TABLE III

COMPARISON OF THE Fe^{II}–Tl^{III} REDUCTION WITH THE Tl^{I}–T^{III} EXCHANGE REACTION

Reaction	Rate constant, $m.^{-1}l.sec.^{-1}$	$E‡$, cal. mole^{-1}	$\Delta S‡$, cal. deg.$^{-1}$ mole^{-1}
(1), exchange	2.60×10^{-5}	14,700	−32
(12), reduction	1.406×10^{-2}	18,400 ± 100	− 7.3
(16), reduction	1.238×10^{-2}	22,060 ± 530	....

Although no reaction path corresponding to reaction (16) has been reported for the exchange reaction, the figures for the exchange reaction (1) and that portion of the reduction which proceeds by way of reaction (12) are subject to comparison. As might have been predicted by those who emphasize the importance of charge interaction,[8] or because of the necessity for the intermediate production of an unstable ionic species in the rate-determining step by those who adhere to the "equivalence change" principle[9] as modified[10] to include the theory of "potential humps,"[11] the experimental activation energy is less for the exchange reaction than for the analogous oxidation-reduction reaction. The entropy of activation for reaction (12) is surprisingly high, in view of the fact that Glasstone, Laidler and Eyring[12] list values from −20 cal. deg.$^{-1}$ mole^{-1} to −32 cal. deg.$^{-1}$ mole^{-1} for a number of reactions between ions of like sign, and is much higher than that reported for the exchange reaction. Although it is not felt that sufficient data are available to permit an adequate explanation of this feature, it is interesting to note that it is this difference in entropy which accounts for the fact that reaction (12) has a velocity which is more than 500 times that of the exchange reaction (1), in spite of the unfavorable difference in activation energies.

[8] J. Weiss, *J. Chem. Soc.*, 309 (1944).

[9] P. A. Shaffer, *Cold Springs Harbor Symposium Quant. Biol.*, VII, 50 (1939).

[10] A. R. Remick, THIS JOURNAL, **69**, 94 (1947).

[11] Bancroft and Magoffin, *ibid.*, **57**, 2561 (1935); **58**, 2187 (1936).

[12] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 435.

URBANA, ILLINOIS RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE HALDOR TOPSØE RESEARCH LABORATORY]

Investigation on Surface Properties of Reduced Iron Catalysts for the Synthesis of Ammonia and Correlation with Crystal Sizes and High Pressure Conversion Activities

BY ANDERS NIELSEN AND HANS BOHLBRO

Two triply promoted ammonia catalysts have been examined by adsorption measurements, and the adsorption data correlated with X-ray data and high pressure conversion measurements. Crystal sizes determined from line broadening in X-ray patterns and surface areas derived from low temperature A and N_2 adsorption are in satisfactory agreement. The more active catalyst has the smaller surface area and the smaller CO chemisorption at −78°. A first order phase transition of adsorbed nitrogen at liquid nitrogen and liquid oxygen temperatures has furthermore been found and isosteric heats of adsorption have been determined.

Introduction

An investigation on high pressure conversion measurements and on the structure of reduced iron catalysts as determined by X-ray analysis has previously been published by one of the authors.[1]

The present paper reports the results of a series of adsorption measurements that have been made with CO, N_2 and A on two of the commercial iron synthetic ammonia catalysts used in the previous investigations.

Experimental

High Pressure Conversion Measurements.—Catalysts used were commercial triply promoted K_2O–CaO–Al_2O_3–iron catalysts, KM I and KM II, made from fused oxides. Conversions were measured at 330 atm., S.V. = 15000 and $H_2:N_2 = 3:1$. For details see reference 1.

X-Ray Technique.—Samples of reduced and tested catalysts were removed from the converter in an atmosphere of nitrogen and transferred to pentane or benzene. Samples for X-ray exposure were ground in the protecting liquid and specimens were prepared by mixing the wet powder with canada balsam in xylene solution. For details concerning the X-ray technique see reference 1. Cobalt and chromium tubes of Machlett manufacture were used.

Adsorption Measurements.—Samples used were the reduced and tested catalysts stored in pentane or benzene as described above. Samples, still wet, were transferred to the adsorption bulb. Evacuation was started at room temperature. When evacuated at room temperature, the sample was slowly heated and the evacuation always terminated with a 9-hour period at 400°. This temperature was chosen so as to ensure that no further sintering of the samples took place. This was verified by re-reducing a sample *in situ* in the bulb, evacuating and repeating the surface area determination (areas of 4.48 $m.^2/g.$ and 4.40 $m.^2/g.$ respectively, were found). Areas always refer to grams of reduced catalyst. Effective cross-sectional area of an adsorbed nitrogen molecule is assumed to be 16.2 $Å.^2$ at liquid nitrogen temperature. The effectiveness of the shielding against oxygen during storage was verified by comparing CO chemisorption at −78° of one of the samples with CO chemisorption of a re-reduced sample and of a freshly reduced sample reduced at atmospheric pressure with pure hydrogen (chemisorptions of 7, 7 and 12% of a nitrogen monolayer were found).

The apparatus was essentially that of Brunauer, Emmett and Teller.[2] For pressure determinations the apparatus was connected to a McLeod gage (10^{-5}–10^{-1} mm.), to a Pirani gage (10^{-3}–0.75 mm.), and to a U-tube manometer provided with a cathetometer (10^{-2}–1000 mm.). The Pirani gage was especially useful during desorption and further to distinguish between condensable and non-condensable gases when used combined with the McLeod gage. A purification train[3] was used for the purification of H_2, He, A, N_2, CO and CO_2 used for the experiments. The evacua-

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[1] A. Nielsen, "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," Jul. Gjellerups Forlag, Copenhagen, 1950.

[2] *Cf.* P. H. Emmett, "A New Method for Measuring the Surface Areas of Finely Divided Materials and for Determining the Size of Particles," Symposium on New Methods for Particle Size Determination in the Subsieve Range, A.S.T.M. (1941).

[3] L. G. Joyner in W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Company, Pittsburgh, Penna., 1949, p. 272.

tion train was capable of yielding 10^{-6} mm. The low temperatures were maintained by use of liquid nitrogen of different degrees of purity, liquid oxygen and dry ice–ethanol-baths. The temperature of 86.7°K. used in one experiment, was obtained by use of a proper oxygen–nitrogen mixture, the composition of which was kept constant by addition of a mixture of the same composition as that of the vapors given off from the bath. Temperatures of the baths were measured by an oxygen vapor pressure thermometer.

Data and Discussion

For the purpose of a quick estimate of the life of ammonia catalysts we operate the catalysts for a shorter period at a temperature 100° above normal operating temperatures and measure the resulting decrease in activity. To this procedure we apply the expression "thermoresistancy test."

In Table I are shown activities and thermoresistancies of samples of each of the two catalysts. The conversions of 23.8 and 25.6% shown initially by KM I and KM II correspond to efficiencies of 0.62 and 0.67, respectively, and to rate constants which according to the theory of Temkin and Pyzhev[4] show a ratio of almost 2. By efficiency is meant according to Larson and Tour[5] "The ratio of the actual per cent. NH_3 in the gas to that theoretically possible under the conditions in question."

TABLE I

THERMORESISTANCY OF AMMONIA CATALYSTS

Conversions are expressed in terms of per cent. ammonia in the exit gas. Conditions for conversion: t = 450°, p = 330 atm., S.V. = 15000.

Catalyst	KM I	KM II
Conversion, catalyst prior to thermoresistancy test	23.8	25.6
Conditions for first thermoresistancy test, °C./hours	550/17	554/17
Conversion, catalyst after first thermoresistancy test	23.8	23.6
Conditions for second thermoresistancy test, °C./hours	557/65	557/17
Conversion, catalyst after second thermoresistancy test	23.8	23.6
Conditions for third thermoresistancy test, °C./hours	..	550/65
Conversion, catalyst after third thermoresistancy test	..	23.6

From Table I it is seen that the more active catalyst has the lower thermostability and further that the rapid decrease in activity shown by KM II during the first few hours at 550° does not continue after the first sintering at 550° at a high speed. We may mention that other catalyst types have shown measurable decrease in activity following repeated thermoresistancy tests, and that such catalysts are known to possess a short life-time in industrial use.

In a separate series of experiments using slightly different procedures in reduction and thermal resistancy tests from those given in Table I, coexisting values of conversion activities and of surface areas have been measured for catalysts KM I and KM II (Table II).

TABLE II

CORRELATION OF ACTIVITY AND SURFACE AREA

Conversions are expressed in terms of per cent. ammonia in the exit gas.

Catalyst	Conversion t = 450° p = 330 atm. S.V. = 15000	Surface area m.²/g. (g. reduced catalyst)
KM I	25.9	12.6
KM I	23.8	7.71
KM II	26.9	8.15
KM II	23.6	4.48

At first it might appear that decrease in activity accompanying a decrease in surface area of a given catalyst type is rather small. By use of the Temkin–Pyzhev[4] equation, one can readily see that this is not the case, as the rate constant decreases at least as much as the surface area, as should be expected. Whether the decrease in activity is greater than the decrease in surface area cannot be definitely answered from our results because of the dependence of the rate constant on the exact method of applying the Temkin–Pyzhev equation and because of the possibility also that slight differences in the temperature distribution in the two catalysts might exist.

Crystal size of reduced KM II catalyst has previously been determined from line broadening in the X-ray pattern of the catalyst. As it appears from Table III—showing constancy of $\frac{\beta \cos \theta}{\lambda}$ the line broadening found in the pattern of reduced KM II can be attributed to a too small crystal size, and the linear dimension of the crystallites was determined to be t KM II = 360 Å. where λ is the wave length of the X-radiation, θ is the Bragg angle and β is the linear breadth of the reflection corrected for experimental conditions.

TABLE III

LINE BROADENING IN THE PATTERNS OF REDUCED KM II CATALYST

θ	λ, Å.	Doublet sepn. d, mm.	b_0, mm.	B_0, mm.	B, mm.	β, mm.	$\frac{\beta \cos \theta}{\lambda}$	β cot θ
38°, 67	1.79	0.32	0.48	1.02	0.90	0.67	0.29	0.84
62°, 00	1.79	0.78	0.57	1.74	1.34	1.13	0.29	0.60
31°, 1	2.08	..	0.32_5	0.81_5	0.82	0.60	0.25	0.98
34°, 5	2.29	0.22	0.36	0.96	0.90	0.76	0.27	1.11

If the crystals are assumed to be cubes, then a linear dimension of 360 Å. corresponds to a surface area of 21 m.²/g. whereas by nitrogen adsorption we found this catalyst to have a surface area of 8 m.²/g. This indicates that for this catalyst roughly one-third of the total surface area is exposed to the gas, whereas two-thirds exists as interfacial layers joining the crystallites.

As is evident from Table II, catalyst KM II has the smaller surface area when compared with catalyst KM I, although KM II is the more active. This is true of the freshly reduced catalyst samples as well as of samples which have been subjected to tests of thermoresistancy. Catalyst KM II not only has the smaller total surface area, but, further, it has the smaller available iron surface as measured by chemisorption of CO at −78°. We found the available iron surface of catalyst KM II, as well as that of catalyst KM I to be approximately 7% of the total surface. This low value agrees qualitatively with the high CO_2

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(4) M. Temkin and V. Pyzhev, *Acta Physicochim.* (*U. R. S. S.*), **12**, 327 (1940).

(5) A. T. Larson and R. S. Tour, *Chem. Met. Engr.*, **26**, 647 (1922).

chemisorption at room temperature which, for KM I amounted to 59% of a nitrogen monolayer. In these calculations, chemisorptions of CO and CO_2 are compared with the volume of nitrogen in a monolayer without correcting for the difference between the area covered by a molecule of chemisorbed CO or CO_2 and that covered by a molecule of physically adsorbed nitrogen. This, of course, is not an exact procedure both because the dimensions of the three molecules are not identical and because the appropriate area of an adsorbed molecule is somewhat influenced by the surface even in the case of physical adsorption, and is greatly dependent upon the spacing of the atoms in the surface of the adsorbent in the case of chemisorption.

Low relative pressure, low temperature, nitrogen adsorption isotherms have been measured in the pressure range from 1×10^{-4} to 50×10^{-4} mm. and at temperatures of 79.8, 86.7 and 90.3° K. The three adsorption isotherms are shown in Fig. 1.

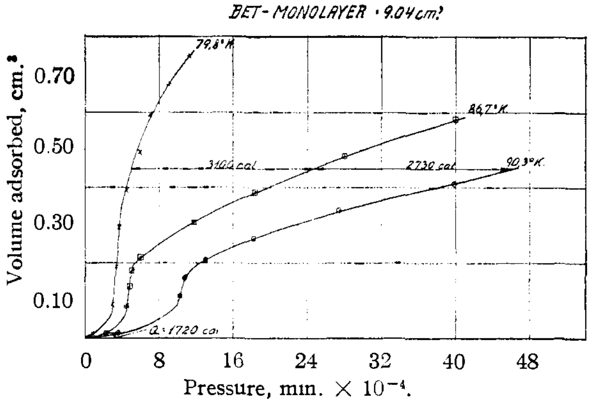

Fig. 1.—Adsorption isotherms for nitrogen on iron synthetic-ammonia catalyst KM I at temperatures 79.8, 86.7 and 90.3 °K. Isosteric heats of adsorptions calculated from the curves are shown.

A sample of catalyst KM I having a surface area of 7.4 m.²/g. and a conversion activity of 22.1% NH_3 at 330 atm., 450° and S.V. = 15000 was used in the experiment.

All three isotherms show a linear and approximately vertical section appearing at different pressures at the different temperatures used. As mentioned by Jura, Loeser, Basford and Harkins[6] such discontinuity of the isotherm *a priori* might be due to chemisorption, to capillary condensation in pores of constant cross section or to a first order phase transition. We believe it is certain that chemisorption can be excluded as the origin of said phenomena, owing to the low values of the calculated heats of adsorption and the fact that all of this adsorbed nitrogen could be pumped off readily at −78°. Furthermore, the vertical portion of the isotherms terminate at different volumes adsorbed depending upon temperature. In our opinion this last point also excludes a normal capillary condensation as the origin of the observed discontinuity of the isotherms and in this connection we wish to mention that mean pore diameters of this type of catalysts are some hundreds of Å. as has been determined by Hall, Tarn and Anderson.[7] We therefore attribute the phenomenon to a first order phase transition of the adsorbed nitrogen.

From the three isotherms we have determined heats of adsorption at surface coverings below and above the phase transition interval. When adsorption takes place to the phase of highest molecular area we found a heat of adsorption of 1720 cal. per mole, and in the case of adsorption to the condensed two-dimensional phase a heat of adsorption of 3100 cal. per mole (79.8–86.7° K.) and 2730 cal. per mole (86.7–90.3° K.), respectively; these last values correspond to a coverage of 5% of a BET-monolayer.

As will be noticed, the vertical parts of the isotherms appear at much lower surface coverings than those reported by Harkins, Jura and coworkers.[6,8] This may be due to the phase transition taking place only on the iron surface and the rest of the surface being only slightly covered. The isosteric heats of adsorption calculated, have magnitudes characteristic for van der Waals adsorption, and attention is specially drawn to the low value found at a surface covering below the phase transition range. This does not agree with the high heats of adsorption of nitrogen on iron reported by Beeck[9] and we, therefore, do not support the theory advanced by Beeck that chemisorption generally makes the BET-nitrogen method unsuitable for the determination of surface areas of metal catalysts—at least not so far as ammonia catalysts are concerned. The differences between

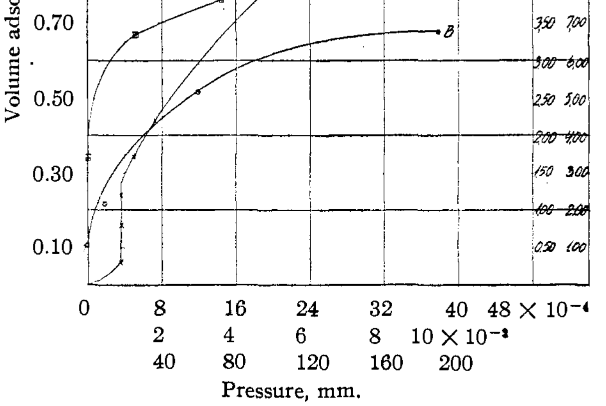

Fig. 2.—Adsorption isotherm for nitrogen on iron synthetic ammonia catalyst KMI at a temperature of 78.5° K. and in the pressure range from 10^{-4} mm. up to 200 mm.

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[6] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **14**, 117 (1946).

[7] W. K. Hall, W. H. Tarn and R. B. Anderson, THIS JOURNAL, **72**, 5436 (1950).

[8] G. Jura, W. D. Harkins and E. H. Loeser, *J. Chem. Phys.*, **14**, 344 (1946).

[9] O. Beeck, "Advances in Catalysis," Vol. II, Academic Press Inc., Publishers, New York, N. Y., 1950, p. 157.

Beeck's results and ours may originate from the fact that Beeck used pure metal films whereas the surfaces of our catalysts are contaminated with promoters and possibly with some residual hydrogen and nitrogen. In Fig. 2 is shown a complete isotherm at 78.5° K. and attention is called to the point that at this temperature the part of curve A corresponding to what is believed to be a first order transition is vertical within limits of experimental accuracy.

It should be noticed that we found a slightly higher value of the heat of adsorption when using the lower temperature interval than at the higher temperature, and we wish to stress the appreciably lower value found for adsorption to the uncondensed phase, which may easily be explained by the transition heat connected with the phase change. The values calculated should be compared with the heat of liquefaction of nitrogen, which is 1336 cal. per mole at $-196°$. We wish to call attention to the fact that the difference in isosteric heats of adsorption to the phases of higher and lower molecular area is of the same magnitude as the heat of liquefaction of nitrogen. This indicates that the heat of adsorption to the phase of highest molecular area is due to adsorbate–adsorbent forces, solely or at least mainly, whereas adsorbate–adsorbate forces become active in the phase transition range. The value of 1720 cal. determined below the phase transition interval may indicate that a potential of not purely van der Waals nature is active. In this connection the "structural" adsorption described by Cook, Pack and Oblad[10] may be mentioned.

The surface areas of a sample of reduced KM I determined by nitrogen adsorption at 78.5° and by argon adsorption at 89.5° K. were 7.71 m.^{2}/g., and 6.25 m.^{2}/g., respectively. As is evident from the above, we do not attribute this difference to the chemisorption of nitrogen, but to the molecular areas used for nitrogen and argon being not quite correct for representing the true cross-sectional areas of nitrogen and argon in the adsorbed monolayers. This observation is similar to the differences in nitrogen and argon areas for adsorption of these gases on silica gel, as described by Brunauer.[11]

As pointed out by Harkins and Jura[12] the appropriate area of a molecule on a surface—even when physically adsorbed—is somewhat dependent on the properties of the surface.

No measurable chemisorption of CO at liquid oxygen temperature could be established. This failure to observe carbon monoxide chemisorption at $-183°$ is very surprising in view of the results that have been published relative to the chemisorption of CO on the surface of iron synthetic ammonia catalysts. Further it should be mentioned that all nitrogen adsorbed at low temperature is readily given off already at $-78°$, one more indication that the nitrogen is physically bound.

Acknowledgment.—The authors feel greatly indebted to Mr. Haldor Topsøe for valuable discussions during the work and for permission to publish the results.

(10) M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

(11) S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1945, p. 158.

(12) W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431 (1943).

HELLERUP, DENMARK RECEIVED MAY 15, 1951

[CONTRIBUTION NO. 1625 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Spectrophotometric Investigation of the Copper(II) Monobromo Complex

BY PAUL S. FARRINGTON[1]

An equilibrium constant for the formation of the monobromo complex of copper(II) in solutions of unit ionic strength has been determined by a spectrophotometric method. At 22 ± 2° the average value for that equilibrium constant was found to be 2.1 ± 0.25. The molar extinction coefficient of $CuBr^+$, ϵ_1, has been determined over the range 260 to 300 millimicrons, and ϵ_1 is reported graphically as a function of wave length.

In the course of the study of the oxidation–reduction equilibrium between cupric copper and bromide made by Farrington, Meier and Swift[2] it became necessary to obtain information concerning the bromide complexes of cupric copper in order to calculate the desired equilibrium constants. For many years it has been known that cupric copper in concentrated bromide solutions (above 3.5 formal HBr) produces a reddish-brown to purple color; however, the only published constant[3] for a bromide complex appeared after the completion of the present investigation. McConnell and Davidson[4] have determined equilibrium constants for both the monochloro and dichloro complexes of cupric copper; the spectrophotometric method which they used is relatively uncomplicated for the determination of a monohalide complex and it was adopted for this investigation. All solutions used for these measurements were adjusted to an ionic strength of unity.

Experimental

Reagents.—A solution of $Cu(ClO_4)_2$ was prepared by dissolving $CuCO_3 \cdot Cu(OH)_2$ in $HClO_4$: the excess $HClO_4$ was very small. A solution of $Na_2S_2O_3$ was prepared and standardized against KIO_3. The $Cu(ClO_4)_2$ solution was then standardized iodometrically and the copper concentration was found to be 1.342 *F*.

A stock solution of NaBr (0.100 *F*) was prepared by dissolving a weighed portion of the reagent grade salt in chloride-free water and diluting to the mark in a volumetric flask. The NaBr had been dried for 1.5 hours at 120°. Solutions 0.0050 *F* and 0.0250 *F* in NaBr were prepared by accurate dilution of the stock solution.

A standard solution of $HClO_4$ (2.673 *F*) was prepared by

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(1) Merck Graduate Fellow in Analytical Chemistry, 1949–50. Present address: University of California at Los Angeles.

(2) P. S. Farrington, D. J. Meier and E. H. Swift, to be published.

(3) R. Näsänen, *Acta Chem. Scand.*, **4**, 816 (1950).

(4) H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).