

## Characteristics of Pt-Rh Gauze Catalyst and Kinetics of the HCN Synthesis

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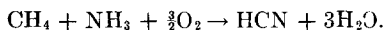
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Investigations were done on the HCN synthesis via the combustion of methane, air, and ammonia over Pt-Rh gauze catalyst. A pack of new catalyst required 60 to 80 hr to be fully activated. It could then maintain its economical life for several thousand hours. The relationships of catalyst activity with morphological change, crystal structure, surface area, and gauze impurities were defined. After external diffusion resistance was eliminated, maximum conversion of  $\text{NH}_3$  to HCN was found at a certain contact time. During this period, the rate of HCN formation was approximately first order each with respect to  $\text{NH}_3$  and  $\text{CH}_4$ .

### INTRODUCTION

The most common process for the synthesis of HCN involves the reaction of methane, air, and ammonia over 90% Pt-10% Rh gauze catalyst. This is an autothermal process and the contact time on catalyst is only several milliseconds. In the common practice of industrial production, the feed composition is within the range of  $\text{CH}_4/\text{NH}_3 = 0.7 \sim 1.7$  mole ratio, and  $\text{air}/(\text{CH}_4 + \text{NH}_3) = 2.80 \sim 3.25$  mole ratio. In addition to some side reactions producing minor by-products, the overall reaction for the HCN formation can be expressed as



Andrussow (1) and Mihail (2) attempted to calculate the number of Pt-Rh gauze layers required for a desired  $\text{NH}_3$  conversion, considering  $\text{NH}_3$  diffusion to or from the catalyst surface as the rate-controlling step. Later, Pan and Roth (3) formulated a method to optimize HCN yields through mathematical correlation of feed ratios and reaction temperature. However, no attempt was ever made to estimate the rate of HCN formation and little information was available on catalyst characteristics.

This paper presents new knowledge in these areas, thereby leading to a better understanding and further improvement of this extremely fast catalytic reaction.

### EXPERIMENTAL METHODS

The data for this study were obtained from operation of a pilot plant having a 4-in. i.d. stainless steel reactor. Procedures for operation of the pilot plant were the same as those (4) described previously, but in the investigation of the effect of contact time, gauze catalysts having 3 to 24 layers were employed and feed throughput to the reactor was varied from 87 to 150 lb/hr. The used gauze samples having 2000 hr on-stream, however, were taken from a commercial HCN reactor.

Several special analytical methods have been utilized in this investigation. The crystal structure and interstitial elements of gauze catalyst were determined by Meta-Chem Laboratory in Houston, Texas. The former was done with X-ray diffraction and the latter with vacuum diffusion and hot extraction.

The surface area of gauze catalyst was measured with a model 212C Perkin-Elmer Shell Sorptometer. Nitrogen was used as

adsorbate and helium as inert carrier gas. The specific surface area was calculated using the BET equation. This method has been described by Wise and Lee (8).

The surface iron concentration on the gauze catalyst was determined using a colorimetric method. After the surface of a catalyst sample was leached by boiling at least 2 hr in concentrated HCl, the solution was filtered and diluted with distilled water. Bathophenanthroline and isoamyl alcohol were added to the diluted solution to extract the dissolved iron. A portion of the organic layer from the solution was taken into an absorption cell. Its absorbance against a blank was measured with a Beckman Model B spectrophotometer. From the calibration of synthetic samples containing various amounts of iron, the surface iron concentration was then calculated from its absorbance and the total sample weight.

It has always been a difficult task to obtain the complete off-gas analysis from the HCN reactor. When only HCN yield and conversion were concerned, chemical titrations were used to determine the concentrations of  $\text{NH}_3$  and HCN in the feed and off-gas. Specifically,  $\text{NH}_3$  was titrated against a standard solution of HCl, whereas HCN was titrated against  $\text{AgNO}_3$ . When a more complete off-gas analysis was required,

both a gas chromatograph (Carbowax 600 column) and a mass spectrometer were used.

## RESULTS AND DISCUSSION

### *Catalyst Activity*

After a pack of new gauze catalyst is installed in a reactor, catalyst activity rises sharply, then declines slowly with on-stream time as shown in Fig. 1 (6). Such a relationship holds for a wide range of feed composition and reaction temperature. In the common practice, the feed is made of  $\text{CH}_4/\text{NH}_3 = 0.7 \sim 1.7$ , and  $\text{air}/(\text{CH}_4 + \text{NH}_3) = 2.80 \sim 3.25$  mole ratios. The corresponding flame temperatures are  $1050 \sim 1250^\circ\text{C}$ . The catalyst activity defined here is  $\text{NH}_3$  conversion to HCN. As the catalyst on-stream time increases, the catalyst activity will increase to a peak of 65 to 70% conversion. The time required to reach the peak is called the activation period ( $t_a$ ). Afterwards the catalyst activity will remain practically constant for several hundred hours and gradually decrease as the on-stream time further increases. The exact activation period and the economical life of the catalyst depend on operating conditions as well as catalyst structure. Usually, activation takes 60 to 80 hr, while the economical life

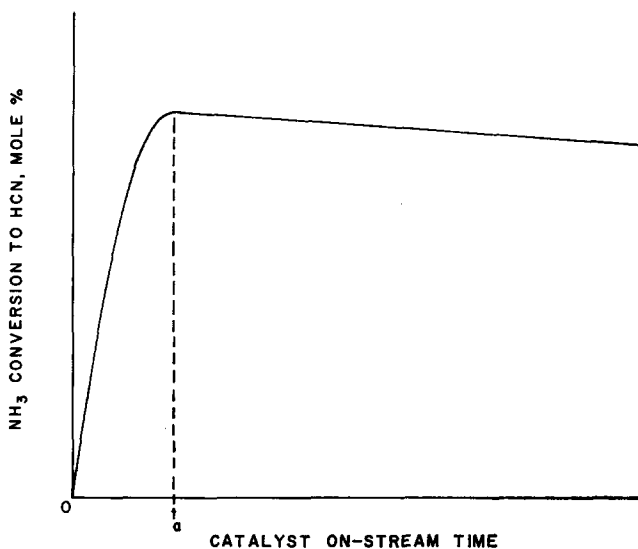


FIG. 1. Catalyst activity versus on-stream time.

can be several thousand hours. No noticeable loss of the Pt-Rh metal during the investigation has been encountered. With regard to the catalyst activity change, it is interesting to examine morphological change, crystal structure, surface area, and gauze impurities.

#### *Morphological Change*

The morphological changes could be clearly seen when gauze catalysts having various on-stream times were examined under a microscope. Figures 2, 3, 4a and b are 200 $\times$  magnification of new, activated, and used gauzes, respectively. The activated gauze has been on-stream for 77 hours and the used gauze has been on-stream for 2000 hours. The same feed ratio of  $\text{CH}_4/\text{NH}_3 = 1.085$  mole ratio, and  $\text{air}/(\text{CH}_4 + \text{NH}_3) = 3.090$  mole ratio was used in both periods.

As shown, the new gauze had a very smooth surface. The activated gauze formed whiskers which should result in an increase of active sites. Later, these whiskers were broken and the gauze wires were pitted as the on-stream time increased.

#### *Crystal Structure*

Crystal structure can be classified according to relative length and inclination of the crystal axes. Three structures can exist in the 90% Pt-10% Rh gauze catalyst: (i) face-centered cubic (f.c.c.) system, having three equal axes at right angles; (ii) face-centered tetragonal (f.c.t.) system, having three axes at right angles with two of equal length; and (iii) face-centered orthorhombic (f.c.o.) system, having three unequal axes at right angles.

Four samples of new gauze were examined by Meta-Chem Laboratory in Houston, Texas. A General Electric XRD-5 diffractionmeter was used. As shown in Table 1, three were f.c.o. and one was f.c.t. The pilot plant operations indicated that the f.c.t. structure demonstrated a better catalyst performance (a higher HCN yield) than the f.c.o. From the viewpoint of metallurgy, the f.c.c. crystal should have the largest catalytic effect and the f.c.o. should have the most brittle structure.

It was believed that interstitial elements,

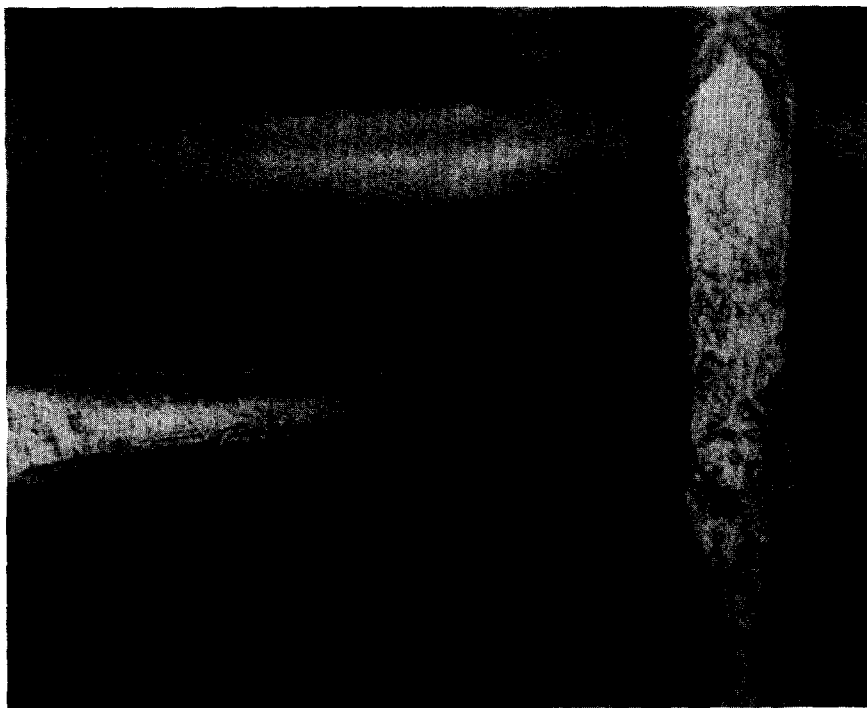


FIG. 2. New gauze, 200 $\times$ .



FIG. 3. Activated gauze, 200 $\times$  (77 hr).

TABLE I  
CRYSTAL STRUCTURE OF 90% Pt-10% Rh GAUZE  
CATALYST LATTICE CONSTANTS ( $\text{\AA}$ )

Condition	A	B	C	Structure
New	3.905	3.914	3.928	f.c.o.
	3.904	3.917	3.941	f.c.o.
	3.903	3.922	3.950	f.c.o.
	3.907	3.909	3.911	f.c.t.
Activated	3.902	3.911	3.913	f.c.t.

such as  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$  and C, contained in the gauze crystal and the residual strain of wire drawing during gauze manufacturing are two factors affecting the crystal structure. Several samples of new and used gauzes were examined for interstitial elements by Meta-Chem Laboratory. It was found that new and used gauzes had almost the same weights of  $\text{H}_2$  (4 to 7 ppm) and  $\text{O}_2$  (110 to 120 ppm), but the used gauze contained a much larger amount of  $\text{N}_2$  (270 ppm) than the new gauze (below 10 ppm). Thus,  $\text{N}_2$  from  $\text{NH}_3$ , HCN and air must have entered gauze crystals in the HCN synthesis.

During activation of a new gauze, probably some interstitial elements can be precipitated out and the residual strain of wire drawing removed, thereby, resulting in an improved catalyst. Another gauze sample from the same batch of the new catalyst was taken from the pilot plant reactor right after the activation period. Although no effort was made to measure the interstitial elements, yet the XRD data in Table I indicated that this particular gauze had already changed from f.c.o. to f.c.t. Along this line, a new gauze having f.c.e. structure should be obtained from the gauze manufacturer and further investigation of the crystal structure could be valuable to improving catalyst performance.

#### *Surface Area*

The specific surface areas of various gauze catalyst are given in Table 2. It is interesting to note that the surface areas of the used gauze Nos. 1 and 2 were much larger than the activated gauze, but after the used gauzes were burned with a methane-oxygen torch, their surface areas reduced to almost

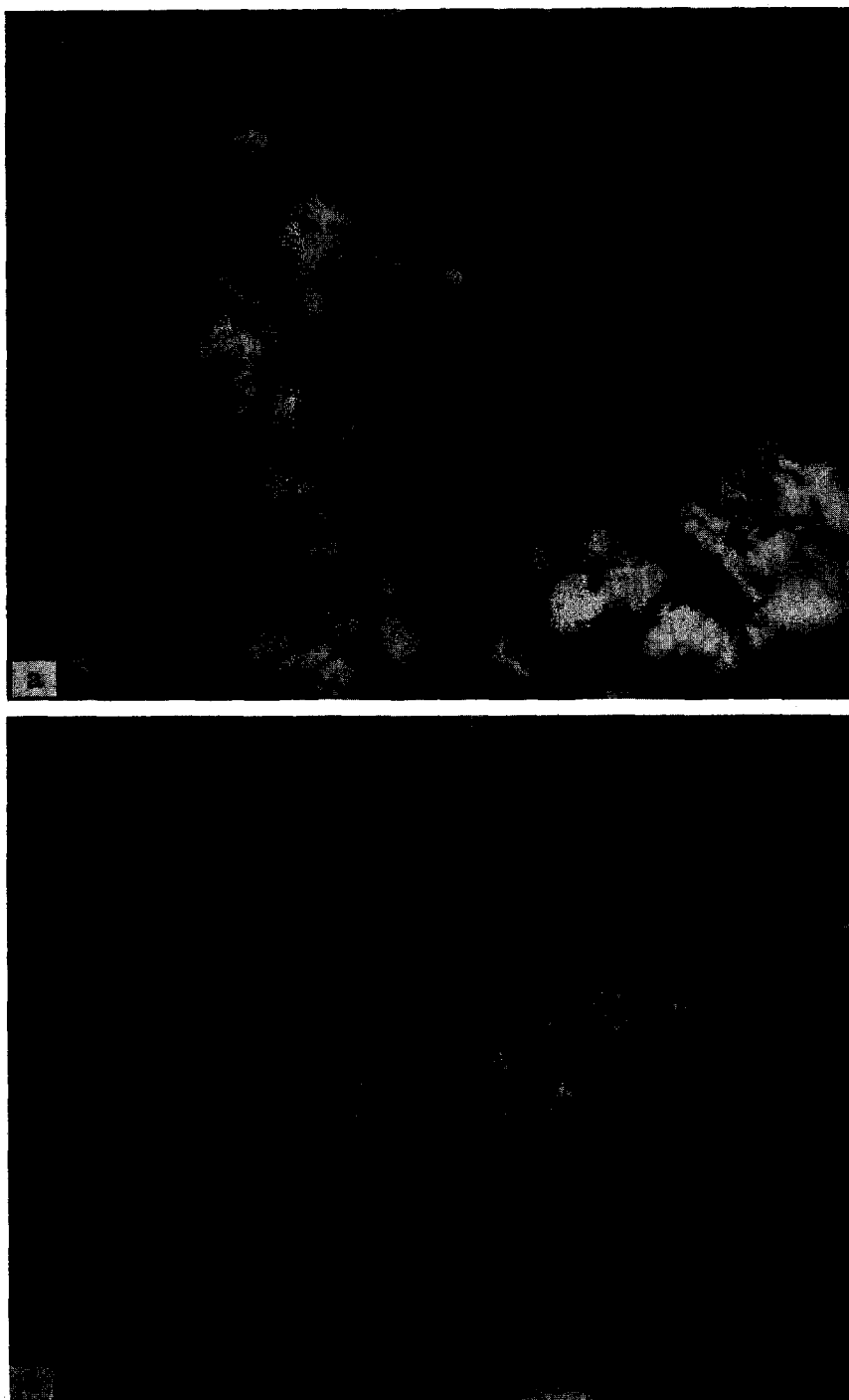


FIG. 4a. Used gauze (upstream),  $200\times$  (2000 hr); (b) used gauze (downstream),  $200\times$  (2000 hr).

TABLE 2  
SPECIFIC SURFACE AREA AND WEIGHT OF  
VARIOUS GAUZES

Sample	Orig. S. A. (cm <sup>2</sup> /g)	Treated S. A. (cm <sup>2</sup> /g)	Wt reduc- tion after treatment (%)
New gauze	55	—	—
Activated gauze	90	—	—
Used gauze, No. 1	220	101	.036
2 <sup>a</sup>	374	110	.085

<sup>a</sup> Burned with oxygen torch and water spraying.

the same as that of activated gauze. The temperature of burning was around 800°C and the weight of used gauze became constant after 5-min burning. It was also found that it was more effective to burn the carbon deposit by the methane-oxygen flame with water vapor than without water vapor. Table 2 shows that the burning with water vapor resulted in a weight reduction of 0.085% for the used gauze.

These results indicate that the increased surface area of used gauze was mainly caused by carbon deposit. Furthermore, samples of the used gauze Nos. 1 and 2 were also sent to the Meta-Chem Laboratory to determine the nature of the deposit on them. They were burned with oxygen at a higher temperature (1200°C). From the weight loss of sample and the collection of CO and CO<sub>2</sub>, it was determined that the carbon content was nearly 80% of the deposited material.

Generally speaking, a new gauze having a small specific surface area exhibits low catalyst activity. The activated gauze having a larger surface area gives a peak activity. The used gauze having the largest surface area, however, shows decreased activity. It is believed that when a pack of new gauze is under activation, its surface area is increased with the formation of whiskers which are responsible for the increased activity; but when the on-stream time continuously increases after activation, carbonaceous deposit gradually accumulates on the gauze surface. Consequently, the number of active sites decreases while the surface area increases.

Based on the data shown above, it is feasible to regenerate the used gauze by removing its carbonaceous deposit. The efficient way is to burn the carbon with water vapor at around 800°C which should not damage the gauze structure.

Two series of tests were conducted in the pilot plant reactor with the used gauze taken from a commercial reactor. The gauze regenerated with water treatment made a 2 to 3% higher HCN yield and conversion than the gauze regenerated without water treatment. The regenerated gauze with water treatment attained the peak activity originally observed in the commercial reactor. Above all, the restored catalyst activity of the water-treated gauze can be maintained for a longer time than the regeneration without water treatment.

It should be noted that in the regeneration of used gauze by removing carbon deposit, it is presumed that the used gauze has not been damaged by other causes. For example, if the gauze is already deactivated or poisoned by some impurity, the above regeneration is not effective.

#### Surface Iron

It has been known that gauze impurities are detrimental to catalyst activity. Among the common impurities, such as Fe, Pd, Ir, Au, and Cu, iron is most harmful. J. Bishop Company reported that their new Pt-Rh gauze contains 20 to 30 ppm by weight of iron which is the total iron analyzed by a spectrographic method. Our laboratory shows that the new gauze has 1.4 to 1.5 ppm by weight of surface iron analyzed by a colorimetric method. The pilot plant data indicate that catalyst activity can be largely affected by variation of the small amount of surface iron. The pilot plant stainless steel reactor was 4-in. i.d. containing six layers of gauze. When the feed throughput of 100 lb/hr at 14.7 psig and with CH<sub>4</sub>/NH<sub>3</sub> = 1.085, and air/(CH<sub>4</sub> + NH<sub>3</sub>) = 3.090 mole ratios was used, the HCN yield and NH<sub>3</sub> conversion to HCN had a linear relationship with respect to surface iron concentration as shown in Fig. 5. The HCN yield, *Y*, is defined as moles of HCN produced per mole of NH<sub>3</sub> consumed; and conversion of NH<sub>3</sub>

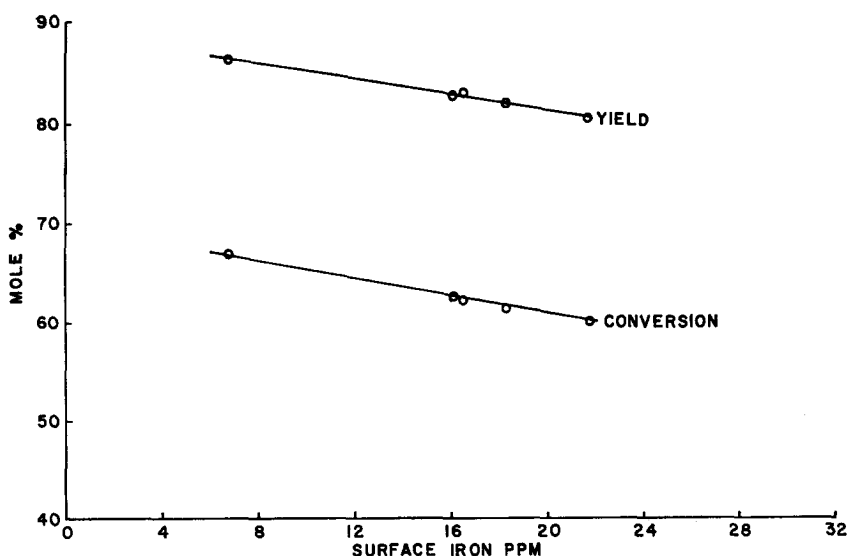


Fig. 5. Relation of HCN yield and conversion with surface iron.

to HCN,  $C$ , as the moles of HCN produced per mole of  $\text{NH}_3$  fed, as shown below:

$$Y = \frac{\text{HCN}}{(\text{NH}_3)_i - (\text{NH}_3)_o} \times 100 (\%),$$

$$C = \frac{\text{HCN}}{(\text{NH}_3)_i} \times 100 (\%),$$

where HCN = HCN produced (moles);  $(\text{NH}_3)_i$  =  $\text{NH}_3$  in the feed gas (mole);  $(\text{NH}_3)_o$  =  $\text{NH}_3$  in the off gas (mole).

On extrapolation, a HCN yield of 89% and a conversion of 69.8% are obtained for this feed composition if the gauze is free from surface iron contamination. Figure 5 also shows that the  $\text{NH}_3$  conversion to HCN decreases faster than the HCN yield. This means that the catalyst activity drops faster than does the selectivity.

It has also been found that if 35 ppm by weight of surface iron is present in a new gauze, it can never be fully activated. If 35 ppm of surface iron accumulates on the already activated gauze, a significant drop in catalyst activity will be observed immediately.

#### External Diffusion

In addition to determination of the physical and chemical properties of the Pt-Rh gauze mentioned above, thermodynamic calculations (5) for this process

have also been made. The results indicate the  $\text{NH}_3$  conversion to HCN would be negligible if the reaction system is allowed to reach thermodynamic equilibrium. This is because the equilibrium constants of several possible reactions in the complex system are larger than that of HCN formation from  $\text{CH}_4$  and  $\text{NH}_3$ . For instance, the equilibrium constant of  $\text{NH}_3$  decomposition to  $\text{H}_2$  and  $\text{N}_2$  is  $1.06 \times 10^4$  at  $1095^\circ\text{C}$  whereas that of HCN formation from  $\text{NH}_3$  and  $\text{CH}_4$  is only  $1.14 \times 10^3$ . However, the rate of HCN formation must be faster than the side reactions, otherwise this process would not be economically feasible. Thus, knowledge of the reaction kinetics is a key to further improve this process.

First of all, the mass transfer or external diffusion resistance between bulk gas phase and catalyst surface should be minimized so that it will not retard HCN formation. If the external diffusion becomes rate controlling, it will not only limit  $\text{NH}_3$  conversion to HCN, but will also adversely affect catalyst activation. As noted before, a pack of new catalyst is activated by surface combustion to increase the active sites. If surface combustion is limited by feed gas diffusion to the gauze catalyst, the activation period will be prolonged and the peak catalyst activity will be lowered (6).

Elimination of external diffusion resistance can be approached experimentally. When feed throughput to gauze catalyst is continuously increased, the formation of HCN will cease to increase beyond a certain throughput. At that point the external diffusion resistance apparently becomes negligible. In addition, the external diffusion resistance of the feed gas to the catalyst surface at various operating conditions can be calculated. This is done using the relationship of mass transfer and chemical reaction rate.

At steady state condition of a flow reactor, we have

$$r = N = K_g a (P_g - P_i), \quad (1)$$

where  $r$  = rate of chemical reaction [lb moles/(hr)(lb cat)];  $N$  = rate of mass transfer [lb moles/(hr)(lb cat)];  $K_g$  = diffusion-rate coefficient, [lb moles/(hr)(atm)(ft<sup>2</sup>)];  $P_g$  = partial pressure of gas diffusion in bulk phase (atm);  $P_i$  = partial pressure of gas diffusion at catalyst surface (atm);  $a$  = external area of catalyst (ft<sup>2</sup>/lb).

For various feed throughputs and gauze layers used in this investigation, the Reynolds number,  $dG/\mu$ , is less than 350. According to a correlation of mass transfer in a fixed bed reactor by Hougen and Wilkie (2), the following equation containing  $K_g$  can be used.

$$\frac{K_g M P_f}{G} \left( \frac{\mu}{\rho D} \right)^{2/3} = 1.82 \left( \frac{dG}{\mu} \right)^{-0.51}. \quad (2)$$

After  $K_g$  is eliminated from the above two equations, the diffusion resistance can be expressed in terms of pressure drop in the following equation:

$$\frac{P_g - P_i}{P_g} = \frac{M P_f r}{1.82 a G P_g} \left( \frac{dG}{\mu} \right)^{0.51} \left( \frac{\mu}{\rho D} \right)^{2/3}, \quad (3)$$

where  $M$  = molecular weight;  $P_f$  = pressure film factor (total pressure) (atm);  $G$  = superficial mass velocity [lb/(hr ft<sup>2</sup>)];  $D$  = molecular diffusivity (ft<sup>2</sup>/hr);  $d$  = diameter of catalyst particles or wires (ft);  $\rho$  = density of air, (lb/ft<sup>3</sup>);  $\mu$  = viscosity of air [lb/(hr)(ft)].

All the quantities involved on the right hand side of Eq. (3) can be calculated from

the feed composition and reaction conditions, and the reaction rate  $r$  can be estimated using the following equation:

$$r = \frac{x}{W/F}, \quad (4)$$

where  $x$  = NH<sub>3</sub> conversion to HCN (lb moles/lb mole of feed);  $W$  = weight of catalyst (lb);  $F$  = feed throughput (lb moles/hr).

For example, when the feed throughput of 100 lb/hr at CH<sub>4</sub>/NH<sub>3</sub> = 1.085, and air/(CH<sub>4</sub> + NH<sub>3</sub>) = 3.090 mole ratios is fed to 6 layers of gauze catalyst in a 4-in. i.d. reactor, at most the conversion of NH<sub>3</sub> to HCN is 70 mole % as shown in the preceding section; i.e., the HCN formation is at most 0.089 lb mole/lb mole of feed. Consequently, the calculated pressure drop from bulk feed gas to catalyst surface is only

$$\frac{P_g - P_i}{P_g} = 0.022 \text{ or } 2.2\%.$$

Such a pressure drop is negligible. In other words, the external diffusion resistance for such a feed throughput is negligible.

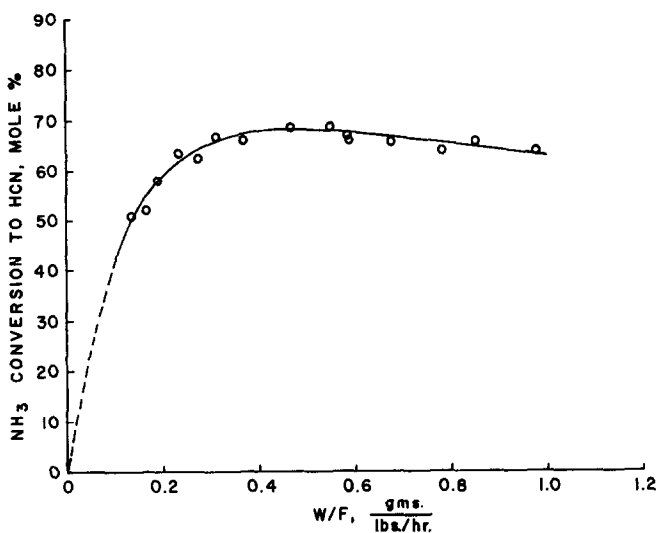
#### Contact Time and Reaction Scheme

After the external diffusion resistance has been reduced to avoid the possibility of its becoming rate controlling, the NH<sub>3</sub> conversion to HCN from a given feed is a function of contact time,  $W/F$ , which can be varied by catalyst weight,  $W$ , and/or feed throughput,  $F$ . Consequently, a maximum HCN conversion can be defined and the proposed reaction scheme can be examined. When feed A having CH<sub>4</sub>/NH<sub>3</sub> = 1.085, and air/(CH<sub>4</sub> + NH<sub>3</sub>) = 3.090 mole ratios was studied, its maximum conversion occurred at around  $W/F = 4.5$  g cat/(lb feed)/(hr) (see Fig. 6). When feed B having CH<sub>4</sub>/NH<sub>3</sub> = 1.417, and air/(CH<sub>4</sub> + NH<sub>3</sub>) = 2.964 mole ratios was tested, its maximum conversion occurred at  $W/F = 7.0$  g cat/(lb feed)/(hr).

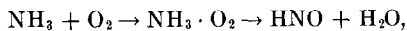
Figures 7 through 9 show the concentrations of major components NH<sub>3</sub>, HCN, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. But H<sub>2</sub>O was not determined quantitatively due to analytic difficulty.

Andrussow (1) assumed that the inter-

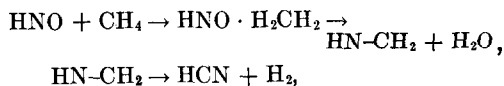


FIG. 6. Effect of contact time on NH<sub>3</sub> conversion to HCN, feed A.

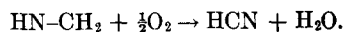
mediate of HCN formation is hyponitrous acid, HNO, which is produced thermally from the oxidation of NH<sub>3</sub>:



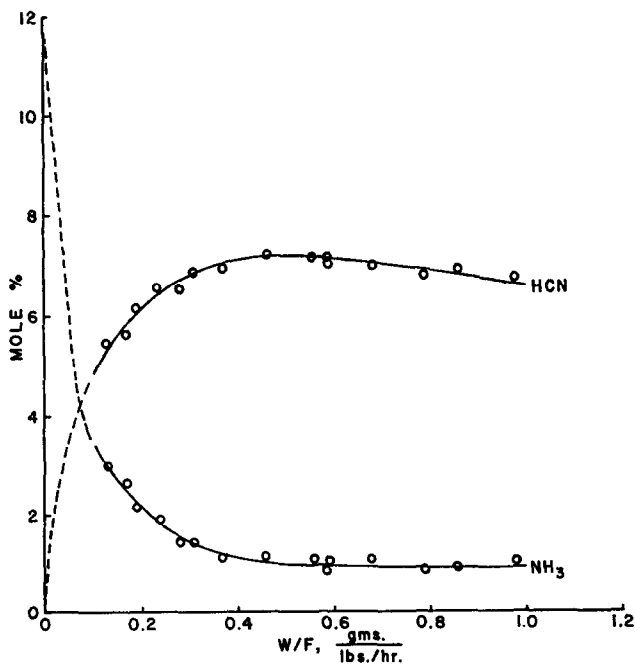
then the HCN formation proceeds through the following sequence:



or



Mihail ( $\beta$ ) assumed that oxidation of NH<sub>3</sub>

FIG. 7. Effect of contact time on HCN and NH<sub>3</sub> concentrations, feed A.

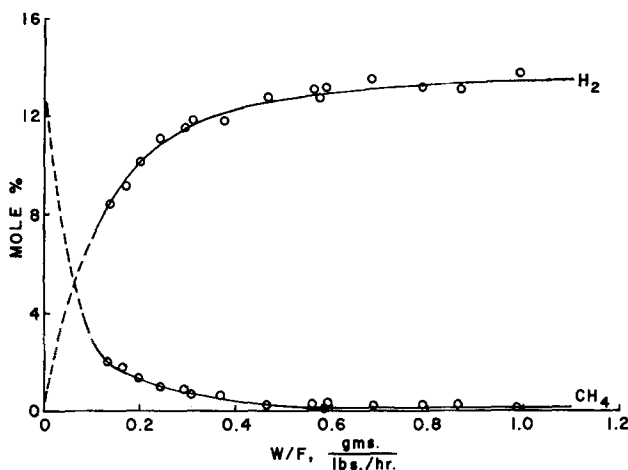
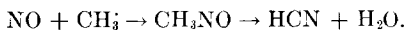


FIG. 8. Effect of contact time on H<sub>2</sub> and CH<sub>4</sub> concentrations, feed A.

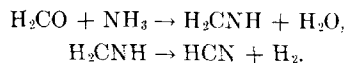
produces nitric oxide, NO, which is the intermediate and reacts with methyl radical to form HCN:



Mihail also suggested that methyl radical is formed in the gas phase and NO is formed through the reaction of adsorbed molecules of NH<sub>3</sub> and O<sub>2</sub> on gauze catalyst surface. Furthermore, the oxidation of NH<sub>3</sub> to NO liberates heat, which can raise gauze temperature to 600 ~ 700°C. It is sufficient to cause the combustion of methane-air mixture. After combustion of methane, the temperature is increased to 900 ~ 1000°C which is favorable for HCN synthesis.

Wendlandt (?) proposed that the inter-

mediate in the HCN synthesis may be formaldehyde, H<sub>2</sub>CO, which is produced by the oxidation of CH<sub>4</sub>. Consequently, HCN is formed as follows:



However, none of the above intermediates, HNO, NO, and H<sub>2</sub>CO, has been detected. Pan and Roth (4) proposed in an earlier paper that there is a preburning of CH<sub>4</sub> and NH<sub>3</sub> before the HCN formation, and the initial rate of CH<sub>4</sub> combustion is faster than that of NH<sub>3</sub>. Now Figs. 7 and 8 show that the disappearance of CH<sub>4</sub> is faster than that of NH<sub>3</sub>. Therefore, Wendlandt's proposal of an intermediate through the oxidation of

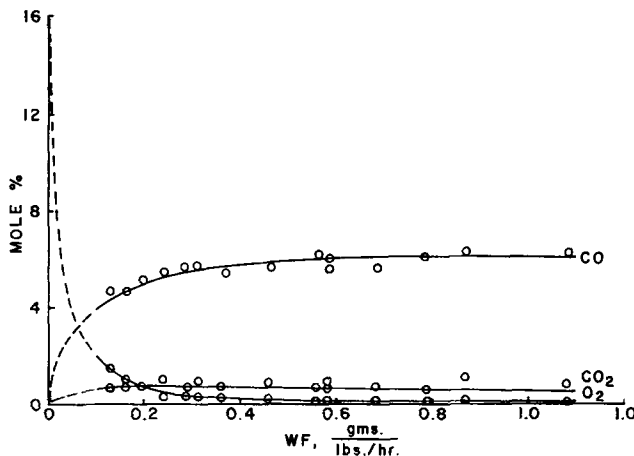
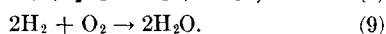
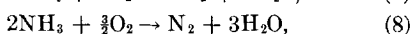
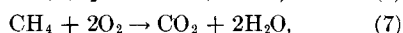
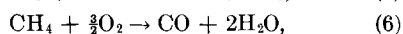


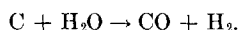
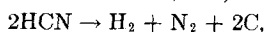
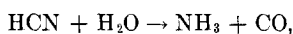
FIG. 9. Effect of contact time on CO, CO<sub>2</sub>, and O<sub>2</sub> concentrations, feed A.

CH<sub>4</sub> instead of NH<sub>3</sub> is in line with our observation.

Without discussing the detailed reaction mechanism, the author (5) proposed a reaction scheme in accordance with the results of 100 lb/hr of feed reacting over six layers of gauze catalyst:

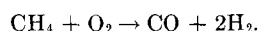


Furthermore, Pan and Roth (4) indicated that CH<sub>4</sub>, NH<sub>3</sub>, and O<sub>2</sub> always compete with one another in the parallel reactions (5) through (8). It is expected that CH<sub>4</sub> should react more rapidly than NH<sub>3</sub> at shorter contact time. These trends are shown in Figs. 7, 8, and 9. When the contact time increases, some consecutive reactions of HCN would occur:



Therefore, a maximum HCN concentration should occur with the formation of more CO and H<sub>2</sub>. It is also possible that the

competition of CH<sub>4</sub> and NH<sub>3</sub> for O<sub>2</sub> would restrict somewhat the oxygen reaction with CH<sub>4</sub> to form CO<sub>2</sub> and H<sub>2</sub>O, then CO and H<sub>2</sub> would also come from CH<sub>4</sub>:



Since nitrogen oxides have never been detected, no similar reaction for NH<sub>3</sub> combustion to liberate H<sub>2</sub> is given.

Based on the above reaction scheme, NH<sub>3</sub>, CH<sub>4</sub>, and O<sub>2</sub> will continue to decrease as contact time increases, and H<sub>2</sub>, CO, and CO<sub>2</sub> continue to increase, but HCN passes through a maximum. These trends are indicated in Figs. 6 through 9.

#### Kinetic Equation

Since there is a maximum NH<sub>3</sub> conversion to HCN, apparently a consecutive reaction of HCN should proceed significantly after the optimum contact time. But the rate of HCN formation from beginning to the maximum conversion should be simply via the reaction of CH<sub>4</sub> and NH<sub>3</sub>. Therefore, the rate equation for this period could be correlated in one of the following three forms:

$$r = k_1 P_{\text{NH}_3},$$

$$r = k_2 P_{\text{CH}_4},$$

$$r = k_3 P_{\text{NH}_3} P_{\text{CH}_4}.$$

TABLE 3  
RELATION OF  $r$  WITH  $P_{\text{CH}_4}$  AND  $P_{\text{NH}_3}$  OF FEED A<sup>a</sup>

$W/F$	$\Delta(W/F)$	$\Delta v W/F$	$C$	$\Delta C$	$P_1$	$P_2$	$\frac{r}{P_1}$	$\frac{r}{P_2}$	$\frac{r}{(P_1)(P_2)}$
0.10			4.15						
	0.05	0.125		1.10	4.20	6.00	5.238	3.667	0.873
0.15			5.25						
	0.05	0.175		0.65	3.00	4.94	4.333	2.632	0.877
0.20			5.90						
	0.05	0.225		0.40	2.40	3.80	3.333	2.105	0.877
0.25			6.30						
	0.05	0.275		0.25	1.80	3.16	2.778	1.582	0.879
0.30			6.55						
	0.05	0.325		0.15	1.30	2.64	2.310	1.136	0.874
0.35			6.70						
	0.05	0.375		0.10	0.90	2.52	2.222	0.794	0.882
0.40			6.80						
	0.05	0.425		0.05	0.50	2.28	2.000	0.439	0.877
0.45			6.85						

<sup>a</sup> Note:  $r = \Delta C / \Delta(W/F)$ ;  $W/F = (\text{g cat})(\text{hr})/\text{lb of feed}$ ;  $\Delta C = \text{conversion } (\% \times 10^2)$ ;  $P_1 = P_{\text{CH}_4}$  (atm  $\times 10^2$ );  $P_2 = P_{\text{NH}_3}$  (atm  $\times 10^2$ ).

TABLE 4  
RELATION OF  $r$  WITH  $P_{\text{CH}_4}$  AND  $P_{\text{NH}_3}$  OF FEED B<sup>a</sup>

$W/F$	$\Delta(W/F)$	$A_v$	$W/F$	$C$	$\Delta C$	$P_1$	$P_2$	$\frac{r}{P_1}$	$\frac{r}{P_2}$	$\frac{r}{(P_1)(P_2)}$
0.10				5.05						
	0.10	0.15			0.75	5.60	6.10	1.339	1.230	0.220
0.20				5.80						
	0.10	0.25			0.45	4.20	4.90	1.071	0.918	0.219
0.30				6.25						
	0.10	0.35			0.29	3.20	4.10	0.906	0.707	0.221
0.40				6.54						
	0.10	0.45			0.20	2.50	3.68	0.800	0.543	0.218
0.50				6.75						
	0.10	0.55			0.15	2.10	3.30	0.715	0.455	0.218
0.60				6.90						
	0.10	0.65			0.12	1.80	3.00	0.667	0.400	0.222
0.70				7.02						

<sup>a</sup> Note:  $r = \Delta C / \Delta(W/F)$ ;  $W/F = (\text{g cat})/(\text{hr})/\text{lb of feed}$ ;  $\Delta C = \text{conversion } (\% \times 10^2)$ ;  $P_1 = P_{\text{CH}_4}$  (atm  $\times 10^2$ );  $P_2 = P_{\text{NH}_3}$  (atm  $\times 10^2$ ).

The rate data,  $r$ , can be evaluated from  $\text{NH}_3$  conversion to HCN for a given feed ratio:

$$r = \frac{d\text{HCN}}{d(W/F)} = \frac{\Delta\text{HCN}}{\Delta(W/F)} = k \frac{\Delta C}{\Delta(W/F)},$$

where  $k$  is also the  $\text{NH}_3$  molar concentration in feed.

Two feed ratios, A and B, were investigated at 2 atm. Feed A had  $\text{CH}_4/\text{NH}_3 = 1.085$ , and  $\text{air}/(\text{CH}_4 + \text{NH}_3) = 3.090$  mole ratios. Feed B had  $\text{CH}_4/\text{NH}_3 = 1.417$ , and  $\text{air}/(\text{CH}_4 + \text{NH}_3) = 2.964$  mole ratios. For convenience, the derivatives were approximated by the first difference shown in Table 3. The rate data of Feed A were taken from Fig. 6. The partial pressures  $P_{\text{CH}_4}$  and  $P_{\text{NH}_3}$ , or molar concentrations were taken from Figs. 7 and 8. Similarly, the rate data of feed B were obtained and tabulated in Table 4. The reaction (flame) temperature of feed A was  $1107 \pm 3^\circ\text{C}$  and that of feed B was  $1092 \pm 3^\circ\text{C}$  at various contact times. The former was  $15^\circ\text{C}$  higher than the latter because of an enriched air mixture. All the data show that the values of  $r/(P_{\text{NH}_3})(P_{\text{CH}_4})$  are approximately constant for a given feed ratio. In other words, the rate of HCN

formation was approximately first order each with respect to  $\text{CH}_4$  and  $\text{NH}_3$  concentrations.

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