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SYNTHESIS OF PRUSSIC ACID

Part 18

Acid or Alkali Treatment of Deactivated Alumina-Thoria Catalyst

By

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Abstract

Catalytic activity of alumina-thoria has been studied at 650°C for hydrogen cyanide synthesis from carbon monoxide and ammonia. The yield of hydrogen cyanide measured at 650°C was decreased by 30–40 per cent by subjecting the catalyst to heat treatment which was conducted at a more elevated temperature of 950°C in a stream of reactants. The reduced yield was restored to a considerable extent not only by the early reported H_2O- or H_2SO_4-treatment (ref. 1) but by HNO_3-, HCl-, or $Ba(OH)_2$-treatment. KOH-treatment increased slightly the reduced yield. The procedures of these water, acid and alkali treatments consisted of boiling the heat-treated catalyst with water or an aqueous solution of the appropriate acid or alkali. The variations in surface area and pore volume caused by each treatment were followed. An investigation also was made as to the effect of catalyst granule size on the catalytic activity.

It is concluded that H_2O- or $Ba(OH)_2$-treatment alters essentially neither surface area nor pore volume of the catalyst so that an enhancement of the activity caused by such a treatment is due entirely to changes in some physical and chemical properties of the catalyst itself, whereas the other acid or alkali treatments increase the average pore radius so that the effect of pore diffusion also may be responsible for the variations in activity caused by such treatments.

Introduction

HORIUTI and his coworkers[2,3] have found that an especially good yield of hydrogen cyanide is obtained by using alumina-thoria catalyst containing a small amount of sulfate. It is already known that[4] at the atmospheric pressure this catalyst maintains a constant cyanide yield for at least 300 hours at 650°C, but that[1,4] the yield at 650°C decreases remarkably accompanied by a remarkable decrease in surface area once it is used several hours at temperatures above 850°C. In the previous work[1], such a deactivated catalyst has been found to be easily regenerated by H_2SO_4- or H_2O-treatment to a consid-

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erable extent accompanied by only a slight increase in surface area.

One objective of the present work was to extend these treatment studies to other acids or alkalis. Another objective was to investigate the influence of catalyst geometry on the activity. The latter objective was accomplished by estimating the average pore radius of the catalysts treated variously and by comparing the catalytic activities of two catalysts different in granule size.

§ 1. Experimental

Two series of experiments were carried out as detailed later corresponding to the two objectives mentioned in the previous section, *i.e.* series 1 mainly for the extention of the treatment studies and series 2 mainly for the investigations of the activity with reference to catalyst geometry.

Materials and Apparatus.—Alumina-thoria catalyst (3 weight per cent thoria) was prepared by drying and calcining gel made by coprecipitation from a mixed solution of ammonium alum and thorium nitrate with aqueous ammonia*). The catalyst was crushed and the 8–14 mesh or 20–40 mesh fraction was used. The detailed descriptions have been given previously[1,2], together with those of preparing reactants, *i.e.* carbon monoxide and ammonia. Guaranteed Grade acid or alkali was used for treating the catalyst.

The flow diagram and the reactor for the synthesis are illustrated in Figs. 1 and 2 of reference 1 respectively.

Treatment of Catalyst.—*Pretreatment.*–A mixture of 10 parts carbon monoxide and 1 part ammonia was passed through the reactor charged with freshly prepared catalyst. Total flow rate was 110 ccNTP/min. The catalyst was heated to 650°C in the stream and kept 8–10 hours at the temperature. This pretreatment has been reported to increase the catalyst activity to a constant value[4].

Heat Treatment.–As in the pretreatment, a mixture of carbon monoxide and ammonia was passed through the reactor charged with catalyst. This was heated to a more elevated temperature of 950°C and kept 9 hours at the temperature.

Treatment with Water, Acid, or Alkali.–Catalyst was boiled five minutes in a quartz beaker with 100 cc of distilled water or of an aqueous solution of sulfuric acid, hydrochloric acid, nitric acid, potassium hydroxide, or barium hydroxide. The liquid was decanted after it had been cooled to a room temperature, and the catalyst was dried one hour at 100°C. The weight of catalyst used and the concentration of the acid or alkali are listed in Table 1.

*) Ammoniacal water was added to the mixed solution until its pH reached 9.

TABLE 1. Conditions of various treatments of catalyst in series 1.

Kind of treatment	Temp. (°C)	Time	Concentration of solution (N)		Weight of catalyst (g)	
			Before treatment	After treatment	Before treatment	After treatment
Pre.	650	10 hr			20.07	15.13
Heat	950	9 hr			13.11	12.73
KOH	b. p.	5 min	0.86	1.39	1.84	1.70
$Ba(OH)_2$	b. p.	5 min	0.22	0.29	1.76	1.79
H_2O	b. p.	5 min			1.66	1.68
HCl	b. p.	5 min	1.07	1.65	1.77	1.66
HNO_3	b. p.	5 min	0.98	1.51	1.86	1.75
H_2SO_4	b. p.	5 min	1.08	1.45	1.91	1.79

The increase in concentration during the acid or alkali treatment is due to vaporization of water by the boiling. The decrease in catalyst weight during the treatment will be discussed later.

Determination of HCN Yield.—A mixture of carbon monoxide and ammonia was passed through the reactor charged with catalyst just in the same way as in the case of the pretreatment. The determination was started as soon as the catalyst had attained to a constant temperature of 650°C, the outlet gas was bubbled one hour through 100 cc of 1 N potassium hydroxide, and the solution was analyzed for cyanide as described in the previous paper[1].

Determinations of Surface Area and Pore Volume.—The surface area of catalyst was measured by the BET method using nitrogen as the adsorbate at the liquid nitrogen temperature. The cross-sectional area of a nitrogen molecule was assumed to be 16.2 Å^2.

The pore volume of catalyst was estimated from the adsorption amount at a relative pressure of 0.98 on the desorption branch of nitrogen isotherm at the liquid nitrogen temperature.

Series 1.—A granular sample (*ca.* 20 g of 8–14 mesh) of freshly prepared catalyst was first subjected to the pretreatment. With *ca.* 1.6 g of thus pretreated catalyst the yield of hydrogen cyanide and the surface area were determined. The remaining portion was heat-treated and then divided into several portions, one of which was used for the determinations of the yield and the surface area. The others were further treated each with one of the acids, alkalis, and water as mentioned above, and then subjected to similar determinations. The yield determination on each portion of the catalyst was repeated three times once every two hours. Every treatment mentioned above

disintegrated a small fraction of the catalyst into fine particles, which were sieved and discarded.

Series 2*).—A granular sample (a mixture of *ca.* 3 g of 8–14 mesh and *ca.* 4 g of 20–40 mesh) of freshly prepared catalyst was first subjected to the pretreatment, and then sieved so as to obtain 8–14 and 20–40 mesh portions discarding disintegrated fractions. The determinations of the yield of hydrogen cyanide, surface area, and pore volume were successively conducted on each portion. These two portions were then mixed together, subjected to the heat treatment, divided again into 8–14 and 20–40 mesh portions, and the yield *etc.* were determined on each portion. The 8–14 mesh portion was now subjected to the H_2O-treatment, while the 20–40 mesh portion to the H_2SO_4-treatment, and then the yield *etc.* of each portion were determined similarly. The yield determinations in this series were conducted twice to five times successively once every hour.

§ 2. Results and Discussion

Series 1.—The experimental results are summarized in Table 2.

TABLE 2. Experimental results of series 1. Variations in surface area and in hydrogen cyanide yield with various treatments of catalyst

W_b, catalyst weight before the measurements of X; W_a, catalyst weight after the measurements of X; S_1, specific surface area of catalyst (referred to W_a); X, yield of hydrogen cyanide in percentage conversion of ammonia into hydrogen cyanide (three figures in a row are arranged from left to right in order of measurement).

Treatment	W_b (g)	W_a (g)	S_1 (m^2/g)	X (%)		
Pre.	1.61	1.60	162	43.1	42.4	41.6
" +Heat	1.61	1.62	110	31.6	31.3	31.6
" + " +KOH	1.61	1.58	124	33.5	32.5	32.8
" + " +$Ba(OH)_2$	1.61	1.58	113	36.7	35.4	34.6
" + " +H_2O	1.60	1.57	115	36.9	36.6	36.0
" + " +HCl	1.59	1.50	123	32.3	38.1	38.3
" + " +HNO_3	1.60	1.51	126	39.9	38.7	38.7
" + " +H_2SO_4	1.62	1.51	120	41.2	40.3	39.6

*) In this series a small amount of asbestos had to be placed between the catalyst bed and the perforated porcelain plate in the reactor to support smaller catalyst granules. The catalytic activity of the asbestos was confirmed by blank test to be quite negligible as compared with that of the alumina-thoria catalyst.

Apparently heat treatment brings about considerable reductions in both surface area and yield of hydrogen cyanide. The subsequent acid, alkali or water treatment increases only slightly the reduced surface area, while its effect on the yield depends appreciably on the sort of treatment. KOH-treatment increases the reduced yield only slightly, $Ba(OH)_2$- and H_2O-treatments more, and HCl-, HNO_3-, and H_2SO_4-treatments restore it nearly to the value before the heat treatment. Three successive measurements of the yield on each of these treated catalysts are generally reproducible or have a slightly decreasing tendency with time with an exception of the HCl-treated one, which gives a poor yield in the first measurement followed by considerably improved ones in the second and the third measurements. This peculiar behavior of the HCl-treated catalyst appears to be related to the evolution of white fume, presumably of ammonium chloride, during the rise of the catalyst temperature to 650°C and for the subsequent one hour at the temperature, suggesting a poisonous effect of hydrochloric acid.

The catalytic activity k per unit weight of catalyst is now defined as

$$k = 0.01 \frac{M}{W} \ln\left(\frac{X_e}{X_e - X}\right), \qquad (1)$$

where M is the inflow rate of ammonia, W the weight of catalyst, X the

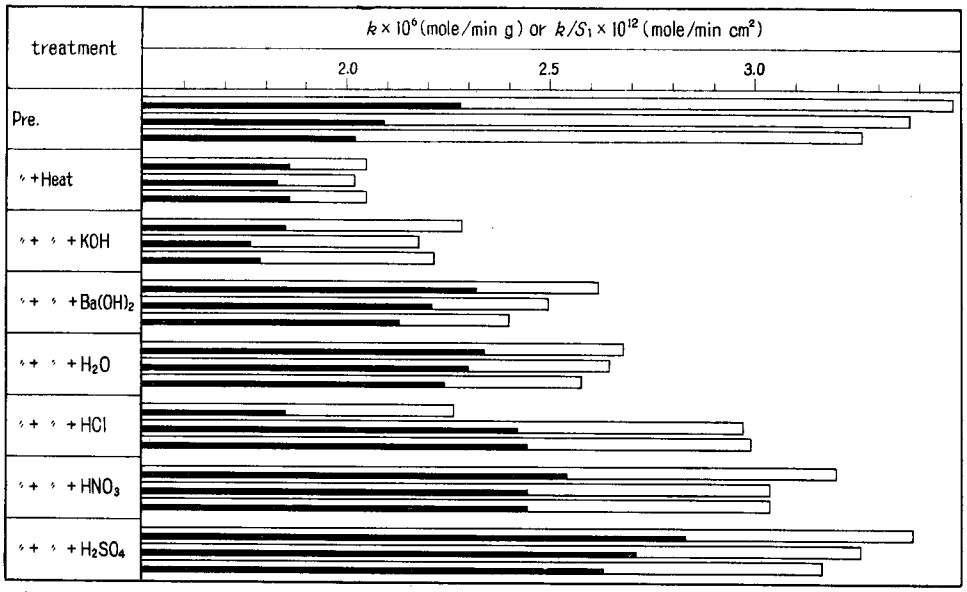

Fig. 1. Variations in activity with various treatments of catalyst (Series 1). White and black bands represent values of k and k/S_1 respectively.

percentage conversion of ammonia into hydrogen cyanide, and X_e the value of X at equilibrium. The value of X_e is taken as 60.4%*) at 650°C. Eq. (1) has been derived in the previous paper[1] on the basis of the rate law $R=k(X_e-X)$ established experimentally by HORIUTI, YANO, and KANAI[5], where R is the moles of hydrogen cyanide produced per unit time per unit weight of catalyst. Fig. 1 shows the calculated values of k and k/S_1, where S_1 is the specific surface area per gram of catalyst. The k/S_1 may be considered to represent the catalytic activity per unit surface area. The calculation of k was made from Eq. (1) by taking M as 4.46×10^{-4} mole/min and by identifying W with W_a in Table 2. The value of k, like the value of X, is highest for the catalyst just pretreated, and lowest for the pretreated and then heat-treated one, respectively denoted in Fig. 1 by "Pre." and "Pre.+Heat". It is of interest that, unlike the k- or X-value, the k/S_1-value of acid or alkali-treated catalyst exceeds that of just pretreated one with an exception of the KOH-treated, whose k/S_1-value is close to that of the "Pre.+Heat".

Here some considerations are given to weight loss of catalyst during the treatments or the synthesis runs. As seen in Table 1 no significant change in weight of catalyst was observed by H_2O- or $Ba(OH)_2$-treatment, whereas a marked loss was found in the cases of the other treatments. The loss brought about by pretreatment or heat treatment would be attributed to the reduction of sulfate contained in the catalyst to sulfide and to its liberation as hydrogen sulfide[1]. On the other hand, the loss by acid or alkali treatment would be attributed to the dissolution of alumina, since the acid or alkali solution with which the catalyst had been treated, deposited white and flocculent precipitate when neutralized with potassium hydroxide or nitric acid respectively. Table 2 shows that the acid-treated catalysts alone among others lost their weights significantly during the synthesis run. This loss appears to be due to the liberation of acid adsorbed by the catalyst during each acid treatment. This is evidenced by the evolution of hydrogen sulfide from the H_2SO_4-treated catalyst and of white fume (presumably of ammonium chloride) from the HCl-treated catalyst as above mentioned.

Series 2.—Table 3 summarizes the experimental results. The effect of granule size on activity is apparent both on just pretreated and the heat-treated catalysts. Surface area decreased when catalyst was heat-treated, and recovered slightly by the subsequent H_2O- or H_2SO_4-treatment. These variations in surface area by the treatments are similar to those in series 1 or in the previous work[1]. Pore volume V_1 per gram of catalyst remained practically

*) An equilibrium constant of 7.18×10^{-3} observed at 650°C for the reaction, $2CO+NH_3=HCN+CO_2+H_2$, was used (ref. 5).

TABLE 3. Experimental results of series 2: Effect of catalyst surface geometry on activity

G. S., catalyst granule size; V_1, total pore volume per gram of catalyst; $\bar{r}$, average pore radius; All other symbols have the same meanings as in Table 2 and Fig. 1.

Treatment	G. S. (mesh)	W_a (g)	X (%)*)	k**) (mole/min g)	k/S_1 (mole/min cm²)	S_1 (m²/g)	V_1 (cc/g)	$\bar{r}$ (Å)
Pre.	8-14	1.52	43.0 42.6 43.3 41.9 42.3	3.61×10^{-6}	2.25×10^{-12}	160	0.26	32
	20-40	1.45	44.6 45.4 43.8 43.3 44.3	4.07 〃	2.67 〃	152	—	—
〃 +Heat	8-14	1.39	27.8 27.5	1.97 〃	1.83 〃	108	0.26	48
	20-40	1.31	30.2 30.1	2.36 〃	2.18 〃	108	0.28	52
〃 + 〃 $+H_2O$	8-14	1.35	34.5 34.2	2.78 〃	2.40 〃	116	0.27	47
〃 + 〃 $+H_2SO_4$	20-40	1.07	36.2 35.9	3.78 〃	3.15 〃	120	0.38	63

*) The figures lie left to right in order of measurement.

**) The constant k is calculated from the appropriate mean value of X by Eq. (1).

unchanged by the heat- or H_2O-treatment, whereas significantly increased by the H_2SO_4-treatment. This is discussed later in connection with the average pore radius.

If a catalyst granule is assumed to have N cylindrical pores all of the same average pore radius $\bar{r}$ and of the same length, the $\bar{r}$ is given by the equation[6],

$$\bar{r} = 2V_1/S_1 . \qquad (2)$$

The values of $\bar{r}$ calculated are shown in the last column of Table 3. Four catalysts different in the final treatment are arranged in the order of increasing $\bar{r}$, Pre.$<$Heat$\simeq H_2O < H_2SO_4$, as designated by the final treatments. A comparison between "Pre." and "Pre+Heat" shows that heat treatment increased $\bar{r}$ leaving V_1 unchanged. This result can be explained by assuming that as catalyst sinters smaller pores vanish while larger pores grow just to compensate for the vanished pore volume. This explanation would be reasonable from a viewpoint of surface energy. Both V_1 and $\bar{r}$ were kept nearly unchanged or considerably increased according as the heat-treated catalyst was then subjected to the H_2O-treatment or to the H_2SO_4-treatment respectively. These results may be attributed to the corrosion of the catalyst by the latter treatment only. This explanation is consistent with the results of series 1 that H_2O-treatment does not alter the catalyst weight whereas H_2SO_4-treatment decreases it as seen in Table 1.

Remarks.—The variations in k/S_1 illustrated in Fig. 1 are now considered in some detail with reference to the data of series 2. Activity per unit surface area of porous catalyst, as measured by k/S_1 in the present case, is not necessarily decided only by the physical and chemical properties of the catalyst itself, but often influenced by gas diffusion in catalyst pores. The pore diffusion influences overall reaction rate as the reaction rate on the catalyst surface is so rapid that a concentration gradient of reactant gas arises in pores. The variation in k/S_1 with catalyst granule size as observed in series 2 may be regarded as an evidence for the effect of this pore diffusion. It would be expected that the larger the average pore radius $\bar{r}$ of porous catalyst is, the less is the reaction hindered, so that the catalyst activity, *e.g.* k/S_1, may increase with increasing $\bar{r}$ even if the physical and chemical properties of the catalyst itself remained unchanged. The decrease in k/S_1 caused by heat-treatment cannot therefore be explained on the basis of pore diffusion, since the heat treatment increases $\bar{r}$. Accordingly the decrease must be attributed entirely to change in some properties of catalyst itself. The enhancement in k/S_1 caused by H_2O- or $Ba(OH)_2$-treatment is a similar case. It was observed that H_2O-

treatment does not vary $\bar{r}$. $Ba(OH)_2$-treatment also is unlikely to vary $\bar{r}$, since $Ba(OH)_2$-treatment as well as H_2O-treatment does not decrease the catalyst weight as seen from Table 1 suggesting that the catalyst walls are not corroded by these treatments. The enhancement in k/S_1 is not thus due to the change in pore diffusion. The enhancement in k/S_1 caused by acid treatment, however, might be due entirely or partly to the change in pore diffusion, since HCl- and HNO_3-treatment would increase $\bar{r}$ similarly as experimentally confirmed in the case of H_2SO_4-treatment as seen from Table 3. This is consistent with the decrease in catalyst weight during each acid treatment as evident from Table 1, suggesting that the catalyst walls are corroded.

Bulk density of the catalyst remained constant at 0.7–0.8 g per cc throughout all the treatments of the present experiment. The catalyst was white when untreated, changed into yellow after pretreated, and into gray after heat-treated. Subsequent acid or alkali treatment caused no change in color.

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