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Chemisorption of Gases on a Promoted Iron Catalyst

I. Hydrogen, Nitrogen, Carbon Monoxide and Carbon Dioxide*

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Chemisorption of H_2, N_2, CO and CO_2 on a promoted iron catalyst has been studied with the aid of temperature-programmed desorption (TPD) technique. TPD of hydrogen showed results similar to those obtained by Emmett and coworkers from isobars (Types A and B), but it gave a finer structure of chemisorbed hydrogen. At least four different types of chemisorption were observed as the different peaks of TPD ranging from −100 to 500°C. Nitrogen gave only one peak at a high temperature, and carbon monoxide gave two groups of peaks: one at low temperatures between −50 and 180°C and the other at about 650°C. Carbon dioxide also gave two groups of peaks but the high-temperature peak was found to result from the decomposition of CO_2.

The effect of preadsorbed gas on the chemisorption of others was also studied. It was thus found that preadsorbed nitrogen showed a selectivity for blocking hydrogen while preadsorbed carbon monoxide did not have selectivity but blocked all types of chemisorbed hydrogen uniformly. It was also found that preadsorbed nitrogen reduced the strong chemisorption of CO but rather enhanced the weaker chemisorption. Amounts of H_2, CO, and N_2 chemisorbed were measured either by TPD or other methods. These are discussed in relation with the results obtained as above.

INTRODUCTION

Since different types of chemisorption of hydrogen were demonstrated by Emmett and Harkness (*1, 2*) on a doubly promoted iron catalyst, Emmett and his coworkers made extensive studies of chemisorption of gases on iron catalysts which brought a great deal of advancement of the knowledge of the surface of iron synthetic ammonia catalysts. It is generally thought that hydrogen, nitrogen, and carbon monoxide are chemisorbed on the metal surface while carbon dioxide is chemisorbed on the surface of alkaline promotor. From the mutual inhibitory effects of gas (*3*), it was concluded that hydrogen and nitrogen are chemisorbed as atoms, but carbon monoxide is chemisorbed as molecules. However, results recently obtained on promoted and unpromoted catalysts (*4–8*) indicate that nitrogen chemisorbed under some conditions, at low temperatures in particular, could be molecular. Apparently more information on the state of chemisorption of gases is needed.

Temperature-programmed desorption, which involves the desorption of chemisorbed gas in a stream of inert carrier gas by increasing the temperature of the catalyst in a programmed manner, has proved to be useful in investigating the state of adsorption, particularly when different sites or adsorbed states exist (*9*). In view of these facts, it was thought to be worthwhile to reinvestigate the classic problem by using the temperature-programmed desorption technique. This paper reports the results of TPD of gases chemisorbed on a promoted iron catalyst including the effect of preadsorption of gases on the chemisorption of other gases.

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EXPERIMENTAL METHODS

Materials

The catalyst used in the present study was a Haldor Topsøe Type KM I catalyst which was kindly supplied by Cominco Ltd., British Columbia, Canada. A typical analysis showed that the catalyst contained 0.64% K_2O, 4.20% CaO, 0.34% MgO and 2.99% Al_2O_3 as promotors. The catalyst was crushed and an amount of 5.17 g of the 25–32 mesh portion was used.

Nitrogen, carbon monoxide and carbon dioxide were all assayed reagent of Air Reduction Co., Inc., and used as adsorbates without further purification. Matheson's Ultra High Purity hydrogen (99.999%) was passed through a spiral type trap cooled by liquid nitrogen and stored in a reservoir as an adsorbate or flown through the reactor to reduce the catalyst. Ultra High Purity helium (99.999%) and argon (99.999%) both purchased from Matheson were used as carrier gas for temperature-programmed desorption after being passed through a Molecular Sieves trap immersed in liquid nitrogen.

Apparatus and Procedure

The apparatus used for the present study was the same as used for the adsorption of hydrogen on alumina previously (*10*). It consisted of two parts: a conventional static system for adsorption measurements; and a temperature-programmed desorption system. The adsorption was measured in a constant volume (45 cc) with a capacitance pressure transducer. The temperature-programmed desorption (TPD) has been described in detail elsewhere (*9*).

At first the catalyst was reduced at 500°C before and after the experiment in a flow of hydrogen at a rate of 50 ml/min at atmospheric pressure. During the preliminary experiments, however, it was found necessary to heat the catalyst up to about 700°C to desorb strongly chemisorbed gases by TPD. Therefore, the catalyst was treated as follows: After each run the catalyst was reduced with flowing hydrogen at 550°C and kept at room temperature overnight with hydrogen sealed in the reactor; the reduction of catalyst with flowing hydrogen was resumed at 550°C before the next experiment (total reduction time at 550°C was 2.5 hr); at the final stage of reduction the temperature was increased to 700°C and the catalyst was evacuated for 30 min; the catalyst was finally cooled to adsorption temperature while pumping was continued. Thus, the catalyst was reduced for 100 hr at 500°C and for 500 hr at 550° in total before the data reported in this paper were taken. The flow of hydrogen was increased sometimes by 10 times, but the adsorption was not affected.

The surface area of the catalyst was measured from time to time by BET with both nitrogen and argon, and it was found that the catalyst sintered gradually and monotonously as expected from the high temperature employed for reduction. The amount of gas adsorbed or desorbed was calculated for the unit surface area of catalyst from the surface-area curve obtained above. It was also found that the monolayer amount of argon was somewhat smaller than that of nitrogen as reported by Huang and Emmett (*8*). The results reported here were all based on the measurements with nitrogen.

Adsorption measurements were carried out manometrically in a constant volume as already described. When the temperature of adsorption was much different from room temperature, a small amount of pure helium was admitted in the reactor prior to the adsorption to stabilize the temperature of the catalyst. After the adsorption, the catalyst was usually evacuated before the carrier gas was diverted into the reactor for TPD. The conditions for adsorption and evacuation will be described for each case. The temperature-programmed desorption was carried out by increasing the catalyst temperature linearly by means of a stainless steel block furnace with a proportional temperature controller–programmer which allowed the temperature to increase continuously from −196 to 800°C. The average speed was about 16°C/min in most cases, although the speed in the very low-temperature region was somewhat different because of the characteristics of the platinum sensor employed for the controller. The gas desorbed in the stream of carrier gas was detected by a thermistor-type thermal conductivity detector. The carrier gas was flown at a flow rate greater than 270 ml/min at which the average residence time in the catalyst bed was less than 0.2 sec.

Argon was used as carrier gas to obtain hydrogen peaks while helium was used for other adsorbates. Since the gases used were not condensable except carbon dioxide, the amount of gas desorbed as peaks was calculated from the peak area by comparing with those of known amount of the gas passed through the detector before and after each TPD experiment.

Results and Discussion

I. Adsorption of Single Gas

(*1*) *Hydrogen*

Adsorption of hydrogen was rapid at all temperatures and no appreciable change of pressure was observed after several minutes. Typical results of TPD carried out after adsorption are shown in Fig. 1. When hydrogen was admitted at −196°C, a large amount of hydrogen was adsorbed but most of it was removed by pumping at −196°C for a few minutes. It is interesting, however, that the subsequent TPD showed a peak at high temperature (strong adsorption) as shown by spectrum A in Fig. 1. It was verified that this peak did not result from hydrogen used for the pretreatment of the catalyst. This strong adsorption must have no or a very small activation energy of adsorption so that it occurs quickly even at liquid nitrogen temperature. In fact, this high-temperature peak did not change when the adsorption temperature was increased up to −100°C, while the total amount of adsorption measured at about 400 Torr of hydrogen (isobar) rapidly decreased with temperature. The amount of the strong chemisorption was about 0.12 ml STP/g or 7.7×10^{13} molecules/cm^2, and this type of adsorption or the peak (at about 200°C) is referred to as H(IV). In the following, the other peaks observed will be referred to similarly without additional identification since they are clear in the figure. The weak adsorption which was removed by pumping is probably a physical adsorption but it may be Type C adsorption found by Kummer and Emmett (*11*).

When hydrogen was adsorbed at tem-

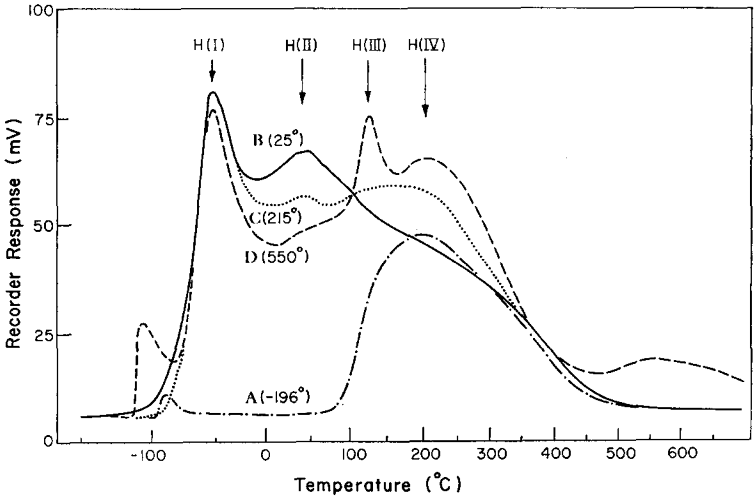

FIG. 1. TPD of hydrogen. Pressure of hydrogen was about 400 Torr except for D which was 740 Torr, and the starting temperature of adsorption was shown on each curve. The catalyst was cooled to −196° in all cases and evacuated briefly before TPD.

peratures higher than −75°, more peaks appeared in TPD at lower temperatures. For example, curve B in Fig. 1 was obtained by adsorbing hydrogen at 25°C for 30 min at about 400 Torr, cooling to −196°C for 15 min in the presence of the hydrogen, and then evacuating at the same temperature for 3 min. Peaks H(I) and H(II) now appear at about −50 and 50°C in addition to the strong adsorption [H(IV)]. Adsorption at −75°C gave exactly the same picture of TPD as B indicating that Type H(I) and H(II) adsorption occurred already at −75°C while Type H(IV) adsorption was saturated at a much lower temperature. The adsorbed amount of hydrogen at about 400 Torr and at 25 or −75°C agreed within 10% with the desorbed amount calculated from the peak area. Therefore, these chemisorptions would not be removed by pumping at −196°C.

As the temperature of adsorption was further increased, the strongest adsorption [H(IV)] developed gradually, but H(I) peak remained almost unchanged as shown by curves C and D in Fig. 1. The conditions for adsorption were: C, at 400 Torr for 30 min at 215°C, for 18 hr at 25°C, and for 15 min at −196°C; D, at 740 Torr for 1 hr at 550°C, for 60 hr at 25°C and for 15 min at −196°C. The catalyst was evacuated for 3 min at −196°C before TPD in both cases. It is seen that a new peak H(III) developed at about 120°C in curve D where high temperature and pressure were employed for adsorption. The H(III) peak becomes clear when the temperature of adsorption is higher than 300°C. It is of interest to compare the desorption spectra B, C, and D. High-temperature peaks H(III) + H(IV) grow as adsorption temperature increases at the sacrifice of H(II). Indeed, the amount of hydrogen desorbed in these spectra coincided within 1.5%. This suggests, firstly, that the sites for the chemisorption of hydrogen are saturated at 25°C or higher and secondly that H(II), H(III), and H(IV) adsorptions are different types of adsorption sharing the same sites rather than adsorptions on different sites. Further support for saturation was obtained by experiments similar to D but varying the pressure and time of adsorption by about 50%, all of which gave the same desorbed amount in TPD within 4% error. The saturated amount of hydrogen was estimated from these experiments as 1.9×10^{14} molecules/cm^2.

A total of about 300 runs were performed on the same sample of catalyst. All the results reported in this paper were obtained from about 40 consecutive runs (Nos. 152–192). The surface area of the catalyst decreased by about 8% from 4.84 to 4.43 m^2/g during the 40 runs, but the saturated amount of hydrogen/cm^2 remained almost constant. In a long-range survey, the H_2/cm^2 value increased rather rapidly in the first 50 runs or so, and then stayed unchanged. In the final stage of the experiments (No. 260), the catalyst was accidentally heated up to 900°C and the H_2/cm^2 value dropped by about 25%, apparently indicating a serious sintering of the metal.

A small amount of alumina or potassium aluminate in promoted iron catalysts covers a rather large fraction of surface (*3*, *12*). The present authors also observed that hydrogen chemisorbed on alumina and the resulting TPD gave peaks between 40 and 500°C (*10*). It is possible, therefore, that some of the peaks observed here are those of hydrogen chemisorbed on alumina. However, the chemisorption of hydrogen on alumina was very slow at room temperature and no chemisorption occurred at −196°C. Although the chemisorption on alumina becomes appreciable at higher temperatures, the maximum amount of hydrogen chemisorbed would be only 5% [1.9×10^{13} atoms/cm^2 (*10*)] of the present saturated amount even if the whole surface of the catalyst was covered by alumina. We also found that a small amount of alkali added to alumina reduced significantly the TPD peaks of hydrogen except for one peak which appeared at about 200°C (*10*). Therefore, the hydrogen peaks observed here should be those on the iron surface although a part of H(IV) peak which was increased at high temperatures could be the adsorption on alumina or alkalies–alumina surface.

It is seen in Fig. 1 that the shape of TPD peaks resembles as a whole the typical isobars of hydrogen observed on a doubly promoted iron catalyst by Emmett and Harkness (*2*). The present results were obtained dynamically by TPD so that the temperature range will shift more or less from that of the isobar. Nevertheless, it seems clear that H(I) peak corresponds to Type A hydrogen which started to adsorb at about −130°C and went through a maximum at about −100°C. Although Type H(IV) appeared at the highest temperature in TPD, a part of it must have been observed as a part of Type A chemisorption since spectrum A in the present experiment was obtained even at −196°C. The isobar of Type B hydrogen was observed by Emmett *et al.* between 0 and 450°C with a maximum at about 80°C, while TPD showed finer structure with three maxima. The difference might be, of course, due to the difference in catalyst. However, the isobar observed on the present catalyst at about 400 Torr showed similar shape with a smooth fall off after 100°C as observed by Emmett and Harkness (*2*).

(*2*) *Nitrogen*

The chemisorption of nitrogen was slow as observed by other workers, and most adsorption was carried out at 300°C or higher. The subsequent TPD gave only one peak starting at about 400°C. The peak maximum appeared between 500 and 550°C depending on the amount adsorbed. The peak did not finish completely at 700°C where TPD was stopped to prevent further sintering of the catalyst, so that it was not quite sure whether a different peak or peaks appeared at still higher temperatures. However, about 90% of adsorbed nitrogen came out in the peak before 700°C and it is unlikely that a separate peak appears at higher temperature.

As already mentioned in the Introduction, some papers published recently suggest the existence of molecular nitrogen particularly when nitrogen is adsorbed at low temperatures (*4–8*). A TPD experiment was carried out by adsorbing nitrogen at 197°C. The TPD gave a similar peak at 510°C as obtained by high-temperature adsorption, although it could not exclude the possibility that molecular nitrogen adsorbed at the low temperature was converted into atomic nitrogen on the surface during heating. Incidentally, TPD carried out after either the ammonia synthesis from a mixture of nitrogen and hydrogen at 200 to 300°C or the decomposition of ammonia at about 100°C gave a nitrogen peak in the same temperature region (between 400 and 700°C).

(*3*) *Carbon Monoxide*

Adsorption of carbon monoxide at −196 and −78°C took place almost instantly. When carbon monoxide was adsorbed at −196°C and 24 Torr and evacuated for 45 min at the same temperature, the subsequent TPD gave a large peak between −160 and −55°C with a shoulder at higher temperatures up to 180°C, and finally a small peak which started at about 550°C. The low-temperature peak was so large that the peak overscaled at the lowest sensitivity available for the detector and this peak was supposed to be a physical adsorption. When the temperature of adsorption and evacuation of carbon monoxide was increased to −78°C, the large low-temperature peak disappeared and the other peaks became clear at a higher sensitivity as shown in Fig. 2a. It is seen in the figure that three peaks appear over a temperature range between −50 and 180°C and one peak at about 650°C. The high-temperature peak did not finish at 700°C so that the total amount of carbon monoxide desorbed could not be measured. The amount of carbon monoxide desorbed in the low-temperature peaks (between −50 and 180°C) was roughly constant (2.3×10^{13} molecules/cm^2) independent of the pressure of CO at adsorption. It is possible that the high-temperature peaks resulted from the dissociation of carbon monoxide on the surface. Although the desorbed gas was not analyzed, it was uncondensable at liquid nitrogen temperature. In any case, it is obvious that this peak is due to very strong chemisorption of carbon monoxide.

Emmett and Brunauer measured the iso-

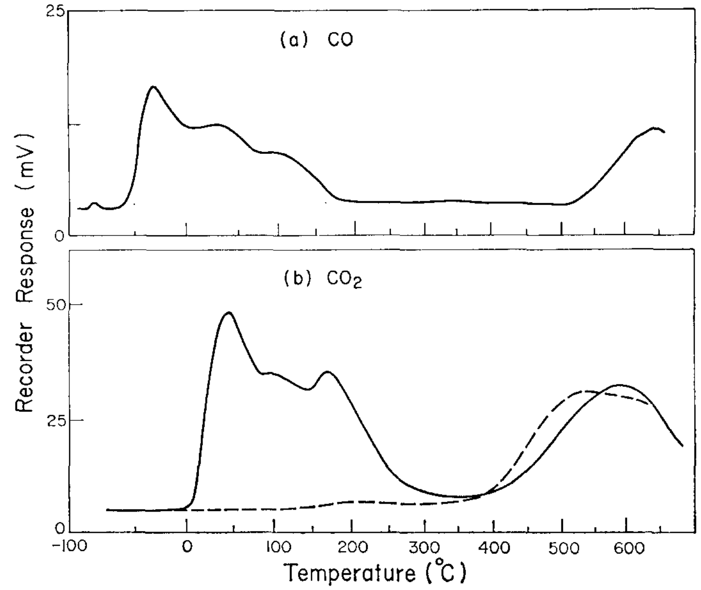

FIG. 2. TPD of carbon monoxide and carbon dioxide. (a) CO: carbon monoxide was adsorbed at −78°C and 15 Torr and evacuated for 15 min at −78°C before TPD. (b) CO_2: carbon dioxide was adsorbed at −78°C and 55 Torr and evacuated for 30 min at 0°C; broken line was obtained under similar conditions but with a liquid nitrogen trap before the detector.

therm of carbon monoxide at −183°C on iron catalysts, pumped at −78°C, and measured the isotherm again at −183°C (*13*). The chemisorption of CO was calculated as the difference of the two isotherms. Later Solbakken, Solbakken, and Emmett determined the chemisorbed amount of carbon monoxide by using a McBain-type balance as the amount remaining on the surface after 4 hr pumping at −196°C following the adsorption of carbon monoxide at the same temperature (*14*). Although they admitted that the pumping at −78°C removed the chemisorbed CO slowly, they suggested that the pumping for 30 min at −78°C employed in the earlier work (*13*) would give the chemisorbed amount within an error of 5%. We measured the isotherm of CO at −78°C twice up to a pressure of 16 Torr between which the catalyst was evacuated for 30 min at the same temperature. The difference of the isotherms was quite constant within ±1% over the entire range of pressure used which gave a surface concentration of 9.3×10^{13} molecules/cm^2. Emmett and Brunauer found that the chemisorption of CO at −78°C was always larger than that at −183°C on all catalysts used by them (*12*). We also found that the high-temperature peak of TPD (at about 650°C) obtained after the adsorption of CO at −78°C was larger than that obtained by adsorbing CO at −196°C. Probably this strong chemisorption of CO is too slow at −196°C to be completed. Therefore, the amount obtained here would be slightly larger than the value which would have been obtained at −183°C or lower.

(*4*) *Carbon Dioxide*

Unfortunately very reproducible results of TPD could not be obtained for carbon dioxide. The reason for it is not yet known, but some of the results are worth describing below.

Carbon dioxide was adsorbed at −78°C in all experiments. A large amount of adsorption was observed at this temperature between 15 and 200 Torr. After evacuation for 30 min at −78°C by condensing carbon dioxide in a trap cooled by liquid nitrogen, an amount of 3.1×10^{14} molecules/cm^2 remained on the surface and this amount was approximately constant independent of the pressure of CO_2 for adsorption. When the evacuation temperature was increased to 0°C as employed by Emmett and Brunauer (*13*) to determine the chemisorption of carbon dioxide, more carbon dioxide was removed and 1.5×10^{14} molecules/cm^2 remained on the surface. The subsequent TPD gave three peaks between 0 and 300°C and one peak at about 600°C as shown by solid line in Fig. 2b.

Emmett and Brunauer (*13*) reported that carbon dioxide physically adsorbed at −78°C could be removed by pumping at 0°C but chemisorbed carbon dioxide was not removed up to 100°C. They also reported that the pumping of CO_2 on a doubly promoted catalyst at 450°C removed about a half of chemisorbed gas but the gas removed contained some carbon monoxide as well as carbon dioxide. We carried out one experiment under similar conditions to those for the solid line in Fig. 2b, but with a liquid nitrogen trap inserted between the reactor and the detector, so that only uncondensable gas was detected in TPD. The results were shown by broken line in Fig. 2b. The low temperature peaks disappeared while the high-temperature peak remained unchanged. Although the desorbed gas was not analyzed, the uncondensable peak at 600°C probably resulted from the decomposition of carbon dioxide in agreement with the findings of Emmett and Brunauer. The present results, however, did not show a clear cut between physical and chemical adsorption, and the first peak at about 50°C in Fig. 2b may be a part of physical adsorption which was not removed completely by evacuation for 30 min at 0°C.

The amount of gas desorbed in the peak which appeared at 600°C could not be measured because it was uncondensable. On the other hand, the amount of CO_2 desorbed in the low-temperature region was measured by condensing in a trap after the detector, and it agreed well with the amount calculated from the area of the peaks. Therefore, the amount of CO_2 decomposed at high temperature was estimated as 8×10^{13} molecules of CO_2/cm^2 from the difference in amount between the gas remaining on the surface before TPD and the gas desorbed in the low-temperature peaks of TPD. When an amount of CO_2 which corresponds to less than 8×10^{13} molecules/cm^2 was admitted in the reactor at −78°C, only one peak appeared in TPD at about 600°C, indicating that the strong chemisorption leading to decomposition preferentially proceeded even at low temperatures. This decomposition peak seems to be due to carbon dioxide chemisorbed either on metal surface or on the boundary of metal and promoters, although carbon dioxide was considered to chemisorb only on the promoters. It may be feared that carbon dioxide strongly chemisorbed on the promoters desorbs at high temperature during TPD and contacts with the metal surface where the decomposition occurs. As will be described later, however, preadsorbed nitrogen reduced the chemisorption of carbon dioxide at −78°C indicating that the metal surface was involved in the chemisorption of CO_2 at the time of adsorption.

Since carbon monoxide and carbon dioxide chemisorbed on the catalyst possibly dissociated at high temperature, carburization of the surface might have occurred. The reproducibility of the surface was examined by the adsorption and the subsequent TPD of hydrogen carried out under similar conditions from time to time. They gave reproducible results not only for the adsorbed amount but also for the TPD spectrum within experimental error, indicating that the treatment of the catalyst with hydrogen at high temperatures described in the Experimental section was adequate to return the catalyst surface to a clean state.

II. Effect of Preadsorbed Gases

(1) Effect of Preadsorbed Nitrogen

(a) **Hydrogen.** Various amounts of nitrogen were preadsorbed at temperatures between 210 and 450°C, and evacuated for about 10 min after the catalyst was cooled to room temperaure. At higher adsorption temperatures, the rate of adsorption was fast enough to adsorb practically all gas admitted. When nitrogen was adsorbed at 210°C, it was allowed to adsorb for 1 hr and the catalyst was cooled for evacuation. The additional adsorption which occurred during cooling was little and the adsorbed amount measured at room temperature was regarded as the amount preadsorbed. After evacuation hydrogen was adsorbed for 35 min at room temperature and at about 430 Torr, then the catalyst was cooled for 15 min in the presence of the hydrogen at −196°C where it was evacuated for 3 min prior to TPD. In some experiments carried out in the middle of this series of experiments, the adsorption and TPD of hydrogen were done under similar conditions but on the fresh surface without preadsorbing nitrogen. The term "fresh surface" will be used in this paper to describe the catalyst on which no gas was preadsorbed.

Most of the TPD experiments were carried out with argon carrier gas to detect hydrogen peaks, but in some experiments helium was used with a liquid-nitrogen trap to see the nitrogen peak. No change was observed for the nitrogen peak whether or not hydrogen was adsorbed subsequently. Also, no ammonia was detected during TPD indicating that reaction between nitrogen and hydrogen was negligible.

Figure 3a shows TPD spectra of hydrogen thus obtained. The spectrum of hydrogen on the fresh surface is shown by solid line while the others are those of hydrogen adsorbed on the surface covered by nitrogen. The amount of preadsorbed nitrogen (molecules/cm^2) is indicated in the figure. It is obvious that chemisorbed hydrogen decreased with the increase in nitrogen preadsorbed in such a way that the peaks were removed from high-temperature side (strong adsorption) and finally only the H(I) peak remained with a large amount of nitrogen preadsorbed. It is also seen in the figure

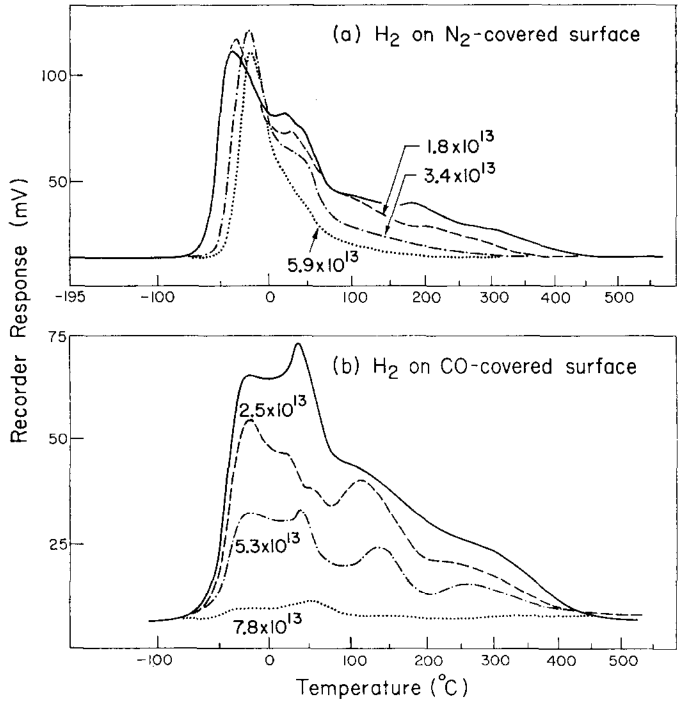

FIG. 3. TPD of hydrogen. (a) TPD spectra of hydrogen adsorbed on top of nitrogen. Nitrogen was preadsorbed at 450 or 430°C and hydrogen was adsorbed for 35 min at room temperature and for 15 min at −196°C. (b) TPD spectra of hydrogen adsorbed on top of carbon monoxide. Carbon monoxide and hydrogen were both adsorbed at −78°C. In both cases the solid line was obtained on the fresh surface, while the amount of gas preadsorbed (molecules/cm^2) was indicated for other curves.

that the H(I) peak first shifted to higher temperature and then began to decrease.

The chemisorbed amount of hydrogen was plotted as a function of the amount of nitrogen preadsorbed in Fig. 4 (upper line) where the temperature at which nitrogen was preadsorbed was indicated. The plot is linear and the temperature of preadsorption does not seem to have any effect at least for hydrogen adsorption. The effect of preadsorbed nitrogen on the chemisorption of hydrogen will be discussed further together with the effect of carbon monoxide.

(b) Carbon monoxide. Nitrogen was preadsorbed mostly at 450°C similarly to (a). Carbon monoxide was then allowed to adsorb for 30 min at −78°C at a pressure of about 10 Torr followed by TPD with helium carrier gas, after evacuation for 30 min at −78°C.

The total adsorbed amount of carbon monoxide at −78°C and 10 Torr was not affected by nitrogen: The total amount of adsorption did not change within 4% with nitrogen from 0 to 9.4 × 10^{13} molecules/cm^2 which inhibited hydrogen chemisorption almost completely as will be discussed later. TPD showed the interesting results that the low-temperature CO peaks appearing between −50 and 180°C became larger with preadsorbed nitrogen as shown in Fig. 5. The high-temperature peak also appeared at about 650°C as it did on the fresh surface (Fig. 2a). This high-temperature peak appeared together with nitrogen over the same temperature range so that the accurate measurement of CO peak was impossible. Nevertheless, it was roughly estimated by subtracting the nitrogen peak obtained with similar amount of nitrogen but without adsorbing carbon monoxide. The results indicated that the high-temperature peak of CO decreased with the preadsorbed nitrogen while those of lower temperature increased as mentioned above.

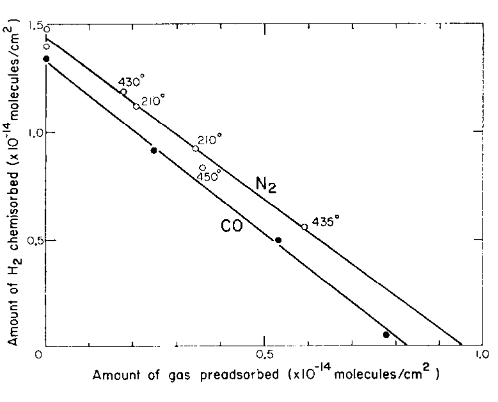

FIG. 4. Blocking effect of preadsorbed gas on the chemisorption of hydrogen. White circle for nitrogen and filled circle for carbon monoxide. The temperature for preadsorption of nitrogen was indicated on each point.

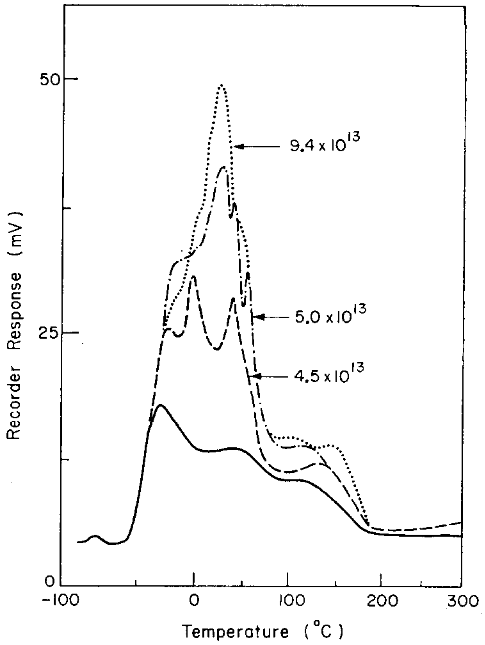

FIG. 5. TPD of carbon monoxide adsorbed on top of nitrogen. The solid line was obtained on the fresh surface without preadsorption, while the preadsorbed amount of nitrogen (molecules/cm^2) was indicated for other curves. Only the low-temperature region was reproduced.

The increase in carbon monoxide desorbed in the low-temperature region of TPD was almost linear with the amount of nitrogen preadsorbed, and the slope gave a value of about 0.5 (mole/mole), in other words, one molecule of CO for every four atoms of nitrogen. In one of the experiments, nitrogen was preadsorbed at 200°C (4.5 × 10^{13} molecules/cm^2) instead of 450°C. The total amount of CO adsorbed at −78°C was the same within experimental error, and the amount desorbed in the low-temperature range (Fig. 5) was in line with those obtained with nitrogen adsorbed at 450°C.

(c) **Carbon dioxide.** Only one experiment was carried out with 8.2 × 10^{13} molecules/cm^2 of nitrogen preadsorbed at 430°C. As shown in Fig. 2b, carbon dioxide gave three peaks in the low-temperature region and one decomposition peak at temperatures higher than 400°C on the fresh surface. On the surface covered by the nitrogen, carbon dioxide was adsorbed at −78°C and then removed at the same temperature by trapping in a trap at −196°C. The amount of CO_2 thus remaining on the surface was about 40% of the corresponding amount obtained on the fresh surface. The subsequent TPD showed that the amount of CO_2 decomposed in the high-temperature peak became also about 40% of that on the fresh surface while the low-temperature peaks remained almost unchanged. The facts suggest that the high-temperature (decomposition) peak is due to carbon dioxide chemisorbed on the sites which involve metal surface as already pointed out.

(2) *Effect of Preadsorbed Carbon Monoxide*

(a) **Hydrogen.** Various amounts of carbon monoxide were preadsorbed at −78°C. The adsorption was so strong that the gas-phase pressure became less than 10^{-3} Torr in most experiments. Therefore, hydrogen was admitted for adsorption without evacuation. Hydrogen was allowed to adsorb for 30 min at −78°C and 380 Torr, and pumped for 3 min at the same temperature prior to TPD which was carried out with argon carrier gas. Although some hydrogen peaks and weakly adsorbed carbon monoxide desorbed over the same temperature range between 0 and 300°C, the sensitivity of detecting CO in argon was so low compared to hydrogen that the peaks obtained by TPD were practically those of hydrogen. The resultant TPD was shown in Fig. 3b, where, similar to (a), hydrogen spectrum on the fresh surface was shown by solid line and the amount of CO preadsorbed (molecules/cm^2) was indicated for others. In contrast with the case of nitrogen, carbon monoxide showed no selectivity for blocking hydrogen, that is, the peaks of hydrogen were uniformly reduced with preadsorbed carbon monoxide.

The lower line of Fig. 4 was obtained by plotting the amount of hydrogen desorbed by TPD against the amount of carbon monoxide preadsorbed. Again, a linear relation was obtained. The two straight lines in Fig. 4 are approximately parallel and the slope gives a value of about 1.5 as the ratio of the decrease in hydrogen chemisorption to the increase in preadsorbed gas (mole/mole).

Since hydrogen and carbon monoxide desorbed simultaneously at temperatures between 0 and 300°C, the gases might have reacted to form a third gas, for example, methane which was not detected in argon. Under the present conditions for TPD, however, the partial pressures of H_2 and CO are so low and the contact time is so short due to the fast flow of carrier gas that the reaction between the gases, if any, would not be serious. Moreover, the plot of Fig. 4 calculated from the area of peaks agreed well with the results obtained from the amount of hydrogen adsorbed at room temperature as will be mentioned later, supporting the above view.

(3) *Effect of Preadsorbed Carbon Dioxide*

(a) **Hydrogen.** Carbon dioxide was preadsorbed at −78°C and weakly adsorbed molecules were removed at the same temperature by trapping them in a liquid nitrogen trap. Thus, 3.2 × 10^{14} molecules/cm^2 of CO_2 remained on the surface. Hydrogen was subsequently adsorbed on it at −78°C for 30 min, and the catalyst was cooled to −196°C in the presence of the hydrogen for evacuation prior to TPD. TPD was carried out with argon carrier gas and with a trap at −196°C inserted between the reactor and the detector, so that only hydrogen peaks were observed.

It was found that the adsorbed amount of hydrogen at −78°C and the amount desorbed by TPD were both decreased by the preadsorbed carbon dioxide compared to those on the fresh surface. The decrease in the desorbed amount was about 8.6 × 10^{13} atoms/cm^2 which was much less than the amount of CO_2 preadsorbed (3.2 × 10^{14}) but close to the amount of CO_2 most strongly chemisorbed and decomposed at high temperature on the fresh surface (8 × 10^{13} molecules/cm^2). The TPD spectrum showed that the front of H(I) (lowest temperature) and H(IV) (highest temperature) were both removed, and the peaks ended sharply at 150°C (refer to Fig. 1). The facts indicate that most of the carbon dioxide molecules adsorb on the promoter surface but those which chemisorb most strongly involve metal surface which corresponds to H(I) and H(IV) peaks.

When the order of adsorption was reversed, that is, hydrogen was preadsorbed at −78°C and carbon dioxide was subsequently admitted at the same temperature, some residual pressure was observed during the removal of CO_2 with the liquid-nitrogen trap. TPD carried out with argon carrier gas gave results similar to those described above. It is apparent that the replacement of hydrogen by carbon dioxide occurred at −78°C.

(b) **Carbon monoxide.** The preadsorption of carbon dioxide, evacuation, the subsequent adsorption of carbon monoxide and its evacuation were all carried out at −78°C. TPD was done with helium carrier gas but with a trap at −196°C inserted between the reactor and the detector so that only uncondensable gases were observed.

Although the total amount of CO adsorbed at −78°C was reduced by the preadsorbed CO_2, the TPD peaks of CO at low temperatures (−50 to 180°C) were not affected even with a large amount of CO_2 which covered more than 60% of the surface. Unfortunately, carbon dioxide strongly chemisorbed decomposed at temperatures higher than 400°C as already described, and this uncondensable peak obstructed the high-temperature peak of carbon monoxide.

III. Sites for Chemisorption

The surface of promoted iron catalyst is complex. As pointed out by Brunauer and Emmett (*3*), the different crystallographic faces of iron will show various types of adsorption and also metal sites adjacent to promoters may have a different nature from the rest of the metal sites. Although no definite conclusion about the nature of sites can be drawn from the present results, some interesting findings in this study are noted below.

As already mentioned, the slope of the lines in Fig. 4 was about 1.5 which was much greater than those found by Emmett and his coworkers on singly and doubly promoted catalysts (*3*, *15*). The maximum ratio of the decrease in Type A hydrogen to nitrogen chemisorbed was 1.28 on a doubly promoted catalyst (*3*). There are differences, of course, not only in the catalysts used but in the method for measurement of hydrogen. They measured the adsorbed amount of hydrogen at −78°C (Type A) while in the present experiments the amount of hydrogen desorbed by TPD was measured. Therefore, we also measured the adsorbed amount of hydrogen at room temperature and at 430 Torr before hydrogen was evacuated at −196°C for TPD. Although the measurement of adsorbed amount at such a high pressure was not very accurate in the present system, the plot of adsorbed amount against the amount of nitrogen preadsorbed gave similar results to those of Fig. 4, namely, the slope was about 1.5.

In this sort of plot, the slope of the plot may vary depending on the conditions under which the adsorption of the second gas (hydrogen) is measured. It is particularly true when the pressure of adsorption is too low or the temperature is too high to saturate the available sites. Since there is no assurance for saturation at present, and moreover, the conditions for the adsorption of hydrogen are different for N_2- and CO-covered surface, the slope in Fig. 4 will not be discussed further. Instead, the amount of preadsorbed gases required to inhibit completely the chemisorption of hydrogen was estimated from the extrapolation of the lines in Fig. 4 as 9.5 × 10^{13} and 8.3 × 10^{13} molecules/cm^2 for nitrogen and carbon monoxide, respectively. These values are listed in Table 1, which also includes the

TABLE 1
AMOUNT OF CHEMISORPTION

Gas	Amount of chemisorption (molecules/cm^2)	Method
H_2	1.9×10^{14}	TPD
CO	9.3×10^{13}	Adsorption–evacuation–adsorption
	8.3×10^{13}	Complete inhibition of H_2
N_2	9.5×10^{13}	Complete inhibition of H_2

saturated amount of hydrogen obtained by TPD after adsorbing hydrogen at a high pressure and over a wide range of temperature, and the chemisorbed amount of carbon monoxide estimated from the cycle of adsorption–evacuation–adsorption at −78°C as already described.

It is of interest that in Table 1 the amount of nitrogen required to block hydrogen is a half of the saturated amount of hydrogen. As pointed out by Podgurski and Emmett (*15*), there would be no solution of hydrogen into the bulk of metal. Indeed, the TPD of hydrogen (Fig. 1) shows that the peaks of hydrogen adsorbed at high temperatures for a long time end similarly as spectrum A in which hydrogen was adsorbed at −196°C. Spectrum D shows a small peak at 550°C, but the contribution of that amount to the total amount desorbed is negligible. The amount of nitrogen listed in the table (9.5×10^{13}) is not, however, the saturated amount of nitrogen. In fact, more nitrogen could be adsorbed in one experiment (1.2×10^{14} molecules/cm^2) and no clear idea was obtained for saturation because of the slow rate of adsorption of nitrogen. The ratio H_2/N_2 of 2 seems to suggest that nitrogen atoms adsorbed weaken the energy of neighboring sites (induced effect) and prevent the chemisorption of hydrogen, or that nitrogen atoms adsorb on some sites preferentially through which hydrogen atoms go to another type of adsorption. The strong selectivity of nitrogen for blocking hydrogen shown in Fig. 3a supports the above views.

On the other hand, carbon monoxide reduced the hydrogen peaks uniformly as shown in Fig. 3b. Carbon monoxide inhibits the chemisorption of hydrogen probably by covering the sites by the large size of the molecule. Thus, it did not show any selectivity for blocking hydrogen (Fig. 3b) and the amount required to inhibit hydrogen completely (8.3×10^{13}) was roughly the same as the chemisorbed amount (9.3×10^{13}) as seen in Table 1. They differ by about 10%, but they are thought to be in reasonable agreement considering the quite different approach employed.

Solbakken, Solbakken, and Emmett (*14*) discussed the area occupied by a molecule of carbon monoxide and found that 14.3 Å^2 gave better agreement for the fraction of surface covered by metal than 16.2 Å^2 usually adopted. If 9.3×10^{13} molecules/cm^2 in Table 1 is taken as the saturated amount of CO on the metal surface, it leads to 13 or 15% as the fraction of the surface covered by metal depending on 14.3 or 16.2 Å^2 employed as the area of a CO molecule. These figures look a little too low as the metal fraction. At the same time, the crystallographic planes (100), (110), and (111) of the closest packing body-centered cubic iron crystal have, respectively, 2.44, 3.46, and 2.12×10^{15} sites/cm^2 as site density, including not only the atoms on the outermost layer but those on the lower layers. Taking 3.8×10^{14} atoms of hydrogen/cm^2 as the saturated amount of hydrogen on the metal as listed in Table 1, the above site densities lead to 15.5, 11.0, and 17.9% coverage for (100), (110), and (111) planes, respectively. The simple average is 14.8% and these figures are in reasonable range of the metal surface assessed by the chemisorption of carbon monoxide.

Preadsorbed nitrogen increased the weaker chemisorption of carbon monoxide while it reduced the stronger one as already mentioned. The reason is not yet clear. It is possible, however, that most carbon monoxide molecules adsorb in bridge form on the fresh surface, but when an amount of nitrogen is preadsorbed the chances for the adsorption in linear form will be increased. The possibility that preadsorbed nitrogen weakened the bonding of chemisorbed carbon monoxide was reported (*8*).

In conclusion, the present results generally agreed with the conclusions obtained by previous authors, and the use of temperature-programmed desorption technique revealed some finer points, in particular the various types of chemisorbed hydrogen. The results also suggested that the saturated amount of hydrogen obtained by TPD can be used to measure the number of metal sites.

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