Studies on Surface Heterogeneity in Adsorption of Carbon Dioxide on Nickel by Use of the Isotopic Desorption Method[1]

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A number of printed works on the active center of catalysts have appeared, since Taylor proposed the idea in 1925. However, though its existence on actual catalysts is recognized unequivocally by most researchers, some ambiguities remain yet as to its nature. In some cases the experimental grounds in favour of the active center may be explained by other causes, i. e., by the "induced heterogeneity" or by the mutual interaction between adsorbed molecules. Such situations regarding this important problem of catalysis may be brought about because researchers have taken it up by the kinetic or calorimetric methods, which are deficient in giving decisive conclusions.

Therefore, in order to attack the problem, now called heterogeneity of catalyst surface, it seems interesting to apply the isotopic desorption method of Roginsky[2], who applied it with success by the use of deuterium to determine the heterogeneity of nickel, when hydrogen was chemisorbed[3]. The process of the method consists in two procedures: firstly successive chemisorption of two gaseous portions of isotopically labelled and non-labelled species, to the catalyst to be investigated, and secondly, determination of the isotopic composition of the gases desorbed from the catalyst. Now, if the isotopic composition of the desorbed gases is the same as that of the mean of the chemisorbed gases, it is highly probable that the catalyst surface is homogeneous, while if it is not the same, the catalyst surface is likely to be heterogeneous. Since then, the method has been applied by others; e. g., chemisorption of carbon monoxide on a promoted iron catalyst by Kummer and Emmett[4] making radioactive carbon as the tracer, and chemisorption of hydrogen on nickel-silica by Schuit[5], who, however refused to accept the result of Roginsky.

Such being the situation it will be interesting to apply it to other systems under the condition of least ambiguity, so as to check the criticism against this method. In the present paper, the heterogeneity of nickel surface will be investigated by use of carbon dioxide,

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[1] Preliminary report: Preprint of the Catalyst Symposium of Japan, Osaka, April, 1959, p. 1.

[2] S. R. Roginsky and O. Todes, *Acta Physicochim.* (*U. R. S. S.*), 21, 519 (1946). This method is called the differential isotopic method in Russian literatures.

[3] M. P. Keier and S. R. Roginsky, *Izvest, AN, URSS*, 1, 27 (1950); Cf., "Advances in catalysts", 5, 247 (1955).

[4] J. K. Kummer and P. H. Emmett, *J. Am. Chem. Soc.*, 73, 2886 (1951).

[5] G. C. Z. Schuit, *Chem. Abstr.*, **48**, 11, 869i (1954). Cf. P. M. Gundry and F. C. Thomkins, *Quart. Rev.*, **14**, 257 (1960).

making heavy carbon dioxide $CO^{18}O$ as the labelled species of adsorbent, and effecting desorption at the adsorbed temperatures. Selection of this adsorbate may be appropriate, because, besides its possible immobility on the surface, it will evolve little adsorption heat, as compared with hydrogen and carbon monoxide hitherto selected, so that the disturbing effect of evolved heat would be small on adsorption.

Experimental

Apparatus.—The apparatus used in the measurement is shown in Fig. 1. During the experiment, caution was always taken that no mercury vapor might penetrate into catalyst A by constant use of trap T kept at ca. −78°C.

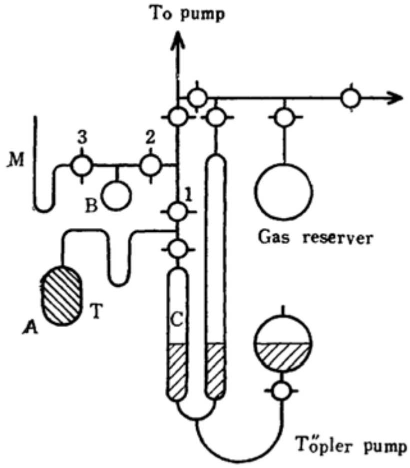

Fig. 1. Apparatus.

Nickel Catalyst.—Nickel carbonate, obtained by the reaction of aqueous nickel nitrate solution with an ammonium carbonate solution, was washed with water, dried and heated in the air for 10 hr. at 300°C. Nickel oxide thus prepared was turned into nickel powders by reducing it with hydrogen for 80 hr. at 350∼380°C. Before each experimental run, the nickel powders were treated with hydrogen followed by evacuation at the same temperature at 10^{-6} mmHg. The specific area of the catalyst determined by the BET method (adsorbate, nitrogen) was 1.18 m^2/g.

Gases.—Heavy carbon dioxide $CO^{18}O$ was prepared in the present laboratory by the thermal diffusion method⁶⁾. Its concentration was 29.9∼15.2 atom %. Normal carbon dioxide was obtained by evaporation of commercial dry ice, and purified with aqueous sodium chromate, followed by dehydration with liquid nitrogen and phosphorus pentoxide. The hydrogen used for reduction was prepared by electrolysis of aqueous sodium hydroxide solution, and was purified finally by being effused through a palladium filter. The last treatment was indispensable for the reproducibility of the result.

Adsorption Isotherm.—For the sake of discussion, the adsorption isotherm for carbon dioxide on the nickel powders (28.1 g.) which were used in the experiment was determined at −78°C. This is shown in Fig. 2. It was found that 0.17_8 cc./g. was necessary in order to complete the monomolecular layer.

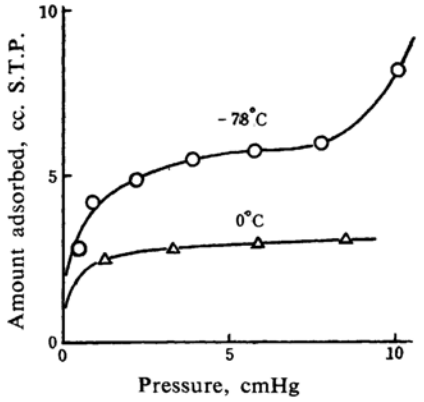

Fig. 2. Adsorption isotherms for carbon dioxide at 0 and −78°C (cat. 28.1 g.)

Reduction of Nickel Surface.—In order to determine the permissible degree of reduction the amount of adsorbed oxygen was measured with the isotopic dilution method by use of $CO^{18}O$, i. e., introducing the gas to the vessel which contained nickel and determining the degree of dilution in the gas collected from the vessel. When the O^{18}% of the original CO_2 was 15.2 atom % and when the reduction at 380°C was continued for 20 hr., the collection was made at two temperature intervals, the result being as follows:—between 0°C and room temperature, 0.3 cc. and 14.2%, and between room temperature and 300°C, ca. 1 cc. and 12.2%. Dilution of the original carbon dioxide occurred to such an extent that the residual oxygen was found not to be negligible by the above treatment of reduction, suggesting that the nickel surface did not reach a state sufficiently free from oxygen. However, it was found that eighty hours of reduction as actually adopted in the experimental runs was found to be satisfactory so that the heterogeneity could be discussed by this method. Such difficulty in cleaning the surface as was found above has been pointed out already, e. g., recently by Roberts and Sykes⁷⁾.

Exchange Reaction.—After the nickel catalyst charged in the reaction vessel A was reduced with hydrogen, it was evacuated and was kept at the adsorption temperature, which was adopted to be −78°C if otherwise not stated. Then a known amount V_1 of heavy carbon dioxide (or normal carbon dioxide) was introduced into the vessel A from the measuring pipette C. After the scheduled time which was set at 30 min. of contact, the gaseous sample was collected by opening the taps

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6) K. Hirota, Y. Kobayashi et al., "Isotopes and Radiation" (Tokyo), **2**, 235 (1959); Y. Kobayashi et al., "Mass-spectroscopy" (Japan), No. 13, 79 (1959).

7) M. W. Roberts and K. W. Sykes, *Trans. Faraday Soc.*, **54**, 548 (1958).

1 and 2, and being condensed in the trap B cooled at −78°C. Amount v of the condensed gas was determined by evaporating it in the known volume of space between the taps 3 and 2 with the manometer M. The residual carbon dioxide adsorbed tightly on the nickel could be calculated as the difference between V_1 and v. Then normal carbon dioxide (or heavy carbon dioxide), the amount of which was measured to be V_2, was again introduced to the catalyst already covered to some extent by heavy carbon dioxide. After the scheduled time of contact, the gaseous part of the carbon dioxide was again condensed in B, and was measured by the same procedure as described above. This procedure was done several times. The first desorption was made at the same temperature as the adsorption, and subsequent desorption was carried out by raising the temperatures gradually up to 300°C. The isotopic abundance and gaseous composition of each collected gas were determined by a mass-spectrometer.

Results

For the sake of making the effect evident, the adsorption was carried out at temperatures as low as possible, i. e., mostly at −78°C and also at 19 and 0°C. However, the amount of the desorbed gas was determined at several temperatures up to 300°C. Experimental data are summarized in Table I in the order of the runs actually carried out. The first and second portions, denoted as I and II in Table I, of the gas introduced into the vessel are heavy and normal carbon dioxide if otherwise not stated. The numerals marked by→after V_1 denote the amount of the gas strongly adsorbed after desorption at the adsorption temperature.

The reproducibility of the experiment may be shown by the residual amount of the gas remaining after evacuation in Nos. 1 and 4, where the adsorbed and desorbed temperatures were the same (−78°C) while other experimental conditions were practically identical with each other. It is noteworthy that such strongly adsorbed gas amounted to ca. 1.85 cc. in both runs in spite of the difference of the first portion introduced. The tendency that

TABLE I. EXPERIMENTAL RESULT

Catalyst: 28.1 g., BET area=1.18 m²/g.=5.0 m²/28.1 g.
Gaseous volume is expressed by STP, while concn. of ^{18}O by atom %.

Run No.	Adsorption procedure				Desorption procedure				
	Temp. °C	Order of addition	Added amount cc.	^{18}O Concn. %	Temp. °C	Evacuated time min.	Desorbed amount cc. v	Residual amount cc.	^{18}O Concn. %
1		I	V_1=1.35	29.9	−78	110	(5.31)	1.87	2.0
	−78		→1.35		0	100	0.21	1.66	11.4
		II	V_2=5.83	0.2	20∼21	80	0.03	1.63	12.8
					150	60	0.06	1.57	12.5
					300	60	0.67	0.90	12.0
2*		I	V_1=11.49	0.2	−78	120	(13.05)	1.44	28.4
	−78		→2.31		0	120	0.25	1.19	10.8
		II	V_2=12.18	29.9	100	90	0.07	1.12	8.0
					300	80	0.94	0.18	7.2
3		I	V_1=2.36	28.4	0	120	(4.35)	2.26	3.5
	0		→2.18		100	90	0.47	1.79	16.3
		II	V_2=4.43	0.2	300	100	1.02	0.77	17.4
4		I	V_1=5.62	29.9	−78	120	(5.01)	1.83	2.8
	−78		→1.88		0	120	0.26	1.57	15.7
		II	V_2=4.96	0.2	100	90	0.09	1.48	17.9
					300	90	0.55	0.93	15.9
5**		I	V_1= 2.32	15.2	(a) Desorbed CO_2 was 0.1 cc. CO_2/CO=1/50, because CO desorbed at −78°C was 5.18 cc.				
	−78								
		II	V_2=12.24 (CO)	0.2	(b) ^{18}O concn. of CO became 1.0%				
6		I	V_1=5.69	29.1	19	120	(4.81)	2.40	3.3
	19		→2.36		100	120	0.42	1.98	10.7
		II	V_2=4.85	0.2	300	120	1.02	0.96	19.0

* The first gas I was normal CO_2 and the second II $CO^{18}O$.
** The second gas was carbon monoxide instead of carbon dioxide.

TABLE II. RESIDUAL AMOUNT OF $C^{18}O_2$ IN NOS. 1 AND 4

No. 1 ($C^{18}O_2$ adsorbed = 0.40 cc.)

Desorbed temp. °C	Heavy carbon dioxide Desorbed cc.	Heavy carbon dioxide Not desorbed cc.
−78	0.096	0.31
0	0.022	0.29
20∼21	0.004	0.28
150	0.007	0.28
300	0.079	0.20

No. 4 ($C^{18}O_2$ adsorbed = 0.56 cc.)

Desorbed temp. °C	Heavy carbon dioxide Desorbed cc.	Heavy carbon dioxide Not desorbed cc.
−78	0.13_0	0.43
0	0.04_0	0.39
100	0.01_6	0.37
300	0.08_6	0.28

the first portion was adsorbed more tightly than the second could be observed in No. 2, where heavy carbon dioxide was made the second portion. From the comparison of Nos. 1 and 4 with No. 2, the residual gas at −78°C is evidently small in the case where heavy carbon dioxide was introduced as the second gas. This may be explained by the isotopic effect of adsorption. Though the discussion along this line is interesting, it will not be taken up in the present report, because there may be some accidental error*.

By comparing the result Nos. 3 and 6 where the adsorption and first desorption were carried out at 0°C and 19°C, respectively, with those of Nos. 1 and 4, it is clear that the strongly adsorbed carbon dioxide increases in amount as the temperature of adsorption becomes higher.

In order to obtain knowledge on the state of adsorption of carbon dioxide, a similar experiment was attempted making carbon monoxide the second gas in No. 5. Since carbon monoxide can be adsorbed on nickel very strongly as shown by the great heat of adsorption (35 kcal.)[8], carbon dioxide which has been adsorbed may be expelled from a nickel surface. Such an effect is moreover possible due to the heat evolution when carbon monoxide is chemisorbed. However, as described in Table I, the amount of the desorbed carbon dioxide was only ca. 0.1 cc., though carbon monoxide was desorbed more than carbon dioxide (5.1_8 cc.). This suggests a firm bonding of carbon dioxide with nickel. However the fact that ^{18}O concentration of carbon monoxide in the desorbed gas could not be neglected will become a matter of discussion; i. e. it was 1.0%. This indicates the occurrence of an exchange reaction such as

$$CO^{18}O + CO \rightarrow CO_2 + C^{18}O \qquad (I)$$

on nikel surface in parallel with desorption.

Such a firm bonding between the first chemisorbed* carbon dioxide and nickel can be concluded also from the isotopic balance of heavy oxygen in each run. According to No. 1, where 0.40 cc. of heavy carbon dioxide was chemisorbed as the first gas, only a part of it could be desorbed at each desorbing procedure, as shown in Table II, where the nautral abundance of ^{18}O was taken to be 0.2%. The same tendency can be seen also in No. 4, where 0.56 cc. of heavy carbon dioxide was first chemisorbed. It will be noteworthy that though the absolute amount of heavy carbon dioxide adsorbed at −78°C is different in both runs, their ratios to those at 300°C is the same i. e., 0.65. A similar result is found easily, in others runs, by the same method of calculation.

Discussion

As pointed out above, a part of the nickel surface has a nature to chemisorb carbon dioxide so strongly that carbon monoxide added as the second gas can not expel the carbon dioxide practically from the surface. This nature of the nickel surface will be supported also from the fact that the molecules once chemisorbed at low temperature were not desorbed even by evacuation at 300°C. By use of the data of No. 1, the situation will be shown quantitatively. The residual amount 1.87 cc at the desorbed temperature corresponds to surface coverage (θ) of 0.37, which decreases gradually down to $\theta = 0.18$ (0.9 cc.) after the desorption process at 300°C, because the amount of carbon dioxide necessary to cover the catalyst surface monomolecularly is 5.0 cc.

Now the nature of such a special surface, which extends to about one third of BET area of the nickel, will be discussed from the standpoint of isotopic exchange of heavy oxygen with regard to possible occurrence of the induced heterogeneity. The data of No. 1 will be taken up again. If the bonding of carbon dioxide to nickel is extremely firm on

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* The residual gas remaining at 300°C is only 0.18 cc. in No. 2. Such a small numeral will probably be brought out by an increased error due to the large amount of the second gas (12.1_8 cc.).

[8] O. Beeck, "Advances in Catalysts", 2, 151 (1950).

* Chemisorption will hereafter be used often as a technical term not defined to be clearly different from adsorption.

some special sites on the surface, it may be possible that ^{18}O concentration in the first portion of desorbed gas is natural, i. e. 0.2%, because V_1 was 1.35 cc., which was less than the volume corresponding to the chemisorption on the special sites (1.87 cc.), leaving some vacant sites for the second gas. Actually, dilution of ^{18}O in the strongly adsorbed carbon dioxide occurred up to 2.0%, as shown in the last column of Table I. The degree of dilution will be given approximately as follows: 0.096/0.40=0.24. This suggests that there occurred some exchange of oxygen between strongly adsorbed carbon dioxide and that which was weakly adsorbed.

Now it is natural to assume that the difference of adsorptive power or the surface mentioned above might be due to the primary property of sites but not induced secondarily by the mutual interaction of absorbed molecules. This is because if the difference is brought about by the latter reason, the degree of the exchange reaction II between adsorbed carbon dioxide would occur much more markedly and increase according as the adsorption temperature rises, and evacuation at 300°C would take away most of the adsorbed carbon dioxide, due to a relatively weak interacting energy. Another fact will be shown against the induced heterogeneity by use of the data of No. 2, where heavy carbon dioxide added as the second gas (3.6_5 cc.) was taken out from the surface practically without exchange by the first desorption at the adsorption temperature, due to the weak bonding of the second gas with adsorptive sites.

Since the surface heterogeneity is confirmed, its nature will be discussed in more detail. According to the analysis of the data, it has been shown that even the special sites extending as much as one third of the total are not of a homogeneous nature in adsorptive power, three fourths of it making firmer bonding to carbon dioxide than the remaining one third. The existence of such heterogeneity is possible also from the data of No. 5, which can be explained by an exchange reaction I of weakly adsorbed carbon monoxide and strongly adsorbed carbon dioxide. Assuming that the amount of the strongly adsorbed carbon dioxide is 1.85 cc. and also that ^{18}O concentration of the strongly adsorbed carbon monoxide (7.0_6 cc.) is the same as that of the desorbed one, ^{18}O lost from carbon dioxide by the contact of carbon monoxide will be approximately equal to $(1.0\times12.24/1.85\times15.2)\times100\%=22\%$. It is noteworthy that this numeral nearly equals that (24%) obtained in the discussion of the above paragraph. Here it will be mentioned that no exchange of this type I could be observed on silver catalyst even at 220°C[9], suggesting that there was a difference in the chemisorped state between nickel and silver. The result may be caused by the chemisorptive power of nickel to carbon monoxide which is so strong that they can form stable carbonyl compounds, though the chemisorptive power of both metals to carbon dioxide is not very different, so that the exchange reaction

$$O_2^* + CO \rightarrow CO_2^* + O_2 \qquad \text{(III)}$$

proceeds at the same order of temperature 100～200°C[10].

In short, it can be concluded that there are two or three types of sites on nickel surface differing in chemisorptive power. It will be our next problem to investigate the real nature of these special sites, e. g., to see whether they exist as groups or as isolated ones. However, the problem of surface heterogeneity is very complicated, and the present data can not give an answer to all the questions to be discussed. Here it will be mentioned that, since the ratio of the active surface to the total is considerably large and reproducibility of the catalytic activity is very good, the heterogeneity here observed may be brought about by the different catalytic activity of each crystal plane and not by isolated sites on some planes. Further discussion concerning the nature of heterogeneity is to be continued in the investigation which will be reported soon.

Summary

By applying the isotopic desorption method of Roginsky under the experimental condition of least ambiguity, heterogeneity of nickel surface has been studied on the chemisorption of carbon dioxide by making heavy oxygen as the tracer. It has been shown that about one third of the surface can chemisorb carbon dioxide very strongly at −78, 0 and 19°C, and a part of carbon dioxide chemisorbed is not desorbed even by the evacuation at 300°C. Considering the isotopic balance of heavy oxygen, it can be said that the above effect is brought about by the primary heterogeneity of surface sites but not by the "induced heterogeneity" of adsorbate. However, it has been found difficult to make the detailed nature of such heterogeneity by the present data alone.

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[9] Hirota and Kobayashi, Preprint of the Catalyst symposium of Japan, Kyoto, April, 1956.

[10] K. Hirota and Y. Kobayashi, This Bulletin., **29**, 996 (1956); Y. Kobayashi, M. Hatada and K. Hirota, unpublished.

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