JOURNAL OF CATALYSIS 24, 101-105 (1972)

The Inhibition by Nitrogen of the Chemisorption of Carbon Monoxide on an Unpromoted Iron Catalyst

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Received March 23, 1971

The effect of chemisorbed nitrogen on the adsorption of carbon monoxide at −195°C was studied on an unpromoted iron catalyst. The results indicate that the adsorption of 1 cm^3 of nitrogen at 300°C causes a decrease of 0.5 cm^3 in the amount of carbon monoxide adsorbed at −195°C. The inhibition appears to be greater the lower the temperature at which the nitrogen is chemisorbed, being as high as 0.75 cm^3 when the nitrogen is adsorbed at 200° and as low as 0.25 cm^3 when it is adsorbed at 400°C. The inhibitive effect of chemisorbed nitrogen is greater on the pure iron sample than previously noted for a promoted iron catalyst, though for both promoted and unpromoted iron the chemisorbed nitrogen at a synthesis temperature of 450°C appears to be primarily in an atomic rather than molecular form on the surface.

INTRODUCTION

The state of adsorbed nitrogen on iron-synthetic-ammonia catalysts has been a subject of many investigations. Dissociation of nitrogen into adsorbed atoms at and above 450°C has been postulated by several authors (*1*, *2*). It was noted, for example, by Brunauer and Emmett, and confirmed by Takezawa and Emmett (*3*), that nitrogen chemisorbed on promoted iron catalysts at 450°C does not inhibit the chemisorption of carbon monoxide at −195 or −183°C, and therefore presumably cannot be present as adsorbed molecules. On the other hand, these latter authors concluded that nitrogen adsorbed at temperatures lower than 450°C on promoted iron catalysts did inhibit the adsorption of carbon monoxide at −195°C, and could therefore be present on the catalyst surface partly as adsorbed molecules. For example, they found that nitrogen chemisorbed at 130°C caused an inhibition of 0.7 cm^3 of carbon monoxide adsorbed at −195°C/cm^3 of adsorbed nitrogen. Very recently, Morikawa and Ozaki (*4*) have published results based on isotopic mixing of $^{30}N_2$ and $^{28}N_2$ which indicated that on a pure iron catalyst as much as 80% of the nitrogen adsorbed at 380°C is in the molecular form. The isotopic mixing experiments on promoted iron catalysts have not been published, but it is our understanding that they show a lower percentage of the adsorbed nitrogen in molecular form than on the pure iron catalyst used by Morikawa and Ozaki. For direct comparison with the isotopic mixing results, the present paper represents an extension to unpromoted iron catalysts of measurements of the fraction of the adsorbed nitrogen present in molecular form as judged by the inhibitive effect of chemisorbed nitrogen on the extent of chemisorption of carbon monoxide at −195°C.

EXPERIMENTAL

Unpromoted iron catalyst No. 927 (about 40 mesh) was reduced at a space velocity of about 1000 hr^{-1} in a stream of hydrogen purified through a palladium thimble. The catalyst was reduced at 240°C for 12 hr, at 340°C for 15 hr, at 390°C for 12 hr, at

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410°C for 30 hr, and finally at 450°C for 72 hr. The reduced catalyst weighed 26 g; it probably contained up to 0.15% Al_2O_3 as an impurity.

The Matheson prepurified-grade argon, which was used for BET surface-area measurements, and CP carbon monoxide were condensed respectively in liquid-nitrogen cold traps and distilled, the middle portions being collected in gas storage bulbs. Nitrogen, Matheson high-purity grade, was passed through a liquid-nitrogen cold trap slowly before being stored in a bulb.

Adsorptions were measured volumetrically after the catalyst had been reduced as described above and evacuated overnight at 450°C. Following the method described by Emmett and Brunauer (*5*), the total CO adsorption was measured at —195°C up to a pressure of 180 Torr. The catalyst was then evacuated at —78°C for ½ hr and at —195°C for 2 hr. Additional adsorption at —195°C following the evacuation procedure is referred to as the physically adsorbed CO. The difference between this volume of physically adsorbed carbon monoxide and the total initial adsorption would then be taken as the volume of chemisorbed carbon monoxide. To investigate the inhibitive effect, a known amount of nitrogen was preadsorbed at temperatures 170–420°C, and at a final pressure of about 380 Torr for a period of 6–30 hr. Gaseous nitrogen in the sample cell together with small amounts of adsorbed nitrogen were then removed stepwise at the same or lower temperature by a gas buret until less than 0.01 cm^3 at STP remained in the gas phase of the sample cell. The catalyst was then cooled down immediately to liquid-nitrogen temperature for the CO-adsorption measurement. At the end of each run, the catalyst was reduced in hydrogen at 400°C overnight. The BET surface area of the catalyst was measured by the adsorption of argon.

RESULTS AND DISCUSSION

The amount of nitrogen that remained on the catalyst before the adsorption of carbon monoxide is shown in Table 1. The time for the adsorption and the temperature at which gaseous nitrogen was removed seem to have little effect. Except at 183 and 172°C the chemisorbed nitrogen in terms of the molecular form corresponds to a surface coverage of 20–30%.

The adsorption of carbon monoxide at —195°C and at 100 Torr and the inhibiting effect of chemisorbed nitrogen are listed in Table 2. Total adsorption and the chemisorption of carbon monoxide were inhibited significantly if measured immediately after BET surface-area measurement by nitrogen (Runs a and c). At the end of the nitrogen-adsorption measurement, the catalyst was evacuated at —195°C for 3 hr in Run a and for ½ hr in Run c. Apparently, some nitro-

TABLE 1
CHEMISORPTION OF NITROGEN ON AN UNPROMOTED IRON CATALYST[a]

Run	Temperature of adsorption (°C)	Time (hr)	Final pressure of adsorption (Torr)	Temperature at which gaseous N_2 is removed (°C)	cm^3	Amount of nitrogen adsorbed (as the No. of nitrogen molecules per $cm^5 \times 10^{-15}$)
b	313	6	384	230	1.43	0.20
h	316	9	377	243	1.01	0.14
i	420	16	380	418	1.08	0.15
j	410	6	392	398	1.32	0.18
l	183	26	392	183	0.31	0.04
n	318	22	390	318	1.14	0.16
o	321	21	385	321	1.07	0.15
p	317	9	381	227	0.92	0.13
r	172	33	365	172	0.29	0.04

[a] Reduced sample weight = 26 g; BET surface area = 0.75 m^2/g (nitrogen).

TABLE 2
THE EFFECT OF CHEMISORBED NITROGEN ON THE ADSORPTION OF CARBON MONOXIDE

	Chemisorption of nitrogen		Adsorption of CO (P = 100 Torr, T = 77°K)			Inhibiting Effect		
Run	Temp. (°C)	(amount adsorbed in cm³)	Total (cm³)	Phys. (cm³)	Chem. (cm³)	ΔCO_{Total} (cm³)	ΔCO_{Total}/cm³ of chemisorbed nitrogen	Monolayer of physically adsorbed N_2 or Ar (cm³)
a	—	—	7.75	5.15	2.60			4.69 (N_2)
b	313	1.43	8.55	5.40	3.15			3.98 (N_2)[a]
c	—	—	7.37	5.28	2.09			4.50 (N_2) 3.78 (Ar)
g	—	—	8.53	5.07	3.46	0.00	0.00	3.53 (Ar)
h	316	1.01	8.48	5.27	3.21	0.05	0.05	
i	420	1.08	8.25	5.38	2.87	0.28	0.26	
j	410	1.32	8.20	5.27	2.93	0.33	0.25	
k	—	—	8.47	5.05	3.42	0.00	0.00	
l	183	0.31	8.23	5.17	3.06	0.24	0.77	3.53 (Ar)
m	—	—	8.42	5.02	3.40	0.00	0.00	
n	318	1.14	7.93	5.15	2.78	0.49	0.43	
o	321	1.07	7.80	5.06	2.74	0.62	0.58	
p	317	0.92	5.12	5.12	2.81	0.49	0.53	
q	—	—	8.12	4.87	3.25	—	—	3.35 (Ar)

[a] On top of chemisorbed nitrogen and chemisorbed CO.

gen was still held on the surface at the end of these evacuations in sufficient quantities to cause the total adsorption of carbon monoxide to be low. Indication of a weak chemisorption of nitrogen on iron films at —195°C has been reported (*6*). It is most likely that adsorbed nitrogen at such low temperature would be in the molecular form. On the other hand, in Run b, the surface area was also measured by nitrogen, but only after the physically adsorbed CO had been pumped off at —78°C. Both chemisorbed nitrogen (1.43 cm³) and chemisorbed carbon monoxide (3.15 cm³) were still on the surface. Yet the decrease in nitrogen adsorption was only 0.71 cm³. Assuming that the decrease is due entirely to the presence of chemisorbed nitrogen, the inhibiting effect would be

$$\Delta V_{N_2}(\text{BET})/V_{N_2}(\text{Chem}) = 0.71/1.43 = 0.50.$$

This is in agreement with the effect of chemisorbed nitrogen on the adsorption of carbon monoxide (Fig. 1 and Runs g–q, Table 2), but this might be fortuitous. At least we can say that a fairly large portion of nitrogen chemisorbed at 313°C is held on such sites or in such form as not to inhibit the adsorption of either carbon monoxide or nitrogen at —195°C. In later runs,

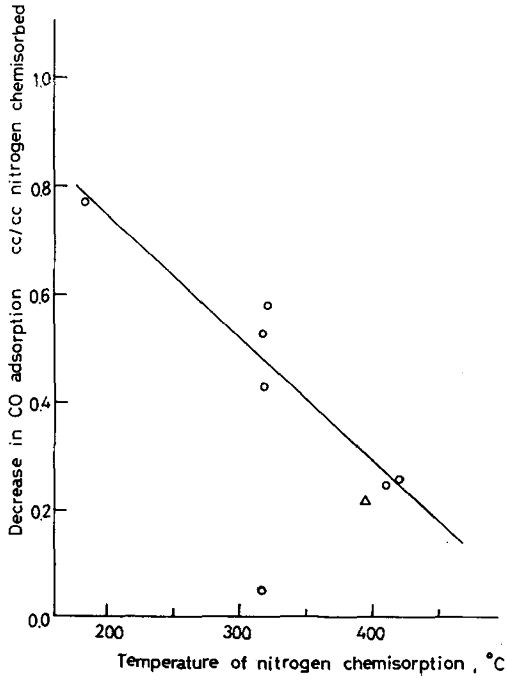

FIG. 1. The inhibiting effect of chemisorbed nitrogen: ○, No. 927 (present work); △, No. 973 (Brunauer & Emmett).

the monolayer coverage of the catalyst was determined by argon adsorption. It is somewhat smaller than that determined by nitrogen.

On the bare surface, the amount of chemisorbed carbon monoxide was found to be quite consistent, and had an average value of 3.4 cm^3. This corresponds to 0.47×10^{15} CO molecules/cm^2 if nitrogen BET surface area is used. In most cases, the ratio of chemisorbed nitrogen to chemisorbed carbon monoxide on bare surface is 1 to 3.

The physically adsorbed CO was also reproducible on bare surface except for the last run, Run q, in which the catalyst might have been sintered slightly during a long period of reduction, as reflected from the argon monolayer. However, whenever nitrogen was preadsorbed on the surface, the amount of physically adsorbed CO was invariably greater than for runs using a bare surface. It is possible that preadsorbed nitrogen atoms might weaken the bonding of chemisorbed CO so that some chemisorbed CO was removed during the evacuation process. Obviously, the assessment of physically adsorbed and thus chemisorbed carbon monoxide in cases in which nitrogen was preadsorbed would be difficult. Therefore, total adsorption of CO was used to estimate the inhibiting effect of preadsorbed nitrogen (Table 2). The decrease in total CO adsorption per cm^3 of nitrogen chemisorbed is given in column (8) and plotted as a function of the temperature at which nitrogen was preadsorbed, in Fig. 1. The result from Brunauer and Emmett (*1*) on No. 973 unpromoted iron catalyst is also indicated. The correlation is quite similar to the result of promoted iron catalysts obtained by Takezawa and Emmett (*3*). In other words, the inhibition of chemisorbed nitrogen is greater at lower temperatures, but becomes negligibly small above 450°C. If the inhibition is caused by the steric hindrance of adsorbed nitrogen, then, even nitrogen adsorbed at 300°C must have a considerable portion that could not possibly be in the molecular form. This is contrary to the work of Morikawa and Ozaki (*4*) who concluded that almost all the nitrogen adsorbed at 350°C is undissociated.

It is of course possible that nitrogen is adsorbed on sites on which carbon monoxide will not adsorb. However, the present work at least agrees with the work of Ozaki in indicating that at a given temperature near 300°C, a larger fraction of the adsorbed nitrogen is held as molecules on a pure iron catalyst than on promoted iron catalysts. In this connection, by means of a field emission microscope, Brill, Richter, and Ruch (*7*) concluded that at 400°C, nitrogen is preferentially chemisorbed on the 111 face of iron. It might then be argued that most of the carbon monoxide is adsorbed on other than 111 faces and that, accordingly, nitrogen in part at least for this reason fails to inhibit carbon monoxide adsorption. However, if CO is not adsorbed extensively on the same face on which nitrogen is adsorbed, the fact that the inhibition by chemisorbed nitrogen increases with decreasing temperature could not be explained. Incidentally, it is not obvious from the work of Brill and his co-workers that nitrogen is adsorbed in molecular rather than atomic form at 400°C. A more direct method for the investigation of the adsorbed state of nitrogen on iron appears to be necessary.

To examine the possibility of having preadsorbed nitrogen displaced when carbon monoxide is added at —195°C, during Run h the gas phase in the sample cell at the highest pressure of the CO adsorption measurement was expanded into the gas burette and collected for analysis. A high-resolution Hitachi mass spectrometer (Model RMU-6E) was used to analyze the possible mixture of carbon monoxide and nitrogen. Previously, a known mixture of both gases was used to ensure good separation of the two peaks. However, no trace of a nitrogen peak was observed. Certainly, prechemisorbed nitrogen is not displaced by carbon monoxide at liquid-nitrogen temperature.

ACKNOWLEDGMENT

We gratefully acknowledge the support of this work by the Atomic Energy Commission through grant number AT(30-1)-2008.

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