[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

PROPERTIES OF PYROPHORIC IRON. II. ADSORPTION OF CARBON DIOXIDE AND AMMONIA AND THE USE OF PYROPHORIC IRON IN THE AMMONIA SYNTHESIS[1]

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In a previous paper,[2] it was shown that the pyrophoric activity of iron prepared by the reduction of ferric oxide in hydrogen was influenced by the method of preparation of the oxide. The greater the degree of dispersion of the ferric oxide, the more easily was pyrophoric iron converted into the non-pyrophoric form when heated to a temperature higher than the reduction temperature.

This investigation is an attempt to find any relationship between the differences in the ease of inactivation of the three samples of pyrophoric iron and their adsorptive and catalytic properties.

Materials for Adsorption

Gases.—Carbon dioxide was prepared by dropping sulfuric acid into a saturated solution of sodium bicarbonate, previously boiled to remove any dissolved air. The gas was dried by concentrated sulfuric acid and phosphorus pentoxide. Pure ammonia was prepared by heating a concentrated solution of ammonium hydroxide, passing the gas through a strongly alkaline solution of pyrogallol and finally over soda lime and flaked caustic soda. Nitrogen, used to determine the free volume of the adsorption bulb, was obtained from a cylinder of the gas. It was passed through concentrated sulfuric acid, over hot copper and finally dried over phosphorus pentoxide. Hydrogen for the reduction of ferric oxide was commercial gas produced by the electrolysis of caustic soda solution. It was purified by passing through concentrated sulfuric acid, soda lime, hot copper, soda lime and phosphorus pentoxide in the order named.

Iron Oxides.—Ferric oxides A and B were precipitated from a ferric nitrate solution by ammonium hydroxide, while ferric oxide C was prepared from a colloidal sol, using ferric nitrate and in one case ferric chloride as a starting material. The preparation of these oxides has been described in Part I.[2]

Preparation of the Iron for Adsorption

The reduction of the iron oxide was carried out in the adsorption bulb, illustrated in Fig. 1 of the previous paper.[2] In all cases pyrophoric iron was prepared by hydrogen reduction at 500°, the hydrogen being passed into the bulb by means of a small capillary tube at a rate approximating 80 cc. per minute. During the reduction the bulb was removed several

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[1] The work in this paper and Part I is from the thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was carried out under his direction. (Manuscript first received November 13, 1928.)

[2] Finzel, THIS JOURNAL, **52**, 142 (1930).

times from the furnace and the material shaken to break up any lumps of material formed during the early stages of the reduction. After about ten hours of reduction a T-tube to which was connected a U-tube containing phosphorus pentoxide was attached to the adsorption bulb. Reduction was stopped when the gain in weight of this U-tube showed that the water liberation had dropped to approximately 0.5 to 1.5 mg. per hour. The iron was degassed at 500° by means of a mercury vapor and oil pump until the pressure dropped to at least 5×10^{-5} mm. pressure. Three to five hours was the usual time for degassing, depending upon the kind of iron in the bulb.

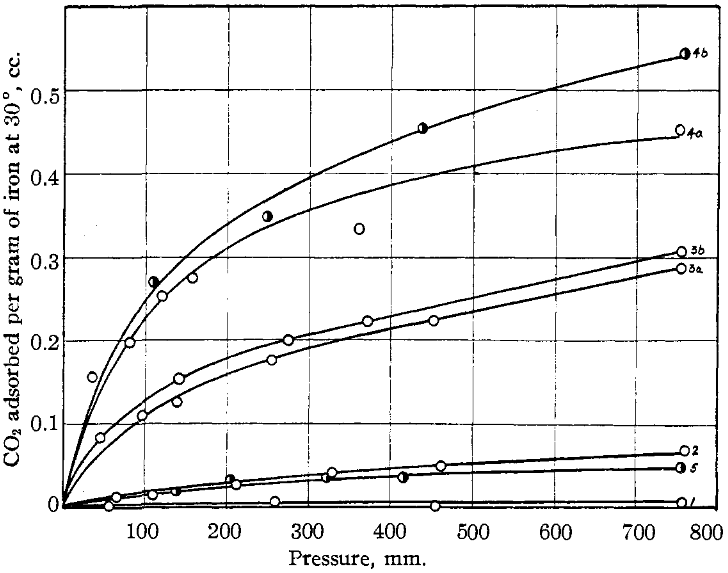

Fig. 1.—Adsorption of carbon dioxide by pyrophoric iron.

Adsorption Results.—The free volume of the adsorption bulb was determined by two methods; in the first the volume of the iron in the bulb was subtracted from the volume of the empty bulb while in the second the volume of nitrogen necessary to fill the bulb containing the iron was determined. Since it was found that the two methods agreed within experimental error, the former was generally used. The adsorptive capacities of the pyrophoric and non-pyrophoric iron samples for carbon dioxide and ammonia at the highest equilibrium pressure and at 30° are given in Table I, the complete isotherms being illustrated graphically in Figs. 1 and 2.

By comparing Curves 2 and 5 (Fig. 1), it is evident that the pyrophoric iron reduced at 500° from oxide C adsorbed less carbon dioxide than the non-pyrophoric iron reduced at 625° from oxide A. It is evident that

TABLE I

ADSORPTION OF CARBON DIOXIDE AND AMMONIA BY PYROPHORIC AND NON-PYROPHORIC IRON AT 30°

Curve	Oxide	Gas	Reduction temp., °C.	Reduction time, hrs.	Pressure, mm.	Cc. ads. per g. of iron	Condition
1	A	CO_2	500	11	757.6	0.004	Non-pyro.
			650	2.5			
2	A		625	12	760.9	0.065	Non-pyro.
3a	A		500	12.5	757.7	.292	Pyro.
3b	A		500	11	757.4	.309	Pyro.
4a	B		500	13	754.4	.454	Pyro.
4b	B		500	11	759.0	.545	Pyro.
5	C		500	12	759.7	.046	Pyro.
6	A-III	NH_3	500	23	758.0	.935	Pyro.
7	B-II		500	22.5	266.4	.950	Pyro.
8	C *ex*		500	12	432.7	.397	Pyro.
	$FeCl_3$		500	22			
9	A-III		650	5	754.2	.188	Non-pyro.

adsorption of this particular gas is not a criterion for judging pyrophoric activity. For the pyrophoric samples, adsorption of both carbon dioxide and ammonia increased in the order C, A, B, the last showing the largest adsorption in each case.

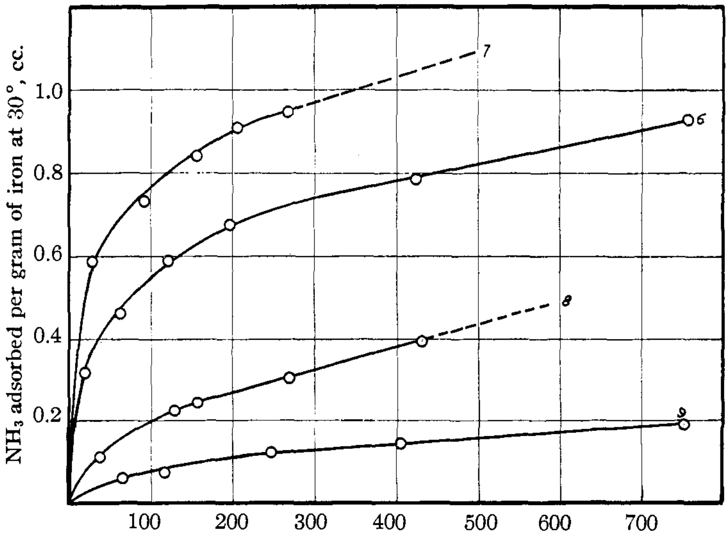

Fig. 2.—Adsorption of ammonia by pyrophoric iron.

It was previously[2] shown that samples of pyrophoric iron reduced from these oxides become non-pyrophoric when heated in nitrogen, hydrogen or helium at 600°. It was found that C became inactive the most rapidly, A next, B taking the longest time. On the basis of von Weimarn's precipitation rule, oxides C and A should have a greater degree of dispersion than oxide B. It was shown by Hofmann[3] that the extent of reduction of iron oxide depends among other factors upon the particle size of the oxide. From these considerations it seemed probable that the reason for the order of pyrophoric inactivation of the iron samples lay in the degree of incomplete reduction of the oxide, so that each particle or cluster contained a residual oxide core varying with the size of the original oxide particle. On this basis it seemed that pyrophoric iron B contained the largest oxide core while C contained the smallest. The definite order for adsorption of carbon dioxide and ammonia could thus be attributed to small amounts of oxide remaining as a core in the iron particles. Taylor and Burns[4] found that finely divided iron reduced from the calcined nitrate for twenty-six hours at 450° in hydrogen adsorbed only 0.25 cc. of carbon dioxide per cubic centimeter of iron. Nikitin[5] reports nearly 4 cc. of carbon dioxide adsorbed per gram of pyrophoric iron at 18° and 732 mm. Since the latter investigator prepared this iron by reducing ferrous carbonate in hydrogen at 515°, this high adsorption value may be attributed to residual oxide or carbon formed by the reaction of the carbon dioxide and iron. Pyrophoric iron produced from the carbonate, moreover, may contain more elementary spaces or fine capillaries[6] especially suitable for carbon dioxide adsorption.

Ammonia Synthesis

Since the iron prepared from oxide C was found to be very sensitive toward heating, becoming thereby non-pyrophoric very readily, and was also found to be inactive with respect to adsorption, it was of especial interest to investigate the behavior of this particular iron in the synthesis of ammonia.

Materials

Gases.—Nitrogen and hydrogen were prepared by the thermal decomposition of ammonia by a method somewhat similar to that described by Larson, Newton and Hawkins,[7] the ammonia being passed over steel wool in a porcelain tube held at a red heat. The gases were purified by the method recommended by Larson and his co-workers.

Ferric Oxide B.—In addition to oxide B, previously described, "Oxide B-dialyzed" was prepared by precipitating oxide B, washing partially, dialyzing the precipitate in collodion bags for one week at 90–95° and finally drying.

Ferric Oxide C.—Together with the colloidal oxide C prepared by the method of Sorum[8] by hydrolyzing ferric nitrate and dialyzing the oxide so formed in collodion

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[3] Hofmann, *Z. angew. Chem.*, **38**, 715–721 (1925).

[4] Taylor and Burns, THIS JOURNAL, **43**, 1276 (1921).

[5] Nikitin, *Z. anorg. allgem. Chem.*, **154**, 130 (1926).

[6] Briggs, *Proc. Roy. Soc. London*, **100A**, 88 (1921).

[7] Larson, Newton and Hawkins, *Chem. Met. Eng.*, **26**, 494–497 (1922).

[8] Sorum, THIS JOURNAL, **50**, 1263 (1928).

bags, an oxide C was dialyzed in parchment bags. Oxide C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$ was also prepared by hydrolyzing 10 g. of ferric nitrate and 1 g. of aluminum nitrate in boiling water, dialyzing in collodion bags and treating subsequently like oxide C. The ignited oxide C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$ contained 95.4% of Fe_2O_3, the remainder being Al_2O_3. All oxides were ground to 5- to 12-mesh.

Method and Results.—The catalyst was prepared by reducing the desired iron oxide in the hydrogen–nitrogen mixture at 400–450° at one atmosphere pressure. The type of catalyst tube used was similar to that described by Almquist and Black.[9] All experiments were carried out at atmospheric pressure with 5000, 11,000 and 16,000 space velocities, 2 cc. of catalyst being used. The ammonia was absorbed in 0.1 *N* sulfuric acid and the excess acid titrated with 0.1 *N* sodium hydroxide, using methyl orange as an indicator.

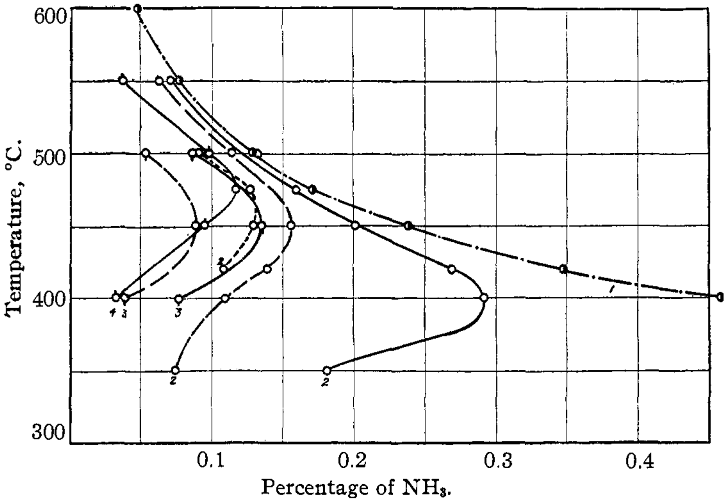

Fig. 3.—Curve 1, equilibrium; 2, oxide B; 3, oxide B dialyzed; 4, C *ex* $Fe(NO_3)_3$·$Al(NO_3)_3$: 5000 S. V.————, 11,000 S. V.— — —, 16,000 S. V.- - - - - -.

Oxide C was reduced at 400° for thirty-six hours and finally at 500°. This oxide proved to be absolutely worthless as a catalyst, no ammonia being formed. Upon examining the reduced oxide microscopically the granules of iron appeared not in the least porous but had a distinctly metallic luster, indistinguishable under a low power microscope from a piece of white cast iron. From the appearance of the iron, an extremely rapid recrystallization must have taken place; however, some poison from the collodion bags may have caused its inertness as a catalyst. To test the probability of poisoning, oxide B and oxide B-dialyzed were used as catalysts. The results obtained are presented in Fig. 3, showing that a cer-

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[9] Almquist and Black, This Journal, **48**, 2814 (1926).

tain amount of inactivation was caused by dialysis since the curves for B-dialyzed lie a greater distance from the theoretical curve than those for catalyst B. With the view that collodion may have had a poisoning effect on iron C, oxide C was dialyzed in parchment bags. Here again no ammonia was produced, the iron after reduction having a decidedly metallic luster. If recrystallization forces caused the inertness of iron C, the incorporation of an oxide of the Al_2O_3 type in the catalyst should prevent such an occurrence. Wyckoff and Crittenden[10] have shown that such an oxide acts as a "guard," inhibiting sintering of the iron. Such a mixed oxide, C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$, was prepared and reduced in the same manner as oxide C. The mixture showed catalytic properties although it was not as active as iron B. The results are given in Table II and shown graphically in Fig. 3. After being in use for more than a day, the catalyst had a bulky black appearance in contrast to the metallic gray of iron C. The material was decidedly pyrophoric when thrown into the air. These experiments, together with the fact that pyrophoric iron C is easily caused to become non-pyrophoric upon heating, point to the fact that the sensitivity and ease of inactivation of iron C is due to extremely rapid recrystallization. The superior catalytic property of iron B could be attributed to the lower degree of dispersion of oxide B. Oxide B would be more difficultly reduced and the resulting iron particles no doubt would contain small oxide cores which tend to hinder coalescence of the iron in a manner similar to the action of aluminum oxide.

TABLE II

AMMONIA SYNTHESIS WITH PYROPHORIC IRON AS CATALYST

Ammonia Concentration—Per cent.

Temp., °C.	Oxide B, space velocity			Oxide B-dial., space velocity		C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$ space velocity	Equilib.[11]
	5000	11,000	16,000	5000	11,000	5000	
350	0.180	0.008	...	...	...	...	...
400	.290	.109	...	0.075	0.038	0.031	0.457
420	.269	.139	0.108	...	...	...	.347
450	.200	.155	.129	.133	.087	.091	.236
475	.159	.136	.126	...	...	.116	.170
500	.130	.112	.089	.088	.052	.098	.128
550	.070	.063	...	...	...	.037	.076

Summary

1. Adsorption of carbon dioxide by pyrophoric iron is no criterion for pyrophoric action, a sample of non-pyrophoric iron adsorbing more gas than a sample of pyrophoric iron.

2. Adsorption of carbon dioxide and ammonia by the samples of pyro-

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[10] Wyckoff and Crittenden, THIS JOURNAL, **47**, 2866 (1925).

[11] Larson and Tour, *Ind. Eng. Chem.*, **26**, 649 (1922).

phoric iron prepared seems to be dependent primarily upon the amount of residual oxide contained in the iron.

3. Iron prepared from colloidal iron oxide by Sorum's method was worthless as an ammonia catalyst. The incorporation of colloidal aluminum oxide in this colloidal iron oxide produced an active catalyst.

4. It appears as though inactivation of an iron catalyst through processes of recrystallization is hindered by an iron oxide core within the iron particles.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

THE EQUILIBRIUM OF THE REACTION BETWEEN NITROGEN AND CARBON DIOXIDE IN THE ELECTRIC ARC

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This study was undertaken as a natural consequence of former work performed in this Laboratory on the equilibrium of gaseous reactions in the electric arc.[1] The reaction between nitrogen and carbon dioxide seemed to offer a very interesting problem because of the appearance of a recent article[2] which indicated that a much higher concentration of nitric oxide could be obtained with a mixture of these gases than could be realized with a mixture of nitrogen and oxygen. The earlier work of Muthmann and Schaidhauf[3] seemed to indicate that this view is erroneous; for they obtained concentrations of nitric oxide from carbon dioxide and nitrogen mixtures which compare unfavorably with those obtainable from air. However, it seemed desirable to collect a more complete series of data in which conditions were varied and in which equilibrium was known to be realized.

Description of Apparatus.—The power supply available was 110-volt, 60-cycle alternating current. The high voltage necessary to maintain the arc was obtained by means of an oil-cooled, closed core transformer of 3.5 kilowatts capacity. Reactance coils in the primary circuit served to stabilize the arc and to give the desired value of secondary current. A milliammeter in the secondary circuit indicated the value of the current. The line voltage varied somewhat, but the current through the arc was substantially constant.

The arc furnace was that used by Colin and Tartar[4] in their study of the equilibrium of the reaction of nitrogen and oxygen in air and other mixtures, to form nitric oxide. It consisted of a 5-liter pyrex flask with platinum electrodes sealed into the neck of the flask. The electrodes were originally of the horn-gap type, and were about 0.8

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[1] (a) Tartar and Perkins, *J. Phys. Chem.*, **30**, 595–616 (1926); (b) Colin and Tartar, *ibid.*, **31**, 1539–1558 (1927).

[2] Krase and Mackey, *ibid.*, **32**, 1488–1494 (1928).

[3] Muthmann and Schaidhauf, *Z. Electrochem.*, **17**, 497 (1911).

[4] Ref. 1 b, see Fig. 2, p. 1544.