EVIDENCE FOR CHEMISORPTION OF NITROGEN ON IRON POWDER AT LOW TEMPERATURES

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IT is known[1] that carbon monoxide is chemisorbed as a complete unimolecular layer at low temperatures (around — 190° C.) on metals like iron, cobalt and nickel and this property has been used to estimate the area of such metal atoms exposed on the surface of catalysts. The total carbon monoxide adsorption at low temperatures consists of a combination of chemisorbed and physically adsorbed gas. The amount of chemisorption has been computed by taking the difference between the total carbon monoxide and the total nitrogen adsorptions, both at the same temperature, on the basis[2] that the physical adsorption of carbon monoxide and nitrogen are the same at the same temperature. A further assumption has been that the chemisorption of carbon monoxide does not affect the subsequent physical adsorption of gases. This assumption has been supported by Joy and Dorling[3] and by Srikant[4] in their investigations on iron catalysts. However, evidence contrary to this has been reported by a number of workers[5,6] in the case of cobalt catalysts. The present work attempts to elucidate the effect of chemisorbed carbon monoxide on the subsequent physical adsorption of nitrogen and also to obtain evidence for the chemisorption of nitrogen at low temperatures on pure iron powder and based on the results obtained a modified method for estimating the active metal atoms on the surface of the catalysts has been suggested.

The catalyst employed in the present study was obtained by thorough reduction of pure iron oxide in a stream of pure dry hydrogen at 500° C. The results reported here refer to adsorption by about 6·35 grams of the reduced catalyst. The adsorption measurements were carried out in an apparatus similar to the one employed by Srinivasan.[7] Solid CO_2 in acetone and liquid nitrogen were used to obtain temperatures of –78° C. and –195° C. respectively. The catalyst was completely evacuated at 500° C. and at 10^{-5} mm. Hg pressure for 8 hours and was then subjected to the following sequence of operations to obtain the isotherms presented in Fig. 1.

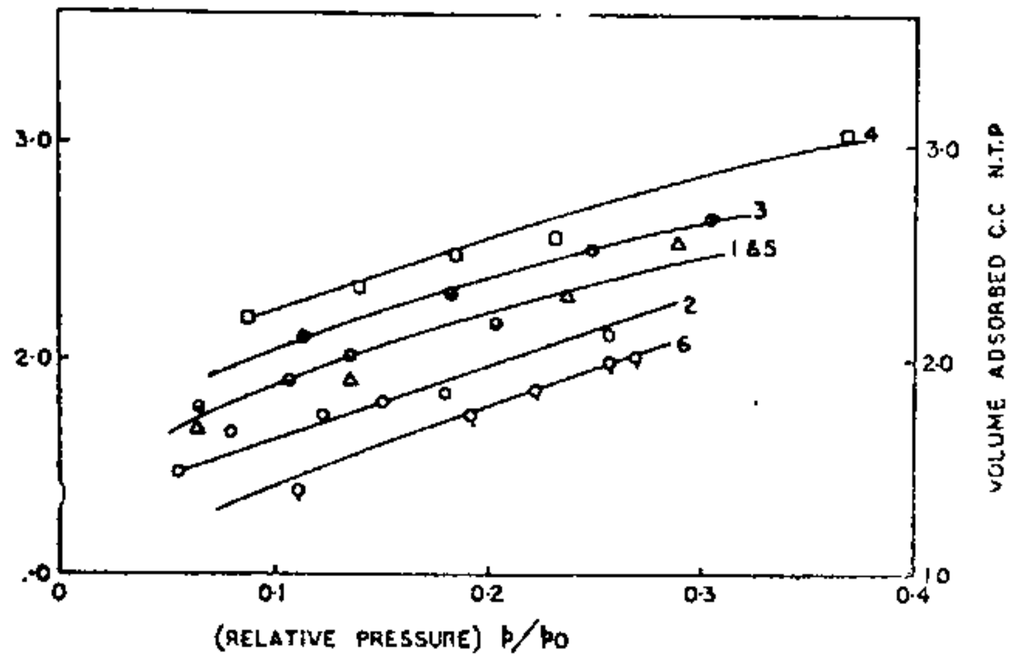

FIG. 1. Adsorption isotherms of nitrogen and of carbon monoxide on pure iron powder at — 195° C.

(1) Determination of the adsorption of nitrogen on the evacuated surface at –195° C. (isotherm 1).

(2) Evacuation at –78° C. for one hour followed by the determination of the adsorption of nitrogen at –195° C. (isotherm 2).

(3) Evacuation at –78° C. for one hour and subsequent determination of the carbon monoxide adsorption at –195° C. (isotherm 3).

(4) Regeneration of the catalyst by evacuation at –195° C. for one hour, soaking in hydrogen and slowly raising the temperature to 500° C. and maintenance at 500° C. for four hours in hydrogen, followed by evacuation at 500° C. for eight hours.

(5) Determination of carbon monoxide adsorption at –195° C. on the bare surface (isotherm 4).

(6) Evacuation for one hour at –78° C. followed by determination of readsorption of carbon monoxide at –195° C. (isotherm 5).

(7) Evacuation at –78° C. for one hour followed by determination of nitrogen adsorption at –195° C. (isotherm 6).

(8) The catalyst was regenerated as in (4) and the experiments (1) to (7) were repeated and the results were found reproducible.

It is seen from Fig. 1, that out of the total amount of nitrogen adsorbed at –195° C. a small amount (0·2 c.c. NTP, difference between isotherms 1 and 2) resists desorption at –78° C. Based on the considerations[1] of heats of adsorption, physically adsorbed nitrogen at –195° C. would be expected to desorb completely at –78° C. The amount resisting desorption may therefore be attributed to chemisorption of nitrogen. Similar observations on nickel catalysts have been interpreted by Kokes and Emmett[8] as being due to a limited chemisorption of nitrogen at –195° C. Kokes[9] has presented evidence indicative of nitrogen chemisorption on iron at –195° C. through a comparison of nitrogen and argon adsorptions. The occurrence of the chemisorption of nitrogen on iron at –195°C. has also been inferred by Ponec and Knor[10] from electrical conductivity measurements.

It is also seen from isotherm (3) that the presence of 0·2 c.c. of nitrogen on the surface results in a decrease of the carbon monoxide adsorption to the same extent [0·22 c.c. NTP, difference between isotherms (4) and (3)] indicating that the chemisorbed nitrogen blocks partially the sites originally available for the chemisorption of carbon monoxide. As the suppression of carbon monoxide is equivalent to the amount of nitrogen present and taking into account that the molecular dimensions of nitrogen and carbon monoxide are almost the same, it can be concluded that the nitrogen chemisorption at low temperatures may be molecular. It is also evident that the chemisorption of nitrogen does not suppress the physical adsorption of carbon monoxide and hence may not be expected to suppress its own physical adsorption.

If the desorption of carbon monoxide at –78° C. had resulted only in the physically adsorbed gas coming off from the surface, then the readsorption isotherm should have coincided with the physical adsorption isotherm of nitrogen (isotherm 2). A perusal of the readsorption isotherm of carbon monoxide (isotherm 5) shows that it coincides with the nitrogen adsorption (isotherm 1) on the bare surface. This would indicate that the desorption of carbon monoxide at –78° C. removes, in addition to the physically adsorbed carbon monoxide, the weakly chemisorbed carbon monoxide [difference between isotherms (5) and (2)] leaving behind only the strongly chemisorbed carbon monoxide [difference between isotherms (4) and (5)]. This conclusion is in accordance with the views of Joy and Dorling and of Sastri *et al.*[6] in the case of *iron and cobalt catalysts.*

A perusal of the adsorption of nitrogen on carbon monoxide covered surface (isotherm 6) indicates that the strongly chemisorbed carbon monoxide suppresses the subsequent physical adsorption of nitrogen as reported by a number of workers.

In conclusion, the present study points clearly to the occurrence of the chemisorption of nitrogen on iron at –195° C. and also indicates that such chemisorption does not affect its own subsequent physical adsorption. This study would lead to an important modification in the method for the estimation of active metal atoms on the surface of a catalyst. On *catalysts where chemisorption of nitrogen* occurs at –195° C. it is suggested that the carbon monoxide chemisorption must be evaluated by taking the difference between total carbon monoxide adsorption (isotherm 4) and the readsorption isotherm of nitrogen at –195° C. after evacuation at –78° C. This would lead to a more accurate estimate of the metal atoms on the surface.

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