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Interaction of Nitrogen and Carbon Monoxide on Iron Synthetic Ammonia Catalysts

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The inhibitive effect of nitrogen chemisorption on the adsorption of carbon monoxide has been studied over a singly and a doubly promoted iron synthetic ammonia catalyst. The adsorption of nitrogen at 450°C did not decrease the amount of carbon monoxide chemisorption capable of taking place at −183° or −195°C. On the other hand, in the temperature range 130° to 300° the inhibition increased with a decrease in temperature and corresponded, at the lowest temperature, to a decrease of as much as 0.7 cc of carbon monoxide chemisorption per cc of chemisorbed nitrogen. The results seem to indicate that in the temperature range 130° to 300°C a considerable portion of the chemisorbed nitrogen on iron synthetic ammonia catalysts is held as nitrogen molecules, or -N=N- or -N—N- groups, whereas at temperatures of about 450° it is held on the surface primarily in the atomic form.

Knowledge as to the state of nitrogen adsorbed on iron synthetic ammonia catalysts is important for elucidating the mechanism of ammonia synthesis (*1*, *2*). Dissociative adsorption of nitrogen was inferred (*3*) from studies of the rate of the equilibration $^{28}N_2 + ^{30}N_2 = ^{29}2N_2$ on iron synthetic ammonia catalysts. It was also deduced (*4*) from the observation that nitrogen chemisorbed at 450°C did not cause any inhibition of carbon monoxide chemisorbed at −195° or −183°C. On the other hand, Scholten *et al.* (*5*) concluded from kinetic studies on adsorption and desorption of nitrogen on an iron synthetic ammonia catalyst, that adsorbed nitrogen is in a dissociated form below a surface coverage of 25%, whereas it is partly in molecular form at higher coverage. To obtain further information on this point, the present experiments were undertaken, in which the state of nitrogen adsorbed on an iron synthetic ammonia catalyst was studied by observing the influence of the temperature of nitrogen adsorption on carbon monoxide adsorption. This influence of preadsorbed nitrogen should differ according to whether it is present in the molecular as compared to the atomic state.

EXPERIMENTAL

A 10.4-g sample of iron synthetic ammonia catalyst No. 234 (containing 0.55% alumina and 1.20% silica) and a 12.5-g sample of No. 416 (containing 0.97% alumina and 0.65% potassium oxide) were reduced in a stream of hydrogen at a space velocity of 2000 hr^{-1} at 360° for 100 hr and at 500° for 100 hr (No. 234) or at 350° for 100 hr and 475° for 100 hr (No. 416).

There is evidence (*6*) that even traces of nitrogen in the hydrogen used to reduce the catalyst would result in a partial coverage of the surface by chemisorbed nitrogen. Therefore, the present reductions were carried out with a stream of hydrogen produced in pure form by passing tank hydrogen through a palladium-silver thimble and a trap immersed in liquid nitrogen.

Tank carbon monoxide and nitrogen were purified by passage over two towers containing potassium hydroxide pellets, then through a chamber containing copper gauze at 500°C, and finally through a trap immersed in Dry Ice–alcohol.

After reduction, the catalyst was evacuated at the final reduction temperature for 3 hr to 10^{-6} mm Hg. The adsorption experiments were then carried out by a volumetric method. The determination of the amount of physically adsorbed nitrogen in a monolayer was made at −195° by the BET method. The total adsorption of carbon monoxide was measured at −195° or −183°C. The amount of chemisorbed carbon monoxide was estimated by the method of Emmett and Brunauer (*7*). All of the runs for nitrogen chemisorption were carried out at temperatures ranging from 130° to 450° and at a pressure of 760 mm Hg.

RESULTS AND DISCUSSION

Each experiment was started by adsorbing nitrogen at some temperature between 130° and 450° or at a series of temperatures. Nitrogen in the gas phase was then removed by a Toepler pump at adsorption temperature down to a value of less than 0.01 cc. The catalyst was then cooled to −195° or −183° and the carbon monoxide was allowed to adsorb on the catalyst on which nitrogen had been preadsorbed. The results thus obtained are listed in Table 1. The last column, "Decrease in CO adsorption," represents the difference between the amount of carbon monoxide adsorbed on a bare surface and that on a surface carrying preadsorbed nitrogen.

Our observations of the effect of nitrogen chemisorbed at 450° on the carbon monoxide adsorption agree with those of Brunauer and Emmett (*8*) obtained under the same conditions, and indicate that there is actually no inhibiting effect. They definitely show, however, that nitrogen chemisorbed at lower temperatures invariably produced considerable inhibition. If the decrease in the carbon monoxide adsorption, ΔCO, divided by the amount of nitrogen preadsorbed, V_{N_2}, is plotted against the temperature of nitrogen adsorption, one obtains the curves shown in Fig. 1. They demonstrate that the decrease in the amount of carbon monoxide adsorption per unit volume of nitrogen preadsorbed decreases as the temperature of nitrogen adsorption increases.

These results seem to be best interpreted by the assumption of the existence of at least two different states of chemisorbed nitrogen on an iron synthetic ammonia catalyst, one that inhibits carbon monoxide adsorption and another that exerts no influence on it. The amount of the former relative to the latter increases with a decrease in temperature.

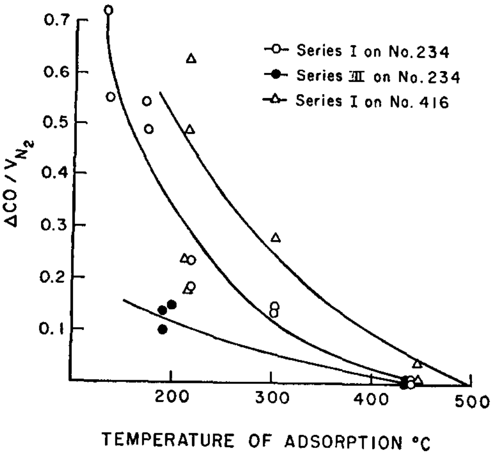

FIG. 1. Influence of nitrogen chemisorbed in the temperature range 130–450°C. on the volume of carbon monoxide chemisorbed at −195 or −183°C on a singly promoted and a doubly promoted iron synthetic ammonia catalyst.

The solubility of nitrogen, *s*, in weight percent in α-iron above 600° was expressed, according to Fast (*9*), as

$$s = 9.8 \times 10^{-2} \exp(-7200/RT)$$

By extrapolation of this equation to 450°C—the highest temperature of nitrogen adsorption in the present experiments—the amount of nitrogen dissolevd in the catalyst was estimated at about 0.05 cc, which is negligibly small as compared to the amount of preadsorbed nitrogen. Also, it can be assumed that there is no formation of nitride under the present experimental conditions because the dissociation of nitride is higher than 1000 atm (*10*). Therefore, it may be concluded that most of the added nitrogen was adsorbed on the surface, and was not contained in the bulk of the catalyst.

TABLE 1

Effect of Chemisorbed Nitrogen on Carbon Monoxide Adsorption

Series No.	Catalyst	Nitrogen monolayer (cc)	Chemisorption of CO (cc)	Chemisorbed N_2		CO adsorption on bare surface vol. (cc)	On top of N_2 vol. (cc)	Pressure of CO (mm Hg)	Decrease in CO adsorption (cc)
				Vol. (cc)	Temp. (°C)				
I	234	14.2	5.2	2.77[a]	130	23.3	21.74	78.5	1.56
						26.25	24.25	123.8	2.0
				2.95[a]	170	23.25	21.79	77.0	1.46
						25.94	24.35	119.1	1.61
				2.34	220	19.34	18.90[b]	107.9	0.44
						20.50	19.95[b]	188.7	0.55
				1.48	440	23.60	23.56	83.0	0.04
						26.59	26.59	127.0	0.00
				3.34	303	19.27	18.81[b]	105.2	0.46
						20.45	19.95[b]	184.0	0.50
I	416	9.58	3.50	1.68	447	17.70	17.62	115.9	0.08
						20.58	20.56	192.8	0.02
				1.73	215	17.39	16.54	106.6	0.85
						20.12	19.03	179.0	1.09
				2.79	302	17.92	17.15	120.5	0.77
						20.95	20.07	202.0	0.88
				2.35[a]	214	17.48	17.06	109.1	0.42
						20.23	19.66	182.7	0.57
III	234[c]	12.13	2.75	1.27	435	18.34	18.34	104.1	0.02
						21.64	21.78	168.0	−0.14
				1.40	190	18.35	18.21	96.4	0.14
						21.51	21.31	155.3	0.20
				1.70	200	18.64	18.38	102.5	0.26
				1.19	450	18.46	18.44	100.0	0.02
						21.82	21.81	159.3	0.01

[a] The two of these runs on Catalyst 234 were made at the end of nitrogen isobar measurements. The catalyst, after many hours exposure to nitrogen at atmospheric pressure and temperatures ranging up to 440°, was then cooled down to the indicated temperature and let stand for about 24 hr. The pressure was then slowly decreased over another 24 hr during evacuation with a Toepler pump. The run on Catalyst 416 was made with nitrogen at 442° to an adsorption of 2.19 cc. It was then equilibrated 40 hr at 1 atm at 214° with an increase in the adsorption of 0.16 cc.

[b] Carbon monoxide was adsorbed both on the bare and the nitrogen covered surface at −183°.

[c] The catalyst No. 234 used in the Series I experiments was exposed to air, i.e., oxidized and then reduced with H_2 at 350°, 450°, and 550° for 100, 50 and 50, hours respectively.

Apparently, nitrogen adsorbed on the iron synthetic ammonia catalyst at high temperatures is present as atoms and is held in such a position that it does not exert any influence on carbon monoxide adsorption. On the other hand, at lower temperature some of the nitrogen atoms appear to be joined to each other as nitrogen molecules or as –N═N– or –N—N– structures and sterically block the carbon monoxide away from the surface. *

Scholten (*11*) and Scholten, Zwietering, Konvalinka, and de Boer (*5*) have defined a term α as equal to the ratio of the number of nitrogen atoms on the iron surface to the

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* There is a possibility, of course, that the inhibition at lower temperatures, as exemplified by the observations plotted in Fig. 1, might have been caused by nitrogen atoms occupying inhibiting positions at the lower temperature and noninhibiting positions at about 450°C. For example, if nitrogen atoms on the (100) faces of iron rest on the body-centered iron atoms, they might be less inhibiting than if they were attached to the uppermost layer of iron atoms. Additional work will be required to really prove that the nitrogen at lower temperatures is present, at least in part, as molecules.

number of chemisorbed carbon monoxide molecules that the surface can hold. A value of unity for α thus means ½ mole of nitrogen per mole of chemisorption capacity for carbon monoxide. They suggest that for α values of 0.25 or less one has nitrogen atoms but at larger values of α, one has structures in which the nitrogen atoms are joined together. It should be noted in the present work, in Table 1, that the four sets of measurements in the range 435° to 450°C all show no inhibition of carbon monoxide even though the α values by their definition are 0.57, 0.96, 0.93, and 0.87. We are inclined to feel, therefore, that the evidence points strongly to atomic adsorption as the prevailing form at 450°C even though at lower temperatures increasing amounts of molecular chemisorbed species occur.

It perhaps, also, should be noted that it was found in previous work of one of the present authors (*12*) that nitrogen adsorbed at lower temperature (150° to 300°C) exhibits a higher activity towards the production of ammonia by reduction with hydrogen at a given temperature, than that adsorbed at higher temperatures (450°C). This is consistent with the existence of nitrogen in a different state at lower temperatures than at 450°C.

The present evidence for the probable existence of chemisorbed nitrogen molecules on an iron synthetic ammonia catalyst in the low-temperature range is in good agreement with conclusions reached in some recent experiments of Ozaki and co-workers (*13*) on the exchange of $^{28}N_2$ with $^{30}N_2$ adsorbed on an iron catalyst. They interpret their measurements as clear evidence that some $^{30}N_2$ molecules initially adsorbed on an iron catalyst at 380° and 355 mm pressure can be displaced by $^{28}N_2$ without being exchanged to form $^{29}N_2$.

It should be mentioned in passing that experimental evidence for molecularly adsorbed nitrogen was obtained by Eischens and Jacknow (*14*) at lower temperatures by infrared spectroscopic studies of the adsorption of nitrogen on nickel. No such observation for nitrogen on iron has as yet been reported.

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