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SYNTHESIS OF PRUSSIC ACID

Part 19

Catalytic Activity of Alumina

By

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Abstract

The rate of hydrogen cyanide synthesis from carbon monoxide and ammonia was measured at 400 and 650°C over three alumina catalysts different in sulfate content in order to investigate effect of sulfuric acid on the catalytic activity. These catalysts were prepared from different materials, *i.e.* ammonium alum, aluminum nitrate, and aluminum isopropoxide respectively. Sulfate contents of these catalysts were 1.5, 0.011, and 0.005 weight per cent in the order of description. Irrespective of this remarkable difference in sulfate content, the three catalysts agreed in activity to within several ten per cent, in activation energy to within 1 kcal, and in surface area to within a few ten per cent. The KOH-treatment of the alumina made from isopropoxide decreased its activity only slightly, whereas the H_3PO_4-treatment reduced it remarkably. The procedures for these treatments consisted in boiling the alumina catalyst for 5 min with aqueous solution of potassium hydroxide or orthophosphoric acid. These results appear to indicate that no sulfuric acid but alumina itself acts predominantly as catalyst.

Introduction

It has long been known that various metal oxides such as alumina, thoria, and urania act as catalyst for hydrogen cyanide synthesis from carbon monoxide and ammonia, *i. e.*

$$2CO + NH_3 = HCN + CO_2 + H_2 . \qquad (1)$$

On the other hand HORIUTI and KINOSHITA[1] had the idea that sulfuric acid also might catalyze the synthesis. With this idea HORIUTI *et al.* prepared alumina-thoria from ammonium alum and thorium nitrate so as to contain an appreciable amount of sulfate. Using this alumina-thoria as catalyst they succeeded in raising the yield of hydrogen cyanide under pressure[2,3]. In the previous work[4] conducted under atmospheric pressure, however, no distinct correlation was found between sulfate content of the catalyst and its activity. The main purpose of the present work is to compare the activity of alumina

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containing a small amount of sulfate with that of alumina of the highest possible purity. The effects of KOH- or H_3PO_4-treatment on the activity are also investigated using the pure alumina catalyst in order to cast light upon the mechanism of the synthesis.

§ 1. Apparatus and Materials

1. 1. Apparatus. The flow diagram and the details of reactor were illustrated in Figs. 1 and 2 of reference 4 respectively.

1. 2. Catalysts. Alumina containing a significant amount of sulfate was prepared from ammonium alum, while aluminas of the highest possible purity were prepared from aluminum nitrate or aluminum isopropoxide.

Catalyst I (alumina from ammonium alum).—A 10 per cent solution of $Al(NH_4)(SO_4)_2 \cdot 12H_2O$ was precipitated with 3 per cent ammonia. The resulting slurry was filtered, and the precipitate was dried 20 hours at 50°C, further 20 hours at 100°C, and finally calcined 3 hours at 750°C. The hard lumps were crushed in a mortar and sieved to obtain 8–14 and 20–40 mesh fractions. This catalyst was pretreated*) 8 hours at 650°C in a stream of carbon monoxide and ammonia, flow rates of which were set to 100 and 10 cc NTP/min respectively. Pretreatment like this is reported[5)] to be necessary to activate catalyst in the case of alumina-thoria catalyst containing a significant amount of sulfate.

Catalyst II (alumina from aluminum nitrate).—Ammonia was bubbled through 10 per cent solution of $Al(NO_3)_3 \cdot 9H_2O$ cooled in an ice-bath. The resulting slurry was filtered. The precipitate was washed with water, dried overnight at 100°C, and calcined 3 hours at 750°C. The rather soft, friable lumps were broken with a spatula and sieved.

Catalyst III (alumina from aluminum isopropoxide).—Redistilled aluminum isopropoxide (80 g) was dissolved in 200 cc of isopropyl alcohol and hydrolyzed by adding dropwise 400 cc of water purified by means of ion exchanger. The resulting slurry was filtered, the precipitate was washed repeatedly with the purified water, then dried and calcined as in the case of catalyst I. The resulting very hard, dense lumps were crushed in a mortor and sieved.

Catalyst III_K (catalyst III treated with KOH).— About 1.6 g of an 8–14 mesh fraction of catalyst III was boiled 5 minutes with 100 cc of 1 N KOH, allowed to stand until the solution comes to room temperature, the supernatant solution decanted, and the residue dried at 100°C for one hour.

Catalyst III_P (catalyst III treated with H_3PO_4).—About 1.6 g of an 8–14 mesh fraction of catalyst III was treated with 3 N orthophosphoric acid and

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*) The pretreatment decreased the catalyst weight from 5.2 to 4.4 g.

dried in the same way as in the preparation of catalyst III_K.

1. 3. Gases. Carbon monoxide and ammonia have been prepared as described previously[4)].

§ 2. Experimental Procedures

Hydrogen cyanide yield, surface area, and pore volume were determined in that order with an 8–14 mesh fraction of each catalyst, and in the case of catalyst I with a 20–40 mesh fraction as well. Sulfur contents of catalysts I, II, and III were measured with portions of freshly prepared catalyst neither pretreated nor subjected to any measurement.

2. 1. HCN Yield. A mixture of 10 parts carbon monoxide and one part ammonia in volume was passed through the reactor charged with catalyst. Total flow rate was 110 cc NTP/min. The catalyst was then heated to a reaction temperature in the stream. As soon as the catalyst attained to the temperature the determination of yield was started. For the determination, outlet gas was bubbled one hour through 100 cc of 1 N or 0.2 N potassium hydroxide. The solution was then analyzed for cyanide as described previously[4)].

On catalyst I, II, or III, the yield determination was conducted at 650°C and then at 400°C for 3 hours respectively, while on catalyst III_K only at 650°C for the same period of time. In the case of catalyst III_P, reaction temperature was raised stepwise to 250, 300, 400, and 650°C, and then lowered again to 400°C. The yield determination was conducted once to three times consecutively at each temperature.

2. 2. Surface Area. This was measured by the BET method with use of nitrogen as the adsorbate at the liquid nitrogen temperature. The cross-sectional area of a nitrogen molecule was assumed to be 16.2 $Å^2$.

2. 3. Pore Volume. A weighed sample of granular catalyst was refluxed 15 minutes with benzene or carbon tetrachloride. The mixture was allowed to come to a room temperature, the liquid was decanted, and the catalyst was superficially dried and weighed. The weight increase divided by the density of benzene or carbon tetrachloride gives the volume of benzene or carbon tetrachloride absorbed into the pore structure.

2. 4. Sulfate Content. For the determination, KIBA's method[6)] was employed which consists essentially of reduction of any form of sulfur to hydrogen sulfide by tin (II)-strong phosphoric acid, absorption of the resulting hydrogen sulfide by zinc acetate solution, and determination of the resulting zinc sulfide by iodometry or colorimetry. Sulfate content was calculated on the assumption that all sulfur in catalyst sample exists as sulfate.

§ 3. Results and Discussion

Table 1 summarizes the experimental conditions and results.

3.1. Geometrical Properties. Bulk density ρ increases in the order catalysts II, III, and I, *i.e.* in the reverse order of the magnitude of pore volume V_1 per gram catalyst. Catalysts I and III are very close in surface area S_1 per gram catalyst, whereas catalyst II has an appreciably less value. The greater S_1-value of catalyst $\mathrm{III_K}$ compared with that of III is likely to be attributed to the corrosion of catalyst surface caused by KOH-treatment. The smaller S_1-value of catalyst $\mathrm{III_P}$, on the other hand, might be due to covering the catalyst surface by glassy metaphosphoric acid which is expected to be formed from orthophosphoric acid adsorbed on the catalyst surface when the catalyst is heated to 650°C. The pore radius was calculated from the equation $\bar{r}=2V_1/S_1$ on the assumption that a catalyst granule has cylindrical pores all of the same pore radius $\bar{r}$ and the same length.

3.2. Sulfate Content. It is seen from Table 1 that even pure alumina catalyst II or III prepared carefully from aluminum nitrate or aluminum isopropoxide still contains a small amount of sulfur. From the amount, the number of sulfates per square centimeters of catalyst surface is estimated at 6×10^{11} and 2×10^{11} molecules for catalysts II and III respectively on the assumption that all sulfur exists solely in the form of sulfate and is located on the surface. These values mean that the surfaces of catalysts II and III are covered only sparsely by sulfate. It should be noted that these estimates are for the fresh catalysts. The sulfate content of the catalyst used for hydrogen cyanide synthesis is expected to be much lower owing to the reduction[4] of sulfate to sulfur or sulfide, which is caused by bringing the catalyst into a reducing atmosphere of carbon monoxide and ammonia at an elevated temperature. This reduction is evidenced by the fact that a small amount of hydrogen sulfide was detected in the outlet gas leaving the reactor during the first one hour of hydrogen cyanide yield determination over catalyst II. In the case of catalyst I, much larger amount of hydrogen sulfide was detected during the pretreatment, which changed the color of catalyst from white to yellow suggesting the formation of sulfur.

3.3. Activity. Each row in the column of "X" in Table 1 shows the yield of hydrogen cyanide (in percentage conversion of ammonia to hydrogen cyanide) in order of measurement from left to right. It is seen that the three values listed in each row agree very closely except in the cases of catalysts I and $\mathrm{III_P}$ kept at 650°C, whose X-values decrease slightly with time. The variable activity of the two catalysts is likely to be due to a significant amount

TABLE 1. Geometrical Property, Sulfur Content, and Catalytic Activity of Various Alumina Catalysts.

Catalyst			Geometrical property				Sulfur content	Activity						
No.	Starting material	Granule size (mesh)	ρ (g/cc)	S_1 (m^2/g)	V_1 (cc/g)	$\bar{r}$ (Å)	Weight per cent as sulfate	Catalyst weight used *) (g)	Reaction temp. (°C)	X (%)			k (mole/min g)	k/S_1 (mole/min cm^2)
I	ammonium alum	8-14	0.70	145	0.28(b) 0.25(c)	37	1.5	1.54	650	40.3	38.9	38.7	3.05×10^{-6}	2.11×10^{-12}
									400	4.7	4.6	4.6	0.29 »	0.20 »
		20-40	0.79					1.23	650	39.6	39.0	38.5	3.78 »	2.60 »
									400	4.8	—	5.0	0.38 »	0.26 »
II	aluminum nitrate	8-14	0.40	119	0.78(b) 0.83(c)	135	0.011	1.56	650	42.4	42.2	42.3	3.45 »	2.90 »
									400	4.8	5.0	5.1	0.31 »	0.26 »
III	aluminum isopropoxide	8-14	0.64	147	0.40(b) 0.39(c)	54	0.005	1.52	650	36.1	36.0	36.3	2.68 »	1.82 »
									400	4.2	4.0	4.1	0.26 »	0.17 »
III$_K$	(KOH-treated III)	8-14		163				1.44	650	30.4	30.3	30.5	2.17 »	1.33 »
III$_P$	(H_3PO_4-treated III)	8-14		118				1.53	250	0.04				
									300	0.24				
									400	1.1	1.0		0.06 »	0.05 »
									650	9.3	8.8	8.5	0.46 »	0.39 »
									400	0.7	0.5	0.5	0.03 »	0.03 »

ρ, bulk density; S_1, surface area per gram catalyst; V_1, pore volume per gram catalyst measured with use of benzene (b) or carbon tetrachloride (c); $\bar{r}$, average pore radius; X, percentage conversion of ammonia to hydrogen cyanide; k, activity per gram catalyst calculated from Eq. (2); k/S_1, activity per cm^2 of catalyst surface.

*) The values given are the catalyst weights measured after the determinations of X. Before the determinations, the weights exceeded these values by 0.03 to 0.08 g.

of the thermally unstable substance contained, *i.e.* sulfate in catalyst I and phosphoric acid in catalyst $\mathrm{III_P}$.

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

$$k = 0.01 \frac{M}{W} \ln \left(\frac{X_e}{X_e - X} \right), \tag{2}$$

where M is the number of moles of ammonia fed per unit time, W the weight of catalyst, X_e the equilibrium percentage conversion of ammonia into hydrogen cyanide, which amounts to 60.4 and 49.1*) respectively at 650 and 400°C. The k has been shown to be constant independent of M in a previous paper[7]. It is seen from Table 1 that catalysts I (8–14 mesh), II, and III agree nearly in k as well as in k/S_1 irrespective of their remarkable difference in the initial sulfate content, where S_1 is the surface area per gram catalyst and hence k/S_1 is regarded as the catalytic activity per unit surface area of catalyst. The values of k and k/S_1 lie at 650°C in a range $2.7\text{–}3.5 \times 10^{-6}$ mole/min g and $1.8\text{–}2.9 \times 10^{-12}$ mole/min cm^2 respectively. These values also are in a good agreement with the previous values[4,8] $3.3\text{–}3.7 \times 10^{-6}$ mole/min g of k and $2.0\text{–}2.5 \times 10^{-12}$ mole/min cm^2 of k/S_1 respectively, which were found over alumina-thoria catalyst containing a significant amount of sulfate. These results seem to indicate that neither sulfuric acid nor thoria but alumina itself acts as predominant catalyst for the hydrogen cyanide synthesis.

If the rate-determining step of hydrogen cyanide synthesis was a proton-transfer process, the KOH-treatment of catalyst would decrease its activity greatly by displacing protons on catalyst surface by potassium ions and the H_3PO_4-treatment might rather activate the catalyst at lower temperatures, where orthophosphoric acid exists stable, since the acid is expected theoretically[9] to be active for proton-transfer reactions. The results contradict these expectations. It is seen from the activities of catalysts III, $\mathrm{III_K}$ and $\mathrm{III_P}$ that the KOH-treatment decreases k and k/S_1 only slightly whereas the H_3PO_4-treatment does severely. These results seem to indicate that a proton-transfer process is not rate-determining. The deactivation by the H_3PO_4-treatment can be attributed to a large fraction of alumina surface being covered with inactive ortho-, pyro-, or meta-phosphoric acid.

3.4. Activation Energy. HORIUTI *et al.*[7] have found on alumina-thoria catalyst that R, the number of moles of hydrogen cyanide produced per unit time per unit weight of catalyst, is proportional to $X_e - X$, *i.e.*

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*) These values are derived from the equilibrium constant 7.18×10^{-3} for reaction (1) at 650°C, the heat of reaction −4560 cal/mole [ref. (7)], and the mole ratio of reactant gas, $CO/NH_3 = 10$.

$$R = k\,(X_e - X)\,. \tag{3}$$

On the other hand it is concluded from general theory[10] of reaction rate that

$$R = \vec{R}(1-\varphi^{\frac{1}{\nu_r}})\,, \tag{4}$$

where $\vec{R}$ is the unidirectional forward rate, ν_r the stoichiometric number of the rate-determining step, and φ the function defined as

$$\varphi = \frac{P_{HCN}P_{CO_2}P_{H_2}}{P_{CO}^2 P_{NH_3}} \Big/ K\,, \tag{5}$$

where P_{HCN} *etc.* are the partial pressures of hydrogen cyanide *etc.*, and K is the equilibrium constant of the hydrogen cyanide synthesis (1). Equating Eqs. (3) and (4), we obtain

$$\vec{R} = k(X_e - X)/(1-\varphi^{\frac{1}{\nu_r}})\,. \tag{6}$$

On differentiation of Eq. (6) with respect to temperature, we have

$$RT^2\left\{\frac{\partial \ln \vec{R}}{\partial T}\right\}_X = RT^2\frac{d\ln k}{dT} + RT^2\left\{\frac{\partial \ln (X_e - X)}{\partial T}\right\}_X$$

$$-RT^2\left\{\frac{\partial \ln (1-\varphi^{\frac{1}{\nu_r}})}{\partial T}\right\}_X\,. \tag{7}$$

At $X=0$, this equation reduces to the form,

$$E_0 = RT^2\frac{d\ln k}{dT} + RT^2\frac{d\ln X_e}{dT}\,, \tag{8}$$

where $E_0 \equiv RT^2(\partial \ln \vec{R}/\partial T)_{X=0}$, which is called activation energy hereafter. The quantity $RT^2 d\ln k/dT$ is calculated from the data of Table 1 for each catalyst. The quantity $RT^2 d\ln X_e/dT$ is evaluated from values of X_e at 400 and 650°C, which have been given in section 3.3. Activation energy is thus calculated for catalysts I, II, and III, and listed in Table 2. It is seen that three catalysts are close in activation energy. These values also agree nearly

TABLE 2. Activation Energy and Related Quantities.

Catalyst		E_0	$RT^2\frac{d\ln k}{dT}$	$RT^2\frac{d\ln X_e}{dT}$
No.	mesh	kcal/mole	kcal/mole	kcal/mole
I	8-14	12.6	11.6	1.0
	20-40	12.3	11.3	"
II	8-14	13 0	12.0	"
III	"	12.5	11.5	"

with 11.6 kcal, the activation energy observed by HORIUTI *et al.*[7] for the same reaction on alumina-thoria catalyst.

It should be noted that activation energy of catalyst I seems to be independent of granule size although both k and k/S_1 depend clearly, even though slightly, on granule size as seen in Table 1. These results are difficult to interprete. The influence of granule size on activity occurs when gas diffusion in catalyst pores is so slow that a concentration gradient of a reactant or product arises in pores, but in such circumstances the activation energy has to decrease with increasing granule size contradicting the observed results. The fact that the activation energy is independent of granule size, however, is likely to indicate that the influence of pore diffusion, if any, is negligibly small.

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