287. *Basic Magnesium Carbonate as a Promoter on a Copper Surface.*

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THE majority of investigations into the problem of heterogeneous catalysis at a gas–solid interface have been carried out by means of velocity measurements, and indicate that a catalyst surface probably consists of areas of different activity, the extent of these areas being changed, not necessarily equally, by the presence of a promoter (Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2235, 2296; Hoover and Rideal, *ibid.*, 1927, **49**, 104; Allan and Hinshelwood, *Proc. Roy. Soc.*, 1928, *A*, **121**, 141; Constable, *Proc. Camb. Phil. Soc.*, 1927, 832; 1928, 291). This difference in activity has been ascribed to the varying unsaturation of the surface atoms of the catalyst (see, *e.g.*, Taylor, *J. Physical Chem.*, 1926, **30**, 147). The probability that the number of different degrees of activity of the surface atoms (and therefore the number of different active areas) is limited, is indicated by the work of Rideal and Wright (J., 1925, **127**, 1347; 1926, 1813), who found only three different active areas on charcoal; in the present work, the postulation of only four such areas is necessary to explain the results obtained.

The present investigation deals with a fuller examination of the adsorptive powers of two surfaces, prepared so as to result in a considerable difference in their properties. The surfaces were "explored" by measuring the adsorption of a number of gases on each at 20°, with the object of obtaining quantitative information regarding the formation, if any, of areas of different properties, due to the incorporation of a second substance (promoter).

Palmer (*Proc. Roy. Soc.*, 1922, *A*, **101**, 175) has shown that, although magnesium itself has little effect on the dehydrogenation of ethyl alcohol, yet a concentration of 2 atoms % of it strongly promotes the activity of copper. This was chosen as a suitable subject and the adsorption of a number of gases on a copper surface and on one promoted by magnesia has been determined. Since it was desirable to obtain as high an activity as possible, the surfaces were prepared at such a low temperature that complete decomposition of the magnesium carbonate, precipitated with the copper oxide, did not take place, either during reduction or during the subsequent out-gassing, and the actual promoter used was therefore a basic magnesium carbonate.

The choice of gases was governed by the restrictions that the possibility of capillary condensation must be avoided, that reaction between the gas and the surface should be absent, and that the gas should be readily prepared in a pure state. The gases used were therefore hydrogen, nitrogen, carbon monoxide, methane, and ammonia. In spite of the high critical temperature of ammonia, it appeared probable, from the results of Dew and Taylor (*J. Physical Chem.*, 1927, **31**, 277), and from the present work, that capillary condensation did not take place at the pressures and temperature used.

EXPERIMENTAL.

The adsorptions of each gas on each of three surfaces (copper, referred to subsequently as A; promoted copper, B; and promoter alone, C) were required. In order to avoid disturbing factors, a given surface was used for one isotherm only. The method consisted in reducing a pptd. CuO, either alone or mixed with $MgCO_3$, by H_2 at 200° under standard conditions; for the control experiments a pptd. $MgCO_3$ was treated similarly. The reduced product was evacuated under standard conditions and known vols. of gas were admitted from a 2-vol. pipette, the pressure being read on a const.-vol. manometer.

For such determinations it is essential to reduce to a min. the ratio free space/mass of adsorbent; this was effected so successfully that accurate measurements could be made on 2—3 g. of Cu. The ppts. (obtained from the sulphates with Na_2CO_3) were washed, suspended in water, mechanically stirred, and filtered into small glass bulbs containing a tiny filter pad of purified asbestos. Very uniform samples of the bulk were thus obtained, and since the only free space in the bulbs was that between the ultimate particles, the free space had been reduced to the min. (70—75% of the total free space). A sufficient number of the bulbs were filled to serve for the whole series of measurements, and were then dried and sealed.

For each isotherm a bulb was sealed to the apparatus, reduction in H_2 at 200° carried out, and the apparatus evacuated at the same temp. for 17 hrs. down to a pressure of *ca.* 0·0004 mm. Hg. Measurements were carried out at 20° ± 0·05°. In order to secure reproduction of the surface conditions on the adsorbent, great care was taken that every detail of the treatment was kept constant. Duplicate determinations were done in most cases.

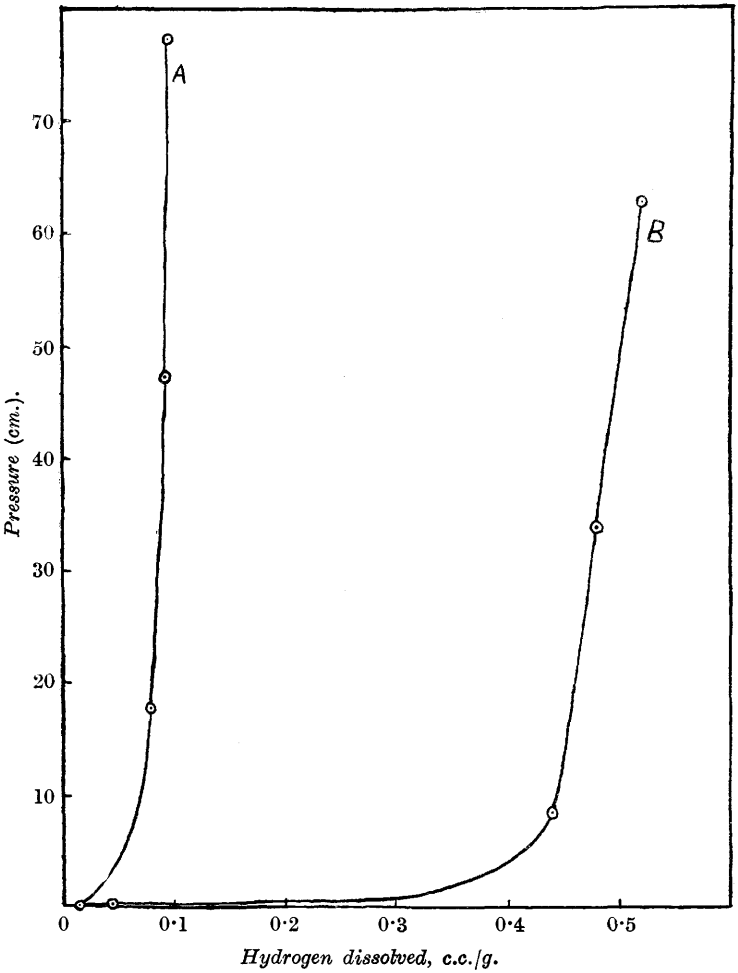
The true densities of each adsorbent were determined separately, for use in the calculations, by exhaustive evacuation at a raised temp., followed by the admission of a liquid under such conditions that air and gases were excluded. For adsorbent A, distilled H_2O was used; for B and C, pure C_6H_6. The densities so obtained (in g./c.c.) were : A, 8·87; B, 6·20; C, 2·157.

The gases used were prepared, purified by the usual methods, and stored over Hg. After their admission to the adsorbent, solution in the adsorbent took place in the cases of H_2, CO, and NH_3 on adsorbents A and B, and of

NH_3 on adsorbent C. This solution was corrected for by extrapolating to zero time pressure readings taken after temp. equilibrium with the bath had again been reached. The time required for this to take place was determined separately and was appreciable only in the cases where considerable heat was evolved by adsorption. A correction was applied to the calculated adsorptions to allow for the desorption occurring during the fall in pressure due to dissolution. Data were obtained for H_2 on adsorbents A and B by allowing up to 6 days for this dissolution to become complete; these results are shown in Fig. 1. It was at first hoped to compare the total areas of the adsorbents by comparing the rates of dissolution of H_2, but it appeared that the final

FIG. 1.

Dissolution of hydrogen in adsorbents A and B.



solubilities were more dependent on the amount of adsorption than on the total areas; the gas thus appears to enter the solid phase more frequently from the adsorbed layer than directly.

Results.—For purposes of comparison the values of the adsorptions have been calculated, in the case of adsorbent B, to a quantity (1·175 g.) containing Cu equal to 1 g. of A; this amount of B contained MgO equal to 0·210 g. of C, and the adsorptions on C have therefore been calculated on this amount. The modified adsorptions are tabulated below, where P represents pressure (in cm.) and x adsorption (in c.c. at N.T.P).

Hydrogen.

Adsorbent A.

P	0·22	17·40	41·05	67·53	0·16	20·30	47·66	78·36
x	0·1208	0·335	0·386	0·418	0·102	0·355	0·406	0·442

Adsorbent B.

P	0·17	10·94	26·30	50·41	0·16	15·38	34·83	63·57
x	0·213	0·921	1·054	1·180	0·202	0·933	1·074	1·193

Adsorbent C.

P	28·42	56·88
x...	0·0065	0·0140

Nitrogen.

	Adsorbent A.			Adsorbent B.			Adsorbent C.	
P	4·62	36·69	68·67	5·70	36·83	68·60	30·92	61·37
x	0·003	0·016	0·029	0·0099	0·056	0·106	0·0071	0·0122

Carbon monoxide.

	Adsorbent A.				Adsorbent C.	
P	0·01	8·46	36·91	67·71	34·43	68·98
x	0·1125	0·698	0·792	0·839	0·0195	0·034

Adsorbent B.

P	0·01	2·13	25·41	55·11	59·31	0·01	3·96	29·88	60·02
x	0·177	1·343	1·661	1·782	1·796	0·192	1·382	1·631	1·744

Methane.

Adsorbent A.

P	4·57	36·88	69·29	4·35	34·99	65·69
x	0·0055	0·038	0·069	0·0051	0·0364	0·066

Adsorbent B.

P	4·31	34·68	65·09	32·14	64·38
x	0·0143	0·1057	0·196	0·1006	0·198

Adsorbent C.

P	33·88	67·95
x	0·016	0·028

Ammonia.

Adsorbent A.

P	0·01	0·06	2·10	10·91	26·98	46·69	66·64
x	0·108	0·867	1·583	2·049	2·414	2·680	2·873

Adsorbent B.

P	0·00	0·12	0·91	2·96	7·32	13·92	22·40
x	0·168	1·347	2·501	3·399	4·377	5·267	6·027
P	31·20	43·16	56·10	70·01			
x	6·629	7·316	7·938	8·544			

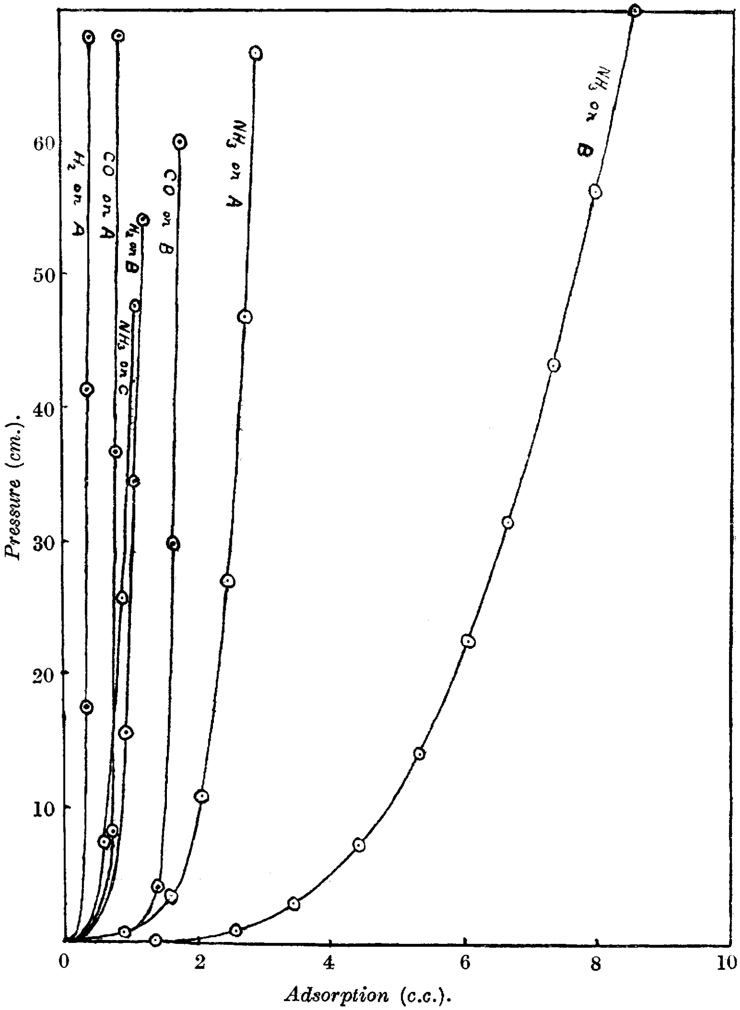
Adsorbent C.

P	7·33	25·66	47·70	72·13
x	0·599	0·852	1·037	1·192

These results, when plotted, give practically straight lines for CH_4 and N_2 on A, B, and C, and for H_2 and CO only on C. For this reason, and because of the confusion which would result from the relatively small values in each

FIG. 2.

Adsorption of hydrogen, carbon monoxide, and ammonia.



of the above cases, these curves have been omitted from the graphs reproduced in Fig. 2, which therefore show only the adsorptions of H_2 and CO on A and B, and of NH_3 on A, B, and C. (For clarity, duplicates have been omitted.) No evidence of discontinuities has been obtained.

For comparison, the values read from the original curves at different pressures have been collected below. They are necessarily less accurate than the individual determinations. The adsorptions are expressed as above, but the values for C have been subtracted from those for B to obtain a probable value for the adsorption on the Cu alone; R represents the ratio of the mean of duplicate determinations on B to that on A.

Gas.	Ad-sorbent.		60 cm. x.	40 cm. x.	20 cm. x.	10 cm. x.	5 cm. x.	2 cm. x.
H_2	A		0·406	0·384	0·343	0·310	0·273	0·22
H_2	A		0·420	0·394	0·352	0·315	0·273	0·22
H_2	B		1·160	1·087	0·976	0·838	0·700	0·555
H_2	B		1·211	1·115	1·013	0·898	0·760	0·585
		R =	2·87	2·83	2·86	2·78	2·67	2·60
N_2	A		0·0255	0·0175	—	—	—	—
N_2	B		0·080	0·054	—	—	—	—
		R =	3·14	3·09				
CO	A		0·83	0·80	0·76	0·72	0·64	—
CO	B		1·71	1·65	1·57	1·51	1·42	—
CO	B		1·77	1·70	1·62	1·56	1·46	—
		R =	2·10	2·09	2·10	2·13	2·25	
*CH_4	A		0·061	0·042	0·022	0·011	—	—
*CH_4	B		0·157	0·1055	0·053	0·0275	—	—
		R =	2·58	2·51	2·39	2·50		
NH_3	A		2·82	2·60	2·30	2·02	1·80	—
NH_3	B		6·98	6·17	5·06	4·13	3·35	—
		R =	2·48	2·37	2·20	2·04	1·86	

* Duplicates practically identical.

Discussion.

The conceptions of Langmuir have been applied to these data by the use of the appropriate relation $x = aPV/(1 + aP)$, where x is the adsorption, P the pressure, a a constant involving the forces between the surface atoms and the adsorbed molecules, and V the adsorption at saturation, taken to represent the area then occupied by the adsorbed gas, a unimolecular layer being assumed.

For nitrogen and methane on all the adsorbents, and for all gases, except ammonia on C, the forces involved (and hence involving a) are so small that the isotherms are almost straight lines, and the calculation of the values of V is so affected by slight changes (or errors) in curvature that only the gases hydrogen, carbon monoxide, and ammonia are useful for estimating the adsorbing areas.

The above relation has been applied on the assumption that the adsorptions at any pressure greater than 20 cm. consist of the sum of two adsorptions, one saturated at that pressure and one unsaturated; *i.e.*, $x = V_1 + a_2V_2P/(1 + a_2P)$. On this basis the values of V_1 and V_2 have been calculated by substituting for x and P in the above relations the three points on the isotherms $(x_1, 20)$, $(x_2, 40)$, and $(x_3, 60)$. The probable errors introduced into the values of V_1 and V_2 by reasonable errors in drawing and reading the isotherms (see above) have been calculated. Since it is assumed that each isotherm may be represented by adsorption on two different types of surface, it follows that information as to the relative areas of six different surfaces may be obtained from the results. The fact that the results are explicable by the postulation of only four different types of surface may be taken as evidence in favour of the basis of calculation.

The values of V_1 and V_2 for the three gases hydrogen, carbon monoxide, and ammonia on the two surfaces A and B are given below, together with the corresponding probable errors. It is

Gas.	Adsorbent.	V_1.	Probable error.	V_2.	Probable error.
H_2	A	0·26	0·06	0·24	0·07
H_2	B	0·86	0·02	1·1	0·2
CO	A	0·71	0·2	0·34	0·1
CO	B	1·50	0·08	0·9	0·3
NH_3	A	1·87	0·4	2·4	0·4
NH_3	B	3·4	0·2	8·6	0·9

clear that the effect of the promoter has been to cause a non-uniform increase in the several values of V_1 and V_2. Unfortunately, these values are very sensitive to small changes in x, so, owing to the large errors thus made possible, any conclusions of a quantitative nature are rendered somewhat speculative.

There are several ways in which the results may be related, of which the one given below is the most probable; the others do not lie well within the errors or involve surfaces capable of adsorbing hydrogen but not capable of adsorbing carbon monoxide, which is contrary to the results of other workers in this field. The most probable distribution of active areas is given in the following relations, in which, under the heading "gas adsorbed," the number of elementary areas occupied by one molecule of gas is given in parentheses.

V.	Gas adsorbed.			V.	Gas adsorbed.		
	Adsorbent A.				*Adsorbent B.*		
0·65	CO (1)	H_2 (2)	NH_3 (1)	1·64	CO (1)	H_2 (2)	NH_3 (1)
0·28	CO (1)	H_2 (1)		1·0	CO (1)	H_2 (1)	
0·9		NH_3 (1)		0·8		NH_3 (1)	
2·4		NH_3		8·6		NH_3	

On this basis, then, the effect of the promoter has been to increase, in different ratios, the extent of each of four different active surfaces.

Summary.

The adsorption isotherms of hydrogen, nitrogen, carbon monoxide, methane, and ammonia on the surfaces copper (A), copper promoted by a basic magnesium carbonate (B), and the promoter (C) alone have been determined at 20°.

The isotherms of nitrogen and methane are too nearly linear to permit calculation of the extent of the areas adsorbing the gases.

From the isotherms of hydrogen, carbon monoxide, and ammonia on the surfaces, calculation has been made of the relative areas adsorbing these gases, and the promoted and unpromoted surfaces compared.

The solubility of hydrogen in A and B has been approximately determined directly.

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