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The Heterogeneous Adsorption of Carbon Dioxide on the Nickel Surface as Studied by the Isotopic Desorption Method

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Further evidence on the adsorptive heterogeneity of the nickel surface has been presented by the use of the technique described in our previous paper. The results support the conclusion already proposed that more than 20—30% of the surface can adsorb carbon dioxide strongly over the temperature range between −78° and 300°C.

The heterogeneity of the adsorptive power of the nickel surface has often been reported by using various physical techniques, e. g., infrared spectroscopy,1) measurements of the electric resistance2) and of the surface potential,3) and electron microscopy.4) Nevertheless, the question why the heterogeneous adsorptivity can be observed at all has not yet been answered satisfactorily. Besides, the fractions of the individual nickel surfaces, which differ in their activity, to the total surface have rarely been determined without ambiguity, though their determination is important to an understanding of the occurrence of heterogeneity in the study of adsorption and catalysis.

Several years ago, the present authors5) applied the isotopic desorption method (or the differential isotopic method) of Roginsky6) to the present problem; they then found that about 20—30% of the BET area of the nickel surface can adsorb carbon dioxide more strongly over the temperature range from −78°C to 300°C than the other fraction of the surface. Since carbon dioxide is soluble into the nickel bulk with much difficulty, the result is free from any ambiguity of absorption, the disturbing effect of which was confirmed in the application of this method by Takeuchi and Asano, when tritium was used as the tracer.7) The heterogeneity observed, therefore, may be suggested as being due to the co-existence of various crystal planes rather than to such peculiar sites as lattice defects on the surface. Selwood et al.8) reported the same conclusion for nickel-kieselguhr on the basis of the method of magnetization-volume isotherms; they concluded the coverage of the stronger adsorption to be one-sixteenth. Quinn and Robert9) and Suhrmann et al.10) also found heterogeneity in the adsorption of carbon dioxide and carbon monoxide respectively on nickel films. Moreover, recently one of the present authors could explain the poisoning effect of carbon dioxide on the self-hydrogenation of ethylene11) in terms of the above findings.

Such being the situation, it will be significant to report here some supplementary data obtained since the report mentioned above,5) which will be denoted hereafter as "Paper I." The object of the investigation is to obtain some knowledge on the physical equilibration of the adsorbed carbon dioxide and also to clarify the adsorbed state, because both points seem to involve some questions, when the previous results are discussed. In the present paper, therefore, two kinds of experiments will be reported, with the desorption time changed on one hand, and with $^{13}CO_2$ and $CO^{18}O$ used as the adsorbate gases on the other.

Experimental

The apparatus and procedure were the same as those adopted in Paper I, except for minor differences to be mentioned below. The reduced nickel powders used as the adsorbent were a different lot from the same source. The weight was 19.8 g., and the BET area, 0.178 cc./g. These powders will be denoted as "Cat. B," if necessary, so as to discriminate them from the "Cat. A" used in Paper I. Heavy carbon dioxide $^{13}CO_2$ (19.7 atom%) was prepared by oxydizing $^{13}CH_4$ which had been given to the authors by Professor S. Horibe.12) It was enriched

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1) R. P. Eischens and W. A. Plinskin, *Advan. Catalysis*, **10**, 1 (1958).

2) W. M. H. Sachtler and G. J. H. Dorgelo, *J. Chem. Phys.*, **54**, 27 (1957).

3) R. Suhrmann, Y. Mizushima, A. Hermann and G. Wedler, *Z. physik. Chem.*, *N. F.*, **20**, 332 (1959).

4) W. M. H. Sachtler and G. J. H. Dorgelo, "Proc. 4th Intern. Conf. on Electron Microscopy," Berlin (1960), p. 802.

5) K. Hirota, Y. Kobayashi and J. Kiji, This Bulletin, **34**, 1213 (1961); "Preprint of the Catalysis Symposium of Japan (Osaka)" (1959), p. 1.

6) N. Keier and S. Roginsky, *DAN USSR*, **57**, 157 (1947).

7) T. Takeuchi and T. Asano, *Z. physik. Chem.*, *N.F.*, **36**, 118 (1963).

8) I. E. Den Besten, P. G. Fox and P. W. Selwood, *J. Phys. Chem.*, **66**, 450 (1962); P. W. Selwood, "Adsorption and Collective Paramagnetism," Academic Press, New York (1962), p. 162.

9) C. M. Quinn and M. W. Roberts, *Trans. Faraday Soc.*, **58**, 569 (1962).

10) R. Suhrmann, H. J. Heyne and G. Wedler, *J. Catalysis*, **1**, 208 (1962).

11) K. Hirota and S. Teratani, *Sci. Pep. Inst. Phys. Chem. Research* (*Tokyo*), **57**, 206 (1963).

12) S. Horibe, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagakaku Zasshi*) **80**, 1206 (1959).

TABLE I. EXPERIMENT TO INVESTIGATE THE EQUILIBRATION OF ADSORBED CARBON DIOXIDE

Catalyst B. Carbon dioxide: $CO^{18}O$ 29.1 atom % in No. 7 and 29.7 atom % in Nos. 8, 9, and 10

	Adsorption procedure			Desorption procedure				
Run No.	Temp. °C	Introduced order	Introduced amount cc.	Temp. °C	Desorption time min.	Desorbed gas amount cc.	Isotopic concn. of the gas %	Residual amount V_r cc.
7	−78	I	$V_1=4.22$	−78	30	(6.74)	1.5	1.61
			$V_1'=1.50$		780	0.20	—	1.41
		II	$V_2=6.85$	17—20	180	0.07	19.2	1.34
				100	180	0.07	19.4	1.27
				300	900	0.78	16.8	0.49
8	−78	I	$V_1=4.36$	−78	120	(5.36)	1.7	1.43
			$V_1'=1.43$	0	90	0.08	17.0	1.35
		II	$V_2=5.36$	100	90	0.12	19.3	1.23
				300	70	0.59	17.5	0.64
9	−78	I	$V_1=4.73$	−78	60	(4.87)	1.9	1.54
			$V_1'=1.44$	0	60	0.15	18.1	1.39
		II	$V_2=4.97$	100	60	0.12	19.3	1.27
				300	70	0.71	19.1	0.56
10	0	I	$V_1=4.12$	0	120	(4.00)	2.9	1.63
			$V_1'=1.55$	100	120	0.41	16.3	1.22
		II	$V_2=4.08$	300	120	0.74	20.2	0.48

N.B. Runs of Nos. 1—6 are shown in Paper I.
Numbers in paentheses denote the desorbed gas after the introduction of the second gas.

TABE II. EXPERIMENT, USING $^{13}CO_2$ AS ADSORBATE

Carbon dioxide $^{13}CO_2=19.7$ atom% Contact of the second gas is always 120 min.

	Adsorption procedure			Desorption procedure					
Run No.	Temp. °C	Introduced order	Introduced amount cc.	Temp. °C	Desorption time min.	Desorbed amount cc.	Isotopic concn., %		Residual amount V_r, cc.
							^{13}C	^{18}O	
11	0	I	$V_1=2.94$	0	120	(4.16)	1.5	14.0	1.64
		($^{13}CO_2$)	$V_1'=1.64$	100	120	0.30	17.5	3.3	1.32
		II	$V_2=4.16$	300	120	0.73	18.2	2.9	0.59
		($C^{18}O$, 14.8 atom%)							
12	−78	I	$V_1=3.89$	−78	120	(3.70)	2.0	—	1.41
		($^{13}CO_2$)	$V_1'=1.41$	0	120	0.11	12.8	—	1.30
		II	$V_2=3.70$	100	120	0.09	15.1	—	1.21
		(CO_2)		300	120	0.61	19.1	—	0.60

by the thermal diffusion column set at the Titani Laboratory of Tokyo Metropolitan University. $CO^{18}O$ was prepared by the present laboratory; its ^{18}O concentration was high enough to fulfill the object of the present research (ca. 29 or 15 atom%). The mass spectrometer used for isotopic analysis was a Hitachi (model RMB).

It might be mentioned that the desorption of carbon dioxide was always carried out by condensing it at the temperature of liquid nitrogen (−195°C), as was done in Paper I; i. e., desorption was continued until the vapor pressure of the adsorbed carbon dioxide decreased to 10^{-5} mmHg.[13] Special care was always taken in materials and manipulation so that no poison appeared on the nickel surface.

Results and Discussion

Table I summarizes the runs (Nos. 7—10) which were carried out to study the effect of the desorption time after introduction of the second gas. In Table II are shown the runs (Nos. 11 and 12) in which $^{13}CO_2$ was used as the first introduced gas, the desorption time being 120 min. In the tables, V_1 denotes the amount of the first gas introduced; V_1', that of the first gas which remained

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[13] Landolt-Börnstein, "physik. u. Chem. Tabellen," II band, 2 Teil (1960), p. 54.

after the desorption; V_2, that of the second gas introduced in the adsorption vessel (A), and V_r, the gas remaining after the second desorption at the same temperature. According to the data of Paper I, all the V_1+V_2 values in these runs are enough to form a monolayer of carbon dioxide on the surface.

No. 7 shows that the desorption time after the introduction of the second gas will not affect the result very much because the change in the residual amount on the surface was small, as is shown in Table II. The first residual gases of No. 7, 8, and 9 agree well with that of Paper I; i. e., 0.72 cc./g. was given for No. 8, while 0.67 cc./g. was given for the mean of Nos. 1 and 4, the desorption time of which was the same (120 min.) as that of No. 8. Thus, the desorption time of the second introduced gas, 110 or 120 min., is enough to make possible the conclusion drawn in Paper I. In other words, the present result means that the second portion of the introduced gas reached a physical equilibration after two hours, but that the isotopic equilibration with the first introduced gas was nevertheless not realized in the present system.

Table II shows that the amount of gas strongly adsorbed was practically unchanged at the same temperature, even if carbon dioxide was labelled by carbon instead of oxygen. (Compare Nos. 12 and 11 with Nos. 8 and 10 respectively.) The second point to be mentioned is the production of $^{13}CO^{18}O$ in the first desorbed gas. However, it could not be identified in the portions of the gas desorbed thereafter, for their quantities were too small. This finding tells us that the following exchange reaction (A) proceeds during the adsorption:

$$^{13}CO_2 + CO^{18}O \rightarrow {}^{13}CO^{18}O + CO_2 \qquad (A)$$

In other words, a kind of dissociative adsorption of catbon dioxide occurs. However, the dissociation may mean the formation of CO (ads)+O(ads), but not of C (ads)+2O(ats), considering the findings of Suhrmann et al.[10] as well as the energetic reason.

As Table II shows, it is now evident that the numerical value of the "strong" area, one-third, becomes more reliable and that carbon dioxide strongly adsorbed may exist as a dissociative state, as has been proposed.[5,9] However, there still exists a possibility of exchange without dissociation, similarly to that proposed by Webb and Eischens[14] in the case of exchange reaction (B):

$$^{13}CO + C^{18}O \rightarrow {}^{13}C^{18}O + CO \qquad (B)$$

The possibility of such a reaction without dissociation will be taken up again in the next section.

General Discussion

As has been mentioned above, there are at least two kinds of adsorption sites on the nickel surface. It is possible, however, that the above conclusion is of an apparent nature, considering that the "induced heterogeneity" may be produced as a result of mutual interactions between adsorbed molecules or between them and catalyst atoms. This possibility, which would be useful in explaining the gradual change in the adsorption heat, cannot be applied to the present findings, however, because since the desorption was carried out after the formation of a monolayer of carbon dioxide, it must occur at random if the surface is homogeneous.*

However, it must be admitted that there was gradual change in the adsorptive power of the strcng sites now observed, because the fraction of the strongly-adsorbed carbon dioxide, reaching ca. 38% over the temperature range from −78°C—100°C, decreased to ca. 10% at 300°C. The above tendency can be explained in run No. 7 as follows. The residual amount of 1.4 cc. at −78°C decreased only by 9% at 100°C, but by 65% at 300°C, the isotopic concentration of the gas desorbed being that of the first gas. Moreover, the desorption at 300°C for 15 hr. could not make the decrease in the amount of adsorbed gas less than 0.49 cc. Now that the presence of stronger adsorption sites seems very plausible, let us discuss its nature.

As has been suggested in Paper I, the difference in the adsorptive power of each crystal plane may be its cause, judging from the magnitude of the ratio of the strong to the weak sites. The word "heterogeneity" must, however, be understood by a conventional standard, because the "strong" adsorption in this research means that the thermodynamical activity of strongly-adsorbed carbon dioxide is less than that of a carbon dioxide trapped at −195°C. Therefore, the strong adsorption sites could be classified in more detail if the relation between the residual amount of $C^{18}O_2$ (last column in Table I) and the desorption temperature could be analyzed more precisely. Thus, the discrepancy in the magnitude of stronger sites between the value of Selwood[8] and that of the present authors may be explained. However, the problem can not be answered quantitatively by the present method of investigation, because there remains a possibility that the decrease in residual $C^{18}O_2$ can be realized to some degree by the slow isotopic exchange (A) without dissociation between the adsorbed carbon dioxide on strong and weak sites. This possibility, if it does occur, may be small, however, considering

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[14] A. N. Webb and R. P. Eischens, *J. Am. Chem. Soc.*, **77**, 4710 (1955).

* This argument owes much to the kind suggestion of Professor Tomiyuki Toya, Hokkaido University.

[15] Cf. G. Ehrlich, *Advan. Catalysis*, **14**, 255—427 (1963).

that the numerical value of the "strong" area determined by the present research coincides well that obtained by the adsorption measurement.⁹⁾

Besides, the difference in adsorptive power between several crystal planes may also be supported by the adsorption measurements obtained on hydrogen by electron microscopy⁴⁾ or by field emission microscopy.¹⁵⁾ The possibility of relating the adsorptive to the catalytic heterogeneity has already been mentioned by one of the present authors¹¹⁾; it will be discussed elsewhere* in connection with the self-hydrogenation of ethylene on nickel.

Summary

The so-called adsorptive heterogeneity of the nickel surface has been studied at $-78°C$ and $0°C$ by the isotopic desorption method, using labeled carbon dioxides ($CO_2{}^{18}$ and ${}^{13}CO_2$). The following results have been obtained:

(i) The fraction of the nickel surface which can adsorb carbon dioxide "strongly" at -78—$300°C$ has been found to be about 20—30% of the total area, a proportion which is unchanged even when the desorption time is varied after the introduction of the second gas; (ii) When ${}^{13}CO_2$ and $C^{18}O_2$ are used as the first and second gas respectively, ${}^{13}CO^{18}O$ can be produced, indicating a dissociation of carbon dioxide on the strong stites of the surface.

These findings seem to offer some new evidence of the surface-heterogeneity which may be brought about by different crystal planes of the nickel surface, judging from the percentage of the area of the strong sites.

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* K. Hirota and S. Teratani, *Z. physik. Chem. N.F.*, in press (1966). (Literature added in proof.)