluidized bed reactor method using a catalyst prepared according to the conditions discovered by the author and his collegues seems to fairly adequately resolve the first two of the three difficulties. Concerning the third problem, that is the problem of whether the diameter of the reaction tube could be enlarged as far as an economic unit, the problem mainly depends on thermal conduction in the fluidized bed reactor, but it could also be strongly influenced by preheating of the raw material gases, and on this point further investigation is necessary.

Since Japan's natural gas resources have been recently found to be more abundant than previously estimated, and also considering the clearly increasing future need for cyanic acid, the authors feel that a method using methane as a raw material warrants serious attention.

References:

(1) L. Andrussow, Angew.Chem., 48, 593 (1935); U.S.P.2, 478, 875 (1949).

(2) Updegraff, Petroleum Refiner, 197 (1953).

(3) Maffezoni, Chimica e Industria, 34, 460 (1952).

(4) Kazuo Sasaki and H. Endo, Kagaku Kogyo (Chemical Industry), 17, 302 (1953).

(5) Brit.P. 220,771 (1923), 279,530 (1926), D.R.P. 1,843,434 (1932).

(6) Japan Patent Announcement 2369 (1950).

(7) Brit.P. 335,585; 349,958, D.R.P. 548,798.

(8) Japan Patent 216341.

(9) Otake, Nakagawa, Ohara, Harada, Ninomiya, Kogyo kagaku zasshi (Journal of Industrial Chemistry), 59, 121 (1956).

(10) Otake, Nakagawa, Ohara, Harada, and Ninomiya, ibid., 59, 151 (1956).

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