

carbon the orientation is in the opposite direction, though why the latter should show such an increased heat of wetting over that of benzene is not obvious.

In the previous work on the densities of these solids a correlation with existing data on heats of wetting is mentioned. How well this is borne out in the present work is indicated in Table II.

TABLE II
DENSITIES AND HEATS OF WETTING OF SILICA GEL AND CHARCOAL

Liquid	Silica		Charcoal	
	Heat of wetting, cal./g.	Density, g./cc.	Heat of wetting, cal./g.	Density, g./cc.
Water	16	2.25 ^a	8.4	1.82
Nitrobenzene	14.3	2.23	27.1	2.00 ^a
Benzene	11.2	2.15	21.0	1.99
Carbon disulfide	6.7	2.21 ^a	29.5	2.02 ^a
Carbon tetrachloride	6.3	2.13	20.0	1.86
Petroleum ether	4.3	2.12	23.8	2.08

^a The values so indicated are due to Culbertson and Weber (unpublished data). Identical silica gel and charcoal were used but the method of Tschapek [*Kolloid. Z.*, **63**, 34-36 (1933)] was employed in making the determinations. This method was compared with that used by Culbertson and Dunbar and satisfactory checks were obtained.

For the most part high heats of wetting accompany high densities though carbon disulfide on silica appears to provide an exception to such a generalization. It is the contention of the writers, however, that such evidence as these data afford

tends to confirm the ideas expressed in the paper by Culbertson and Dunbar,¹ *e. g.*, that differences in the apparent density of a porous solid as indicated by measurements made with different liquids as filling fluids are due either to differences of penetration of the pores of the solid by the liquids or to differences in the amount of compression of the liquid film at the interface, in either case the determining factor being the decrease in surface energy when the liquid wets the solid. Quantitative correlation is of course lacking in Table II, but in consideration of the fact that if the above view of these phenomena is correct, then the specific areas of the solids, the compressibilities and the heats of compression of the different liquids, satisfactory data for most of which are unavailable, would have to be taken into consideration in developing such quantitative ideas and therefore the irregularities found are quite within the expected magnitude.

Summary

The heats of wetting of charcoal and silica gel by water, nitrobenzene, benzene, carbon tetrachloride, carbon disulfide and petroleum ether have been determined. A correlation is noted between the order in which these values fall and that of the apparent densities of the solids as determined in the same liquids.

PULLMAN, WASH.

RECEIVED OCTOBER 6, 1936

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Accumulation of Alkali Promoters on Surfaces of Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND S. BRUNAUER

It has been pointed out repeatedly that the high pressure activity of iron synthetic ammonia catalysts containing a per cent. or so of potassium oxide in addition to an approximately similar amount of aluminum oxide is considerably greater than that of a catalyst promoted with aluminum oxide alone.¹ So far as we are aware, however, no evidence has ever been published concerning the fraction of the catalyst surface actually covered by the few per cent. of the alkali oxide promoters contained in typical iron synthetic ammonia catalysts. It is the purpose of the present paper to show that some recently determined low

temperature adsorption isotherms of nitrogen, carbon monoxide and carbon dioxide on five different synthetic ammonia catalysts, enable us to conclude that 1% or so of potassium oxide in a catalyst actually covers a large fraction of the catalyst surface.

Experimental

The adsorption apparatus used was similar to that already described² except that parts F, E, C', C, M, A, N, L, K, J and trap H of the apparatus shown in Fig. 1 of that paper were eliminated, and a manometer made of 10-mm. tubing was attached at the top of buret B. Stopcocks 1 and 2 were replaced by mercury sealed vacuum cocks, and catalyst bulb A was replaced by one of 25-cc. capacity.

(1) Larson, *J. Ind. Eng. Chem.*, **16**, 1002 (1924); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

(2) Emmett and Brunauer, *THIS JOURNAL*, **56**, 35 (1934).

The Toepler pump used in some of the experiments was attached essentially as shown in Fig. 1 of the above paper.

The iron synthetic ammonia catalysts were samples that had been prepared as oxides about ten years previously by the fusion method of Larson and Richardson³ and kept in stoppered bottles since that time. According to their procedure, the promoters (pure potassium nitrate and Norton R. R. Alundum) were incorporated into the fused oxides at about 1540°. The catalyst composition, weight, reduction schedule and activity toward the high pressure synthesis of ammonia are presented in Table I for each of the five different types of synthetic ammonia catalysts used.

TABLE I

Mesh size, 8 to 14. Apparent volume of catalysts, 25 cc. Hydrogen flow during reduction, 500 cc. per min.

Catalyst	Sample as oxide, g.	Promoter content, %	Reduction schedule Time, hrs.	Temp., °C.	Activity ^a toward ammonia synthesis (% NH ₃ at 450°, 100 atm. and 5000 space velocity)
930	64.5	1.07 K ₂ O	48 between 350 and 450		5.3
931	61.0	1.59 K ₂ O	18 at 300 to 350		12.3
		1.3 Al ₂ O ₃	65 more 350-450 18 more 450-530		
954	66.8	10.2 Al ₂ O ₃	48 at 350 to 450		8.2
			48 more at 450-500		
958	71.9	0.35 Al ₂ O ₃	36 at 350 to 450		10.4
		.08 K ₂ O	36 more at 450-500		
973-I	63.4	.15 Al ₂ O ₃	124 at 300 to 350		3.3
			54 more at 375-500		
973-II	67.0	.15 Al ₂ O ₃	96 at 300 to 400		

^a The high pressure activities given here were determined about ten years ago on other samples of these same catalysts. They are included in this table merely as illustrations of the approximate relative activities of the various catalysts.

Hydrogen from large electrolytic cells in operation at this Laboratory was used after being passed over hot copper and dried by phosphorus pentoxide. All copper purifiers were first heated in hydrogen for several hours at 750° to remove traces of sulfur that might be present. Tank nitrogen was passed slowly over hot copper and dried by passage over phosphorus pentoxide. Carbon monoxide prepared according to the method of Thompson⁴ was taken from tanks and passed through liquid air traps to remove iron carbonyl and any traces of carbon dioxide. Tank carbon dioxide was dried by passage through a trap immersed in an alcohol-dry ice bath at -78° and was used without further purification after it had been shown to contain only a negligible amount of non-condensable gases.

The liquid oxygen used as a constant temperature bath was prepared immediately before use by passing tank oxygen into a condenser cooled in liquid air. The only two tanks of the oxygen analyzed contained 2.0 and 3.4% nitrogen; oxygen liquefied from the latter of these two tanks was found to retain 0.9% nitrogen. The Dewar flask used as a container for the liquid oxygen during the adsorption experiments was not silvered and permitted

rapid evaporation of oxygen. Apparently quite a constant temperature was obtained during a given run, the temperature change during the day being less than 0.05° as judged by a ten-junction copper-constantan thermocouple used in conjunction with a type K potentiometer. The temperature of the cold bath was obtained by noting the barometric pressure and using the tables of Dodge and Davis⁵ for the vapor pressures of liquid oxygen. The temperature of -78.5° was obtained by using an alcohol-dry ice bath stirred only by the bubbling caused by the gradual evaporation of carbon dioxide. It is realized that such a bath might have been a degree or so warmer at the top than at the bottom, though the temperature at the bottom of the bath opposite the catalyst bulb was close to -78.5° as indicated by a calibrated thermocouple and a pentane thermometer. The adsorption measurements were carried out in the usual fashion, helium⁶ calibrations of the dead space in the catalyst bulb being made before each series of runs. The catalyst was always first cooled in helium to the desired low temperature before admitting either carbon monoxide or carbon dioxide. After sufficient time had been permitted for temperature equilibration between the catalyst and the surrounding bath the helium was removed and the catalyst evacuated to about 10⁻⁴ mm. immediately before each run. To avoid the possibility of traces of oxygen contaminating the catalyst overnight, a uniform reduction period of one hour, in a stream of about 500 cc. of hydrogen per minute, was carried out every morning at 450°.

The gas contained in the "dead space" around the catalyst was corrected in each case for deviations from the perfect gas laws with the help of data from the "International Critical Tables." The corrections used were 3.2% for carbon monoxide at -183°, 2.97% for nitrogen at -183°, 2.0% for carbon dioxide at -78.5° and 0.58% for carbon dioxide at room temperature. Values for the first three of these corrections were also obtained through the kindness of Dr. A. F. Benton from some measurements that he and his collaborators have made recently. His results are in substantial agreement with the above corrections.

Results and Discussion

The carbon dioxide adsorption on the various iron catalysts at -78.5° was found to have many of the characteristics to be expected for a purely physical type of adsorption. For example, the rate of adsorption is rapid at all pressures; furthermore, it is no slower for catalysts promoted with alkalis than for those promoted with aluminum oxide alone. However, even a cursory comparison of the adsorption isotherms for carbon dioxide and for nitrogen shows that the ratio of the volume of carbon dioxide capable of being adsorbed at -78.5° to the volume of nitrogen that can be adsorbed at -183° on the same catalyst is

(5) Dodge and Davis, *THIS JOURNAL*, **49**, 610 (1927).

(6) We wish to express our thanks to Dr. R. Wiebe of this Laboratory for furnishing us a supply of helium that he had purified by passing through charcoal tubes immersed in liquid air. His analysis by use of an interferometer showed that the helium was 99.94% pure.

(3) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

(4) Thompson, *ibid.*, **21**, 389 (1929).

much higher on a catalyst promoted with alkali than on one to which no alkali has been added.

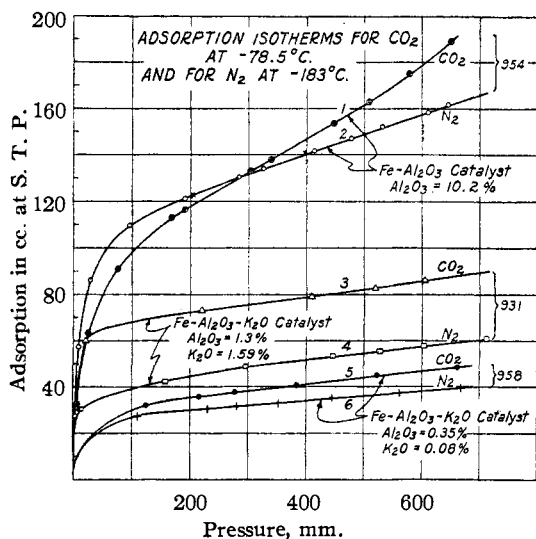


Fig. 1.—Comparison of the adsorption isotherm for carbon dioxide at -78.5° on a given iron synthetic ammonia catalyst with that for nitrogen at -183° on the same catalyst.

Figures 1 and 2 afford such a comparison between the isotherms of carbon dioxide at -78° and nitrogen at -183° , for the various catalysts. It is evident that at 300 mm. pressure⁷ the volume of carbon dioxide adsorbed by catalyst 954 (10.2% Al_2O_3) at -78.5° is exactly the same as the volume of nitrogen adsorbed at -183° . On the other hand, at this same pressure in the case of catalysts 930, 931 and 958, which as pointed out above contain 1.07, 1.59 and 0.08% K_2O , respectively, the carbon dioxide isotherms at -78.5° exceed those for nitrogen at -183° by 78, 55 and 20%. For catalyst 973, to which no promoter had been added, the carbon dioxide adsorption for sample II is 10% larger at 300 mm. than the nitrogen adsorption at -183° and for sample I, 8% larger. In view of the marked influence of 0.08% K_2O in catalyst 958 on the total carbon dioxide adsorption it seems probable that the results on "pure iron" catalyst 973 may actually indicate the presence of a few hundredths of a per cent. of alkali even though none was intentionally added. Presumably, then, something other than the physical adsorption of carbon dioxide was

(7) 300 mm. was arbitrarily chosen as the pressure at which to make this comparison between catalysts promoted with alkali and those to which no alkali had been added. Any pressure in the range in which sufficient observations had been made to fix the shapes of the isotherms (roughly 100 to 700 mm.) would have served equally well.

occurring on the alkali-promoted catalysts at -78.5° .

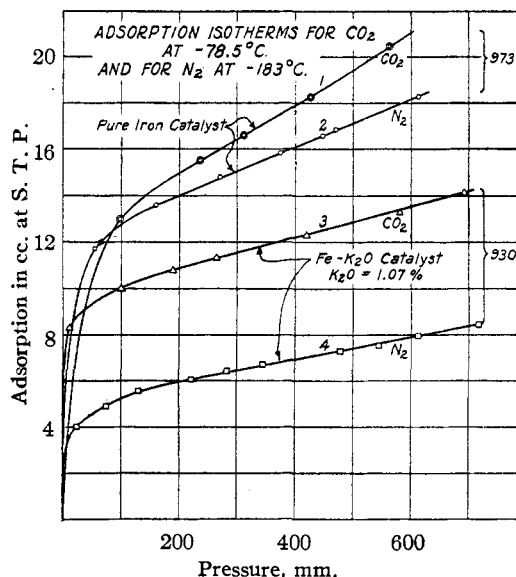


Fig. 2.—Comparison of the adsorption isotherm for carbon dioxide at -78.5° on a given iron synthetic ammonia catalyst with that for nitrogen at -183° on the same catalyst.

A reasonable interpretation of the large excess of carbon dioxide taken up by the catalysts containing potassium oxide appeared to be that the surface alkali was causing a very rapid⁸ chemisorption of carbon dioxide to occur in addition to about the usual amount of physical adsorption. To obtain further evidence regarding the existence of such chemisorption and to ascertain the approximate amount of it that might be occurring, the catalysts were degassed by a diffusion pump for thirty minutes at 0° at the end of an isotherm determination, in order to remove the physically adsorbed carbon dioxide, after which the -78.5° isotherms were repeated. The slopes of the straight line portion of these second isotherms were in all cases practically the same as the slopes of the carbon dioxide isotherms shown in Figs. 1 and 2. However, the actual amount of adsorption occurring at -78.5° following the evacuation at 0° was smaller than the original carbon dioxide adsorption by 5 cc. for catalyst 954, 30 cc. for catalyst 931, 8 cc. for catalyst 958, 4.2 cc. for catalyst 930 and 2 cc. for catalyst 973. (For the

(8) Only a few desorption points were taken on the runs with carbon dioxide at -78.5° . They showed, however, that on catalyst 931 at least 93% and possibly all of the chemisorption of carbon dioxide occurring during an entire isotherm determination had completed itself in the first fifteen minutes of the run and at a pressure of 25 mm. or less.

original carbon dioxide adsorption values see the curves in Figs. 1 and 2.) These values for the decreases in adsorption following the evacuation at 0° correspond to 67, 62 and 25% of the -183° nitrogen isotherm adsorption values at 300 mm. for the alkali-containing catalysts 930, 931 and 958, but only 4.7 and 13.5% in the case of catalysts 954 and 973 to which no alkali had been added. A comparison of these percentages with those given in the previous paragraph shows clearly that the volume of carbon dioxide that is rapidly adsorbed at -78.5° but not removed from the catalysts upon half an hour of evacuation at 0° is about sufficient to account for the amounts by which the total carbon dioxide adsorptions at -78.5° on the alkali-containing catalysts exceed the nitrogen adsorption at -183° and 300 mm. pressure. There seems to be little doubt, accordingly, that a considerable portion of the carbon dioxide adsorbed by the catalysts containing alkali is actually held to the catalyst by a process of chemisorption rather than physical adsorption.

An exact determination of the amount of chemisorption of carbon dioxide occurring on the various catalysts could be made only in case some temperature could be found at which all of the van der Waals adsorption would be removed by evacuation without any of the chemisorption being removed. If it could be shown, for example, that evacuation at 100° for a half hour removed none of the carbon dioxide that could not be removed by a similar period of evacuation at 0°, then the numerical values previously found for the differences between the initial total carbon dioxide adsorptions and the adsorptions following an evacuation at 0° would be considered correct values for the chemisorption of carbon dioxide at -78.5° on the various catalysts. This indeed proved accurately to be the case for most of the catalysts studied. Thus, three and one-half hours of evacuation of catalyst 931 at 0° removed no more carbon dioxide than had been removed in half an hour. Furthermore, pumping at 100° for half an hour removed no greater amounts of carbon dioxide from this catalyst or from catalysts 954 or 930 and only 0.2 cc. more from catalyst 973 than had been removed at 0°. Only from catalyst 958 did it appear possible by pumping at 100° to remove considerable carbon dioxide that could not be removed by pumping for a similar period at 0°. In this instance evacuation at 0° left 8 cc. of carbon dioxide on the sur-

face whereas two 100° evacuations in separate runs left 7.1 and 5.0 cc. of carbon dioxide on the catalyst. Accordingly, one can merely say that out of the total carbon dioxide adsorption shown by curve 5, Fig. 1 (catalyst 958), between 5 cc. and 8 cc. is chemisorption. It may be of interest to point out that evacuation of catalyst 931 with a diffusion pump for thirty minutes at as high a temperature as 450° removed only about one-half the carbon dioxide that could not be removed at 0°. Analysis of the first 2 or 3 cc. of gas coming off the catalyst at 450° indicated the presence of both carbon monoxide and carbon dioxide, the latter predominating. The carbon monoxide probably came from the reaction of carbon dioxide with the iron atoms of the catalyst surface. It appears, therefore, that the chemisorbed carbon dioxide is very tightly bound to the catalyst surfaces containing alkali.

No definite evidence exists in the present work as to the number of carbon dioxide molecules that are chemisorbed on the catalysts by each alkali molecule on the catalyst surface. Neither is there any information concerning the nature of the surface alkali though presumably it cannot be present as potassium atoms since Brewer⁹ has shown by photoelectric experiments that the concentration of free potassium atoms on the surface of promoted iron synthetic ammonia catalysts is very small. It seems probable that the alkali concerned in the chemisorption of carbon dioxide in the present experiments is in the form of an oxide or a complex with iron or iron oxide. By making the plausible assumption that each alkali molecule present on the surface of the catalyst is capable of holding one molecule of chemisorbed carbon dioxide, and by taking into account the amount of carbon dioxide needed to form a monolayer of physical adsorption on the catalyst as a whole, one is led inevitably to the conclusion that during the preparation or reduction of the catalyst alkali has accumulated to a marked extent on the catalyst surface. In fact, on the basis of our best estimates of the surface area¹⁰ the alkali covers about 71 and 75% of the surface of catalysts 930 and 931, respectively, although the

(9) Brewer, *THIS JOURNAL*, **53**, 74 (1931).

(10) The principle of the method used in measuring the surface areas has already been presented [see Brunauer and Emmett, *ibid.*, **57**, 1754 (1935)]. A detailed discussion of the method with its application to a number of synthetic ammonia catalysts and other catalytic substances will soon be submitted for publication. The estimates of the surface areas used in the present paper are based on the final revised estimates of the surface areas resulting from this more comprehensive work.

alkali contents of these two catalysts as a whole are only 1.07¹¹ and 1.59%.

A fortunate characteristic of the adsorption of carbon monoxide on iron catalysts at -183° enabled us to obtain evidence regarding the fraction of the total surface that consists of iron atoms rather than alkali molecules and to confirm thereby the above conclusions in regard to the accumulation of alkali on the catalyst surface. Early in the work upon the determination of catalyst surface areas by the use of low temperature isotherms it was noted that on pure iron catalyst 973 (Sample I) the carbon monoxide adsorptions were roughly twice as large as the nitrogen adsorptions at the same temperature and pressure, although the carbon monoxide adsorption equilibrated as rapidly as that of nitrogen. To ascertain whether chemisorption of carbon monoxide

immediately following this evacuation at -78° showed an amount of physical adsorption of carbon monoxide comparable to that of nitrogen at -183° . It was therefore concluded that on the iron catalyst at -183° a practically instantaneous chemisorption of carbon monoxide was occurring which could not be removed by pumping for half an hour with a diffusion pump at -78° . Furthermore, the fact that this chemisorption reached a saturation value instantaneously at pressures of only a few mm. of carbon monoxide and did not continue during the subsequent determination of the superimposed physical adsorption up to 760 mm. led us to believe that at -183° a complete monolayer of chemisorbed carbon monoxide was formed on the catalyst surface.

If the chemisorption of carbon monoxide takes place on the iron atoms on the surface, then it should follow that the same catalysts that are capable of large chemisorptions of carbon dioxide should have low chemisorptions of carbon monoxide and *vice versa*. In Fig. 3 are presented curves showing the total adsorption and the van der Waals adsorption of carbon monoxide on a doubly promoted catalyst compared with an unpromoted catalyst. The isotherms designated as "van der Waals CO" were obtained at -183° immediately after determining the "total CO" isotherms at -183° and then evacuating the catalyst with a diffusion pump for a half hour at -78° . The difference between the two curves may be taken as the amount of chemisorbed carbon monoxide in each case because, as mentioned above, it was found that the chemisorbed carbon monoxide could not be removed by pumping at -78° . It is apparent that the doubly promoted catalyst, which had a large carbon dioxide chemisorption, has a small carbon monoxide chemisorption, whereas the pure iron catalyst with little or no chemisorption of carbon dioxide has large carbon monoxide chemisorption. The carbon dioxide and carbon monoxide chemisorptions therefore each leads independently to the conclusion that the 1 or 2% K_2O present in promoted iron synthetic ammonia catalysts covers a large fraction of the surface of the catalyst.

Throughout the present paper we have generally referred to the irreversible carbon monoxide and carbon dioxide adsorptions as chemisorptions. At present we do not wish to enter into an extended discussion in regard to the most appropriate nomenclature for sorptions of a chemi-

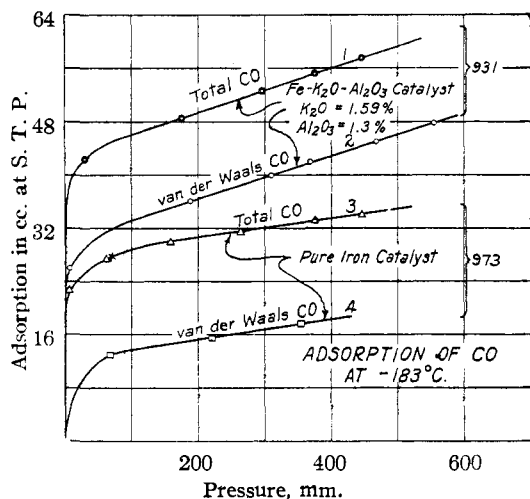


Fig. 3.—Comparison of the total carbon monoxide adsorption at -183° with the van der Waals adsorption for doubly promoted catalyst 931 and for pure iron catalyst 973. The X on curve 3 represents a desorption point.

was occurring the catalyst was evacuated by a diffusion pump at temperatures up to -78° immediately following a run at -183° . Carbon monoxide adsorption isotherms made at -183°

(11) In the course of the reduction of catalyst 930 the glass adsorption bulb became heavily frosted, presumably due to the volatilization of alkali from the catalyst. Analysis of the alkali on two of these frosted catalyst bulbs showed that 65 and 54%, respectively, of the 1.07% alkali had volatilized onto the glass. Hence, the alkali remaining in the catalyst was only 0.4 to 0.5% in all the runs on catalyst 930 rather than the 1.07% reported in the present paper. It was also shown by a blank run on a third such catalyst bulb from which the catalyst had been removed immediately after reduction that no carbon dioxide (less than 0.1 cc.) was taken up at -78° by the alkali on the glass. Any chemisorbed carbon dioxide reported in the present paper was therefore adsorbed by the catalyst or by the alkali on the catalyst and not by the alkali on the glass reaction vessel.

cal type. In those instances in which a surface adsorption can be shown to be a slow surface process whose rate is very sensitive to temperature, the name "activated adsorption" suggested by Taylor¹² is certainly descriptive and therefore appears to serve a useful purpose. However, in the present instances, the irreversible adsorptions of carbon monoxide on the iron catalysts and of carbon dioxide on the alkali promoted iron catalysts were not slow processes; they appear to be about as rapid as the accompanying van der Waals adsorption. The name "chemical adsorption" or "chemisorption" which has been used frequently in the past therefore appears to be a more descriptive one to apply to the present examples in order to emphasize their rather unique adsorption characteristics.

An accurate assessing of the present work as a contribution to a better understanding of the action of promoters in iron synthetic ammonia catalysts seems desirable at this point. Almquist¹³ summarized the ways in which promoters may affect the activity of a catalyst by pointing out that they may serve either (1) to maintain a large surface area by retarding the growth of crystals in the catalysts, or (2) to change the qualitative nature of the surface by furnishing a promoter-catalyst interface that is more active as a catalyst than the same surface area of the pure catalyst. Furthermore, from the results of Almquist and Black,¹⁴ as well as from previous work by Wyckoff and Crittenden,¹⁵ it may be concluded that in the case of iron synthetic ammonia catalysts aluminum oxide alone, or aluminum oxide together with potassium oxide function in part at least in the first of these two ways. Recently determined² adsorption isotherms for nitrogen at -183° confirm this view by showing that catalysts promoted with either aluminum oxide or a combination of potassium oxide and aluminum oxide have much larger surfaces than have pure iron catalysts; however, they also show that a typical doubly promoted catalyst containing both potassium oxide and aluminum oxide has only about one-third as much surface as a catalyst promoted with aluminum oxide alone, even

though the former is much more active at high pressures than the latter. It therefore seems very probable that an alkali such as potassium oxide, when added as a promoter to an iron catalyst together with a per cent. or so of aluminum oxide functions predominantly in the second of the two ways mentioned above, namely, by changing the qualitative nature of the catalyst surface. The present work, by indicating that about 70% of the surface of a doubly promoted catalyst is covered with alkali, brings to light the fact that only about one-third as much iron but about forty times as much alkali goes to make up the surface of a doubly promoted catalyst as one would have had reason to suspect heretofore. The precise mechanism through which the alkali when present with aluminum oxide so radically increases the activity of the surface per unit area is still a matter of conjecture and is not revealed by the present work.

Adsorption isotherms at -183° previously reported by Benton and White¹⁶ for a sample of the same pure iron catalyst (973) as used in some of the present experiments agree qualitatively with our results in indicating that the total adsorption of carbon monoxide at -183° is much larger than that of nitrogen at -183° . However, their adsorption of carbon monoxide at -183° is only about 40% larger than that of nitrogen, whereas our results yield a total carbon monoxide adsorption that is consistently at least 100% larger than that of nitrogen. No explanation of this discrepancy between their results and ours is evident at this time.

Summary

With the help of adsorption isotherms for carbon monoxide and nitrogen at -183° and for carbon dioxide at -78.5° evidence has been obtained to show that a per cent. or so of potassium oxide in an iron synthetic ammonia catalyst actually covers more than 50% of the total surface of the catalyst. Apparently at -183° carbon monoxide rapidly forms a monolayer of chemisorbed carbon monoxide on the iron atoms of the catalyst, whereas at -78.5° carbon dioxide rapidly forms a layer of chemisorbed carbon dioxide on that portion of the surface that is covered by alkali.

WASHINGTON, D. C.

RECEIVED NOVEMBER 21, 1936

(12) Taylor, *THIS JOURNAL*, **53**, 578 (1931).

(13) Almquist, *ibid.*, **48**, 2820 (1926).

(14) Almquist and Black, *ibid.*, **48**, 2814 (1926).

(15) Wyckoff and Crittenden, *ibid.*, **47**, 2866 (1925).

(16) Benton and White, *ibid.*, **54**, 1806 (1932).