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THE CHEMISORPTIONS OF GASES ON WELL-REDUCED IRON SYNTHETIC AMMONIA CATALYSTS

By

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Abstract

The chemisorption of nitrogen, hydrogen, and carbon monoxide and the mutual influence of these species on each other were studied on two iron catalysts carefully reduced in hydrogen diffused through a palladium thimble. The chemisorption of nitrogen was found to occur more extensively on the present carefully reduced catalysts than was found in earlier work in which reduction was made with hydrogen that was not diffused through a palladium thimble. This is consistent with the idea that even 0.001% nitrogen in a hydrogen stream can leave an appreciable amount of chemisorbed nitrogen on the surface of iron during the reduction process.

Hydrogen adsorbs in three different types within the range −195 to 450°C. Type A extends from −100 to 0°C; type B, from 100 to 450°C, and type C from −195 to −150°C. In agreement with prior work, type B strongly inhibits type C adsorption. Type A has no influence on type C adsorption. Nitrogen adsorbed at 450°C inhibits molecule per molecule the type B adsorption of H_2 at 100°C on doubly promoted catalysts whereas on singly promoted, the inhibition is less and decreases steadily with the time of exposure to hydrogen. Thus, the presence of NH or NH_2 groups on the singly promoted catalysts is more prevalent than on the doubly promoted in accordance with earlier observations.

Introduction

The adsorption of nitrogen and hydrogen on synthetic ammonia catalysts has been widely studied in connection with ammonia synthesis[1,2]. Emmett and his coworkers studied previously the chemisorptions of various gases on promoted iron synthetic ammonia catalysts.[3~6] Furthermore, the influence

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of one adsorbed species upon the adsorption of the other was studied to obtain information related to the nature of adsorbed species as well as that related to the nature of the catalyst surface.[5]

A few years after the earlier work was completed, it was shown[7,8,9], that even a trace of nitrogen in the hydrogen used to reduce the iron oxide would build up a partial layer of chemisorbed nitrogen on the iron surface. This raises the question as to whether results gotten with catalysts already containing a partial layer of nitrogen would be different from those reduced in pure hydrogen. To investigate this, the experiments described in this paper have been carried out on iron synthetic ammonia catalysts reduced in hydrogen purified by diffusion through a palladium thimble. The adsorption of nitrogen and hydrogen and the mutual interaction of several combinations of gases on adsorption have been determined.

For convenience, the influence of the reduction by pure hydrogen will be assessed with regards the adsorption of nitrogen, the adsorption of hydrogen, and the influence of one adsorbed species on another.

Experimental

The experiments were carried out over two iron synthetic ammonia catalysts: doubly promoted catalyst 416 (0.97% alumina and 0.65% potassium oxide) and singly promoted catalyst 234 (0.35% alumina and 1.20% silica). These were crushed to 8–14 mesh granules before use. The catalysts were reduced in a stream of pure hydrogen at a space velocity of 5000. The weight and the reduction schedule are listed in Table 1. Between the runs, the catalyst was reduced for 15 hr at the final temperature of the reduction for each series of experiments in the tables. At the end of the reduction, the catalyst was evacuated to 10^{-6} Torr for 2 to 10 hr at the same temperature as that of the reduction. The amount of adsorption was measured with a conventional volumetric apparatus.

Table 2 shows the amount of carbon monoxide chemisorbed on the catalysts. The column headed "N_2 monolayer physical adsorption" represents the number of cc STP of nitrogen necessary to cover the entire surface with a complete monolayer of physically adsorbed nitrogen. It was estimated from nitrogen adsorption at −195 or −183°C by using the BET method.[9] The amount of chemisorbed carbon monoxide listed in the fourth column was estimated by the method proposed previously by Emmett and Brunauer.[10] The isotherm of carbon monoxide adsorption was obtained at −195° or −183°C. After physically adsorbed carbon monoxide had been removed by the evacuation of −78°C for 1 hr, the isotherm was again determined

TABLE 1.

Number of series	Catalyst	Unreduced oxide (g)	Reduction time (hr)	Temperature (°C)
I	234	10.41	100	260
			100	500
III	234[a]	9.68	100	350
			50	450
			50	550
IV	234[b]	11.32	94	330
			108	450
			87	550
I	416	12.51	100	350
			100	475
II	416	10.01	23	360
			107	450
			94	550

a) Singly promoted catalyst 234 used in series III experiment was exposed to air at room temperature after series II, not listed.

b) This was a mixture of fresh catalyst and a part of the catalyst used in series III.

TABLE 2. Chemisorption of Carbon Monoxide

Number of series	Catalyst	N_2 monolayer physical adsorption (cc STP)	CO chemisorption (cc STP)	Temperature of CO adsorption (°C)
I	234	14.2	5.2	−183
		14.2	5.2	−195
III	234	12.15	2.75	−195
I	416	9.58	3.50	−195
II	416	—	3.00	−195
		7.14	2.75	−195

at −195 or −183°C. The difference between two isotherms thus obtained was practically independent of the partial pressure of carbon monoxide so that it was assumed to be the amount of carbon monoxide chemisorbed on the surface iron atoms.

Hydrogen was carefully purified by passage through a palladium thimble.

Carbon monoxide, and nitrogen were purified by passage through potassium hydroxide, heated copper (600°C) and finally through a trap immersed in dry ice-alcohol. Helium was purified in a similar fashion but instead of dry ice-alcohol, liquid nitrogen was used as a refrigerant.

Results and discussion

Nitrogen Adsorption:

Table 3 shows the results of the nitrogen adsorption as a function of time and temperature. The ratios of chemisorbed nitrogen (at 440°C) to chemisorbed carbon monoxide (at -195°C) (referred to as N_2 chem/CO chem) are 0.5 and 0.64 for singly promoted catalyst 234 and doubly promoted catalyst 416, respectively. When the nitrogen adsorption is carried out at lower temperature *i. e.* around 300°C, higher ratios of N_2 chem/CO chem are obtained: 0.66 for catalyst 234 and 0.81 for catalyst 416. On the other hand, the ratios obtained in the previous work[5] were 0.34 and 0.51 at 391°C for singly promoted catalyst 954 and doubly promoted catalyst 931, respectively whereas

TABLE 3. Chemisorption of Nitrogen

Catalyst	Number of series	N_2 monolayer physical adsorption	CO chemisoprtion		N_2 chemisorption		Ratio	
		(cc STP)	(cc STP)	temp. (°C)	time (hr)	volume (cc STP)	$\frac{N_2 \text{ chem}}{\text{CO chem}}$	$\frac{N_2 \text{ chem}}{N_2 \text{ mono}}$
234	I	14.2	5.20	217	0.083	0.57	0.11	0.04
					0.86	1.09	0.21	0.077
					2.7	1.67	0.31	0.11
					4.4	1.90	0.36	0.135
					19.5	2.44	0.47	0.17
				303	0.033	1.40	0.27	0.097
					0.8	2.43	0.46	0.17
					1.5	2.76	0.53	0.19
					8.5	3.33	0.64	0.23
					19	3.42	0.66	0.24
				440	0.083	2.24	0.43	0.157
					0.33	2.42	0.47	0.17
					0.59	2.45	0.47	0.17
					0.93	2.54	0.49	0.18
					1.8	2.57	0.49	0.18
					2.5	2.61	0.50	0.18

TABLE 3. (*cont*)

Catalyst	Number of series	N_2 monolayer physical adsorption	CO chemisorption		N_2 chemisorption		Ratio	
		(cc STP)	(cc STP)	temp. (°C)	time (hr)	volume (cc STP)	$\frac{N_2\text{ chem}}{\text{CO chem}}$	$\frac{N_2\text{c hem}}{N_2\text{ mono}}$
416	I	9.55	3.50	307	0.19	1.22	0.35	0.13
					1.9	1.76	0.50	0.18
					9.4	2.52	0.72	0.26
					19.5	2.83	0.81	0.30
				217	0.1	0.49	0.14	0.051
					1.4	0.92	0.26	0.095
					4	1.11	0.32	0.12
					16	1.63	0.47	0.17
					23.8	1.81	0.52	0.19
				440	0.13	1.91	0.546	0.2
					0.68	2.24	0.64	0.235
			3.35[a]	307	0.166	1.07	0.319	—
					3.90	1.90	0.567	—
					6.20	2.13	0.636	—
					9.4	2.33	0.696	—
					20.4	2.66	0.759	—
			3.25[a]	437	0.11	1.51	0.465	—
					0.28	1.76	0.542	—
				410	0.63	1.78	0.548	—
					1.63	1.92	0.591	—
			3.15[a]	232	0.23	0.45	0.143	—
					1.0	0.67	0.213	—
					9.1	1.22	0.387	—
					20.3	1.36	0.432	—
				232	1.26	0.72	0.241	—
					2.9	0.94	0.298	—
					16.05	1.32	0.419	—
416	II	—	3.00	232	0.283	0.86	0.315	—
					1.45	1.21	0.404	—
					3.05	1.40	0.467	—

a) The amount of chemisorbed carbon monoxide was decreased by repeated reduction of the catalyst.

the ratio obtained at 440°C was 0.26 for catalyst 954.*) Huang and Emmett recently studied the state of nitrogen chemisorbed on unpromoted catalyst which was reduced with highly purified hydrogen.[11] The N_2 chem/CO chem ratio which is estimated from their results is fairly large (>0.42 at 313°C) compared to that previously obtained for unpromoted catalyst 973 (0.22 at 395°C).[5] Therefore, it is evident that the chemisorption capacity of the catalyst for nitrogen is enhanced when the catalyst is reduced with highly purified hydrogen.**)

In series I experiments, adsorption isobars of nitrogen were determined at atmospheric pressure. The maximum N_2 chem/CO chem ratios obtained are 0.943 and 0.674, respectively for catalysts 416 and 234. When the catalyst is further reduced according to the schedule in Table 1, the free iron surface as well as the surface area decreases to some extent probably due to the sintering of the catalyst (Table 2). The maximum ratio obtained in Series III experiment is 1.16 for catalyst 234. Here again one must remember that if the CO chemisorption values were obtained at −78°C instead of −195°C all of these ratios of chemisorbed nitrogen to chemisorbed carbon monoxide would be about 15% smaller and would therefore lie in the range 0.5 to 1.0.

The question naturally arises as to whether the observed nitrogen adsorption as judged by the N_2 chem/CO chem ratio is larger than one might expect. First we have to answer the question of whether nitrogen is adsorbed as atoms or molecules. From measurements of the inhibitive effect of adsorbed nitrogen on the low temperature chemisorption of CO, Brunauer and

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*) Not obtained for Catalyst 931.

**) Caution has to be used on comparing the results in the present paper and the paper by Huang and Emmett with the older work by Brunauer and Emmett.[5] In the recent work the CO chemisorption was measured at −195 or −183°C. Brunauer and Emmett[5] showed that the chemisorption of CO at −78°C was about 10 to 15% greater than the chemisorption at −183°C. Therefore, in comparing the old work and the new work one has to take into account that 10 to 15% higher value for N_2chem/COchem should be obtained in the present work compared to the older work because of the CO values being 10 to 15% smaller in the present work than they would have been if the chemisorptions were measured at −78°C. Eeven when this correction is made, however, it is still true that the chemisorption of nitrogen is considerably greater on catalysts reducecd in hydrogen that had been purified by diffusion through palladium than they were when the hydrogen had not been so diffused. In this connection, it should be noted that the reduction of iron synthetic ammonia catalyst by hydrogen containing as little as 0.001% nitrogen could result in final catalyst having about 15% of its surface covered with chemisorbed nitrogen.[8,9] This results from the fact that the equilibrium adsorption values for nitrogen on iron catalysts vary as the 1/6th power of the pressure of nitrogen.

Emmett[5)] concluded that at 400°C and above substantially all the nitrogen adsorbed on iron catalysts is present in the atomic form. It is interesting to note that recent experiments by Ertl and coworkers show that on single[16,18)] crystals of iron the combination of LEED, Auger electron spectroscopy, and ultraviolet photoelectron spectroscopy enabled him to conclude that all detectable nitrogen chemisorption in the temperature range 0 to 400°C at pressures equal to or less than 10^{-4} Torr is present as atomic and not molecular adsorption. Only at 140°C on the Fe (111) surface were molecules detectable. This is perhaps the most convincing and direct evidence that has been obtained in regard to the nature of nitrogen adsorbed on iron surfaces. It should be noted that Takezawa and Emmett[14)] did find evidence of adsorption as molecules at temperatures below 400°C, the ratio of molecules to atoms increasing as the temperature is lowered. This is not considered to be in disagreement with Ertl's results because the work was carried out at atmospheric pressure rather than the 10^{-4} Torr used by Ertl. It should be noted in passing that Takezawa[15)] has provided some convincing additional evidence that nitrogen molecules are present on an iron catalyst at low temperatures. He found that nitrogen (presumably largely molecular) adsorbed at 200°C reduced several times as rapidly at about 200°C as nitrogen adsorbed at 440°C. The kinetics of reduction were also different for the low temperature as compared to nitrogen adsorbed at high temperatures.

Most comparisons would lead one to expect the ratio of chemisorbed nitrogen to chemisorbed carbon monoxide to be in the range 0.5 to 1. For example Ertl and coworkers[16)] find that nitrogen atoms occupy a $c\,(2\times 2)$ structure on the (100) face of iron. This is equivalent to occupying one half of the C-8 sites.[22)] Furthermore they point out that at atomospheric pressure the other half would also be occupied. This would correspond to one nitrogen atom per surface atom of iron total nitrogen pickup. It is a little uncertain as to whether one or two surface atoms would be required per carbon monoxide molecule. Each surface iron atom in the 100 plane occupies 8.14 A^2.[17)] Ertl and coworkers have shown that on Ni the closest packing of CO corresponds to about 9 A^2, so he might not be able to pack CO molecules into an atom having an area of 8.14 A^2. At any rate, if CO occupies two atoms, the N_2 chem/CO chem would be 1.0, and if it occupied one iron atom, this ratio would be 0.5. On the (110) faces each molecule of nitrogen and of CO should require two surface atoms, so that the expected ratio would be 1.0. Finally, for the (111) faces presumably one CO molecule would be adsorbed per surface C-4 site whereas two C-7 sites[22)] are available for nitrogen atoms. Such location of CO and N atoms would then yield a 1 : 1

ratio of N_2 chem/CO chem. Of course, if the type of surface reconstruction takes place that was found by Ertl and coworkers[16] on single crystals of iron (111) face, it becomes difficult to predict the ratio of chemisorbed nitrogen to chemisorbed CO. Since on these polycrystalline iron catalysts we have many faces present, we can conclude that the observed N_2 chem/CO chem ratios are well within the range of expected values.

If there were any need to account for extra nitrogen adsorption, one might take refuge in the recent Ertl experiments[16] in which evidence is obtained for the existence of a "surface nitride" which may involve both the first and second layer of iron atoms, particularly on the (111)[16] and (110)[18] faces of iron.

Hydrogen Adsorption:

Table 4 shows that the maximum type A hydrogen to carbon monoxide ratios are 1.24 and 0.9~1.15 for catalysts 234 and 416, respectively. The maximum ratio of type B adsorption to CO chemisorption for series I and III of catalyst 234 are 0.834 and 1.06 respectively, whereas for catalyst 416 the ratio is 1.06. The maximum mixed hydrogen to carbon monoxide ratios were observed to 1.25 and 1.52 for catalysts 234 and 416, respectively.

If as is usually assumed at saturation each surface metal atom retains one hydrogen atom and that CO will occupy single atoms on the (111) plane (14.16 A^2 per iron atom) but will require two atoms on the (110) (5.76 A^2 per iron) and possibly on (100) (8.14 A^2 per iron atom), then the ratio of chemisorbed hydrogen to CO will be in the range 0.5 to 1.0. This is in agreement with the adsorption values cited above for type A and for type B adsorption.

How does one account for the high values of the mixed adsorption -1.52 on catalyst 416? (This would drop to 1.37 if allowance is made for the CO chemisorptions being at $-195°C$ instead of $-78°C$.) There are several possibilities. First of all, if there is a large proportion of (111) faces on the sample, the occupation of the C-4 sites and the two sets of C-7 sites by hydrogen atoms could contribute to high H_2/CO ratios. A second possibility is that diffusion of some of the hydrogen under the promoter takes place. Boudart and Reed[19] recently found that both the hydrogen chemisorption and oxygen chemisorption were the same size on a Pt black sample before removing a 0.5% K_2O impurity as after. The total BET area of the sample was not changed by the removal of the alkali. Presumably, the hydrogen and oxygen diffused under the K_2O molecules. Still a third possibility is that a little hydrogen "spillover" onto the alumina promoter molecules might be occurring.[20]

As pointed out above, in previous work it was found that a very small partial pressure of nitrogen in the hydrogen gas used for reducing the iron oxides to make iron ammonia catalysts would cover 10 to 20% of the surface with chemisorbed nitrogen. Furthermore, it was found that nitrogen on the surface would inhibit type A adsorption at −78°C on both singly pro-

TABLE 4. Chemisorption of Hydrogen

Catalyst	Number of series	N_2 monolayer physical adsorption	CO chemisorption		H_2 chemisorption		Ratio
		(cc STP)	(cc STP)	temp. (°C)	time (hr)	volume (cc STP)	$\frac{H_2 \text{ chem}}{\text{CO chem}}$
234	I	14.2	5.2	103	0.1	3.74	0.72
					0.33	3.81	0.773
					0.6	4.01	0.722
					1.5	4.09	0.786
					13	4.25	0.817
					15	4.35	0.837
416	I	9.58	3.50	100	0.083	2.99	0.855
					1.5	3.34	0.955
					3.5	3.46	0.988
					5.5	3.53	1.01
					20	3.70	1.06
				−78	0.11	3.07	0.878
					2.0	3.53	1.01
					3.3	3.64	1.04
			3.35	−78	0.366	3.17	0.946
					1.63	3.30	0.985
			3.25	−78	0.3	2.65	0.816
					1.4	2.93	0.902
			3.15	235	0.31	1.63	0.517
					1.03	1.74	0.552
				−78	3.6	3.34	1.06
					15.88	3.63	1.15
234	III	12.10	2.75	−78	0.8	3.40	1.24
				110	0.183	2.66	0.967
					0.783	2.79	1.01
					2.783	2.92	1.06
					5.503	2.86	1.03
					7.05	2.89	1.05
					16.77	2.92	1.06

moted and doubly promoted catalysts. It also inhibits molecule per molecule type B hydrogen adsorption on double promoted catalysts. However, on singly promoted catalysts chemisorbed nitrogen tends to increase adsorption at 100°C rather than inhibit it. Clearly therefore, on a pair of catalysts reduced with nitrogen free hydrogen, one would expect the ratios of hydrogen adsorption at -78°C to hydrogen adsorption at 100°C to be the same as for nitrogen contaminated H_2 for doubly promoted catalysts. However, this ratio on singly promoted catalysts should be larger for the pure hydrogen than for the hydrogen not purified by diffusion through a palladium thimble, because the nitrogen increases the relative amount of hydrogen adsorbed at 100°C. This is clearly born out by the data in table 4 of this paper and table of the paper by Brunauer and Emmett.[5] Thus, the ratio of hydrogen adsorption at -78°C to that at 100°C is approximately one for doubly promoted catalyst 416 of the present work and catalyst 931 of the previous work. It also has a value of unity for singly promoted catalyst 954. For catalyst 234 of the present work, this ratio is in the range 1.23 to 1.5 for comparable adsorption time.

Mutual Effect of Adsorbed Species on Each Other:

i) *Influence of chemisorbed nitrogen on type B hydrogen adsorption*:

The influence of nitrogen chemisorbed at 450°C on the chemisorption of hydrogen at 100°C was thoroughly studied by Brunauer and Emmett.[5] It was established that on a doubly promoted catalyst the hydrogen chemisorption at 100°C decreases as much as the amount of nitrogen chemisorbed at 450°C. As Table 5 shows, this is confirmed in the present results on catalyst 416. On singly promoted catalyst 954 containing 10.2% Al_2O_3 an initial inhibition of 54% in hydrogen adsorption at 100°C was observed. This decrease in hydrogen adsorption rapidly disappeared, so that within an hour or so hydrogen adsorption was as great or greater on the surface partially covered with adsorbed nitrogen than it had been on the surface containing no adsorbed nitrogen. Table 5 reveals a similar behavior for catalyst 234 which contains 0.35% Al_2O_3 and 1.2% silica except that the initial inhibition disappears much more slowly than on catalyst 954. In only one instance was the experiment continued sufficiently long (65 hr) to reach the point at which the adsorption of hydrogen was larger on the surface containing nitrogen than on the nitrogen-free surface. The reason for the much slower disappearance of the inhibiting effect of nitrogen on type B hydrogen adsorption on catalyst 234 as compared with catalyst 954 is not known. It is to be noted that the recovery is more rapid the larger the fraction of the surface covered by the adsorbed nitrogen. Perhaps, the influence of the 10.2% Al_2O_3 on the tendency to stabilize NH or NH_2 groups is very much greater than that of the 0.35% Al_2O_3 and 1.2% SiO_2 contained as promoters in catalyst 234 of the present work.

TABLE 5. Effect of the Chemisorption of Nitrogen on Type B Hydrogen Adsorption

Catalyst	Number of series	Type B H_2 on bare surface (cc STP)	time (hr)	Inhibiting chemisorption (cc STP)	Type B H_2 on inhibitor (cc STP)	time (hr)	Ratio $\frac{\text{Decrease in type B } H_2}{N_2 \text{ chemisorption}}$
234	I	3.77	0.13	2.76 N_2[a)]	1.91	0.13	0.674
		3.84	0.44		2.18	0.44	0.602
		4.01	0.6		2.33	0.6	0.609
		4.06	1.8		2.56	1.8	0.544
		4.10	2.5		2.66	2.5	0.522
		4.13	3.5		2.69	3.5	0.522
		4.41	4.7		2.86	4.7	0.464
		4.15	6.6		2.96	6.6	0.452
		4.18	23.5		3.28	23.5	0.326
		3.74	0.1	2.05 N_2[b)]	2.14	0.1	0.780
		4.04	1.1		2.68	1.1	0.665
		4.17	12.5		3.10	12.5	0.522
		4.17	14		3.13	14	0.517
		4.17	17.7		3.18	17.7	0.482
234	III	2.66	0.18	1.08 N_2[c)]	1.64	0.18	0.945
		2.83	1.2		1.85	1.2	0.915
		2.90	5.83		2.16	5.83	0.685
		2.92	16.77		2.18	21.9	0.685
		2.66	0.183	1.45 N_2[d)]	1.62	0.183	0.718
		2.85	1.6		1.94	1.583	0.628
		2.89	3.8		2.15	3.81	0.510
		2.91	8.7		2.40	8.7	0.352
		2.92	16.77		2.63	21.6	0.20
					2.64	24.6	0.20
		2.65	0.23	1.24 N_2[e)]	1.71	0.25	0.76
		2.89	2.85		2.04	2.85	0.686
		2.90	5.8		2.22	5.8	0.548
		2.92	15.8		2.45	15.8	0.379
		2.65	0.2	3.22 N_2[f)]	1.53	0.2	0.325
		2.87	2.0		1.97	2.0	0.28
		2.90	3.7		2.14	3.7	0.236
		2.92	17		2.84	27.0	0.034
					3.03	65.8	−0.034
416	I	3.04	0.33	1.70 N_2[g)]	1.60	0.33	0.850
		3.32	1.4		1.75	1.4	0.925
		3.46	3.2		1.97	3.2	0.877
		3.62	13.6		2.04	13.6	0.936
		3.68	17.6		2.05	17.6	0.960

The nitrogen adsorptions are carried out at: a) 450, b) 440, c) 441, d) 220, e) 437, and g) 449°C. f) The amount of nitrogen after the isobar run.

ii) *The effect of chemisorbed nitrogen or carbon monoxide on type A hydrogen adsorption*:

When type A hydrogen was adsorbed at −78°C on top of the chemisorbed nitrogen or carbon monoxide, it was found that the nitrogen and carbon monoxide decreased type A hydrogen adsorption in the ratio 1 : 1.[5] In the present work these results are confirmed. Specifically, the inhibition per cc of chemisorbed nitrogen was 1 and 0.92 for catalyst 234 and 416, respectively. The CO chemisorption yielded inhibitive ratios of 0.9 and 0.94 respectively for catalyst 234 and 416.

iii) *The effect of various adsorbed species upon type C hydrogen adsorption*:

Three types of chemisorption of hydrogen have been found on iron synthetic ammonia catalysts, named types A, B and C. Type A refers to the adsorption of hydrogen that is capable of reaching equilibrium over the temperature range −78° to 0°C in a reasonable time. Type B adsorption becomes fast enough to reach an equilibrium curve over the range 100 to 450°C.[5] At atmospheric pressure of hydrogen these two types of adsorption appear to be distinctly different from each other. At pressures of 10^{-2} mm[11] type B disappears, so it may be associated with the promoter content. Type C hydrogen adsorption is defined as the chemisorption that occurs on iron catalysts at −195°C. It was first discovered[6] following the observation that the reaction of hydrogen and deuterium to form HD was three orders of magnitude faster over a singly promoted catalyst at −195°C than over a catalyst containing both aluminum oxide and potassium oxide as promoters (doubly promoted catalyst). On studying adsorption isotherms for singly and doubly promoted iron catalysts at −195°C, it was found that singly promoted catalyst at pressures smaller than about 0.1 mm Hg chemisorbed

TABLE 6. Effect of the Chemisorption of Nitrogen on Type B Hydrogen Adsorption

Catalyst	Number of series	Inhibiting type A H_2 adsorption[a]	Type C H_2 Adsorption[b]		Decrease in type C H_2 adorption
			on pure surface	on top of inhibitor	
		(cc STP)	(cc STP)	(cc STP)	(cc STP)
234	III	2.99	1.23[c]	1.19[c]	0.04
			1.62	1.64	−0.02
			1.93	1.87	0.06

a) Adsorption at −78°C, b) Adsorption at −193°C, and c) Partial pressures of hydrogen for these three points were 85, 130 and 175 mm of Hg, respectively.

hydrogen to an extent equivalent to covering about 12% of the metallic surface. The chemisorption on doubly promoted catalysts was only about 1/4 as extensive. Furthermore, evacuation of the catalyst at −195°C for an hour and a half removed about 50% of the chemisorbed hydrogen on the singly promoted catalyst but none of it on the doubly promoted catalyst. So the picture emerges that the hydrogen chemisorbed at −195°C (called type C adsorption) is responsible for the rapid H_2-D_2 reaction for form HD over singly promoted catalysts. The binding energy seems to range up to 6 kcal or more for part of the hydrogen and to be in the range 3 to 5 kcal for a portion that can be pumped off. In view of the importance of this type C adsorption, experiments were carried out to ascertain the extent to which type A chemisorption might inhibit type C adsorption. The results are shown in Table 6. Clearly, there is no effect of type A on the type C adsorption.

Type B adsorbed hydrogen has already been shown to exert a marked poisoning effect on type C adsorption on a singly promoted catalyst.[16] In the present work the inhibitive effect of type B adsorption was not studied but a mixture of type A and type B hydrogen adsorption produced a marked inhibition. Since type A is not inhibiting the mixed adsorption, effect is interpreted as being due to the type B adsorption present. For example, on the singly promoted catalyst (catalyst 234) the adsorption of 4.3 cc at 100°C and 2.2 cc at −78°C caused a decrease of 3.03 cc in the type C (plus van der Waals) adsorption. On the doubly promoted catlayst 3.5 cc adsorbed at 100°C (mostly type B) and 1.8 cc adsorbed at −78°C (mostly type A) caused a decrease of 2.75 cc in the type C (plus van der Waals) adsorption. It should be noted that the decreases here mentioned include the decrease that may have occurred in the van der Waals physical adsorption as well as the chemisorbed type C species. Unfortunately, there is no way of differentiating between these without additional measurements permitting the isotherms to be extrapolated to low pressures, or measuring the rate of H_2-D_2 interaction.

The exact nature of types A, B and C adsorption for hydrogen on iron ammonia catalysts is now known. Presumably, one would conclude from the present measurements that type C and type A adsorptions occur on different sites on the catalysts. This has already been extensively discussed in connection with types A and B adsorption.[5] It seems meaningless to speculated further until additional experimental data become available.

One concluding observation from the present work in regard to type C adsorption should be noted. Both Kummer[6] and Podgurski[11] found the singly promoted iron catalysts chemisorbed about 4 times as much type C hydrogen adsorption as the doubly promoted catalyst. On the singly promoted catalyst, Kummer found 12 and Podgurski 30% coverage of the metal surface. In the present experiments the type C adsorpiton at pressures of 0.1 mm or lower was equivalent to about 40% coverage of the metallic surface for both the doubly and the singly promoted catalysts. These findings are in agreement with the idea that the small nitrogen content of the hydrogen which was not diffused through palladium becomes chemisorbed during reduction and capable of inhibiting the amount of type C hydrogen adsorption that can occur on a catalyst. It should also be noted that Amenomiya and Pleizier on triply promoted catalyst (containing K_2O, Al_2O_3, and CaO as promoters) reduced with very pure hydrogen found a chemisorption at −196°C equivalent to 40% of the total hydrogen chemisorbed by exposing the catalyst to 25 or 210°C and cooling the catalyst to −196°C in hydrogen.[23)]

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