

Studies on Solid Catalysts with a Basic Character

III. Nature of Acidic and Basic Centers on the Surface of Sodium-Silica Catalysts

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CO₂ adsorption has been measured on seven silica catalysts containing different amounts of sodium. The results are compared with those of a previous study of ammonia adsorption. As with NH₃, the adsorption of CO₂ increases with sodium content, but evidence is presented to show that the centers for adsorption of CO₂ and NH₃ are different. The adsorption of CO₂ is about one-tenth that of NH₃ under similar conditions.

I. INTRODUCTION

On the basis of our earlier studies (1, 2) the surface of sodium-silica catalysts was assumed to have both acidic and basic centers. The acidic centers were the subject of a previous investigation (3); we now proceed to a study of the basic centers.

The adsorption of carbon dioxide was chosen for this purpose; CO₂ has the character of a Lewis acid and should be adsorbed on basic centers. However, we realized that in the presence of strong acidic centers on the catalysts carbon dioxide could be adsorbed by the oxygen free electron pairs and the assumptions made would no longer be valid. Nevertheless, we came to the conclusion that, at least to a certain degree, such investigations would indicate the type of centers adsorbing the carbon dioxide molecules.

II. EXPERIMENTAL METHODS

Granulated silica was impregnated with identical volumes of sodium hydroxide solution of varying concentrations to obtain seven catalysts differing in the amount of sodium on the surface. The amounts of sodium, surface area, pore volume and mean pore radius are shown in Table I. Adsorption of carbon dioxide was studied in a conventional BET apparatus.

The seven catalysts were degassed under identical conditions. For adsorption studies at temperatures up to 300°C the catalysts were degassed for 3 hr at 6×10^{-5} Torr at 300°C. For still higher adsorption temperatures the specimens were degassed at the measurement temperature. Adsorption of carbon dioxide was investigated at pressures from 80 to 200 Torr and temperatures from -23 to 600°C. The measurements were made after 3 hr as equilibrium was reached. The adsorbed amounts were converted to the number of molecules adsorbed per square meter.

III. RESULTS AND DISCUSSION

CO₂ adsorption as a function of temperature is shown in Fig. 1. The curves exhibit minima, maxima and inflection points. The adsorption isobars exhibit two adsorption maxima: (1) at 0 to 100°C, (2) at 300°C. For this reason most of our experiments were carried out at 100 and 300°C. The adsorption curves obtained with sodium-impregnated catalysts follow similar courses, but that for the sodium-deficient gel is different.

The lack of any relation between the number of adsorbed carbon dioxide molecules and the catalyst degassing temperature proves the adsorption centers to be stable.

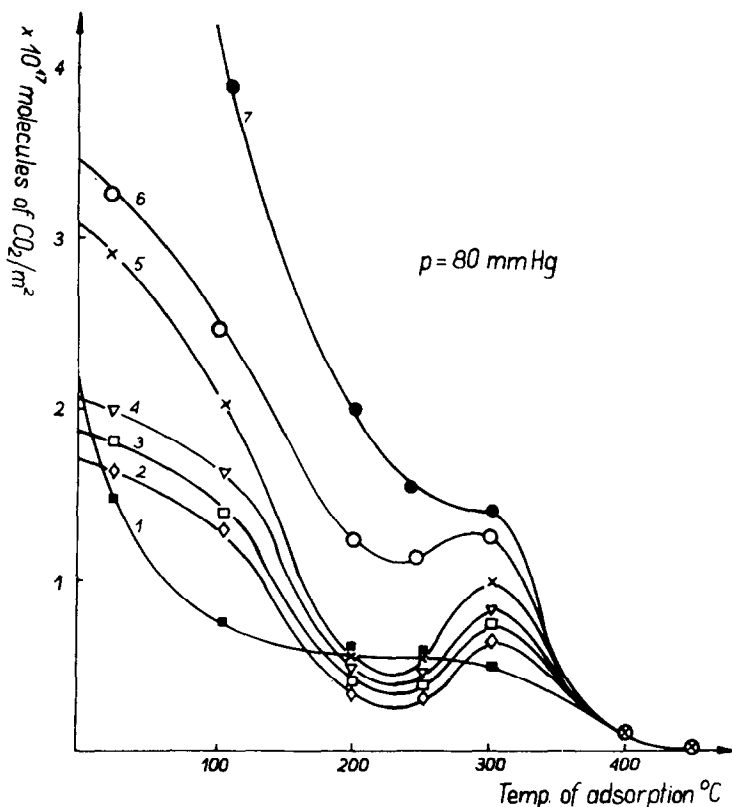


FIG. 1. The number of adsorbed CO_2 molecules/ m^2 as a function of temperature. For key to curve numbers, see Table 1.

The number of adsorbed carbon dioxide molecules is plotted in Fig. 2 against the amount of Na^+ mg-ions per square meter of the catalyst surface area. Aside from a break point occurring at very low sodium concentrations, the plot is linear, which

TABLE 1

Nr	Amount of sodium ($\times 10^{-3}$ mg-ions Na^+/m^2)	Surface area (m^2/g)	Vol of pores (cm^3/g)	Mean pore radius (μ)
1	0.00	225.0	1.58	13.8
2	0.79	215.0	1.63	15.2
3	1.49	167.0	1.55	18.7
4	2.54	141.5	1.52	21.7
5	4.57	120.5	1.45	38.0
6	9.26	87.5	1.35	35.0
7	22.7	55.0	1.18	42.6

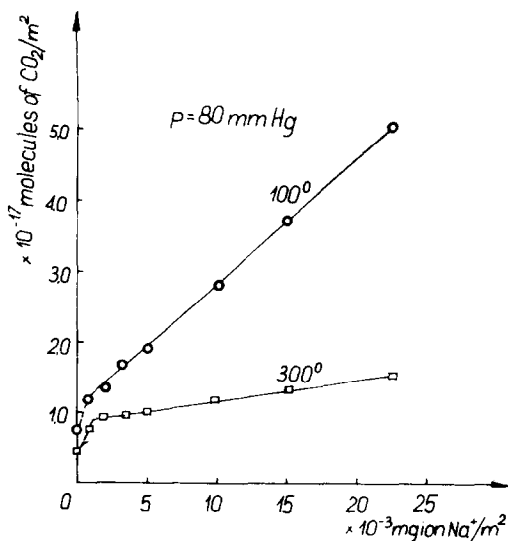


FIG. 2. The number of adsorbed CO_2 molecules/ m^2 as a function of mg-ions Na^+/m^2 .

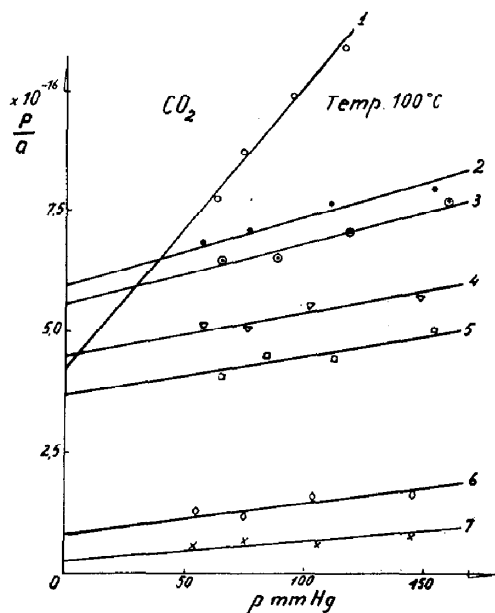


FIG. 3. Carbon dioxide adsorption isotherms at 100°C as Langmuir plots of p/a vs p .

suggests a proportional increase in carbon dioxide adsorption with rise in the sodium content on the catalyst surface.

The above results prove that adsorption of carbon dioxide is quantitatively and qualitatively affected by the presence of sodium ions on the silica gel surface. This notwithstanding, the adsorption of carbon dioxide is fairly consistent with the Langmuir and Temkin adsorption isotherm equations. Plots of (p/a) vs p at two temperatures are presented in Figs. 3 and 4. In all cases we have obtained straight lines. Nevertheless, the adsorption is supposed to be of mixed character and the consistency with the Langmuir isotherm should be explained either by prevalence of one type of adsorption or by formation of different bonds between the carbon dioxide molecules and the catalyst surface, which are energetically approximately equivalent.

The infrared studies of carbon dioxide adsorbed on beryllia and magnesia made

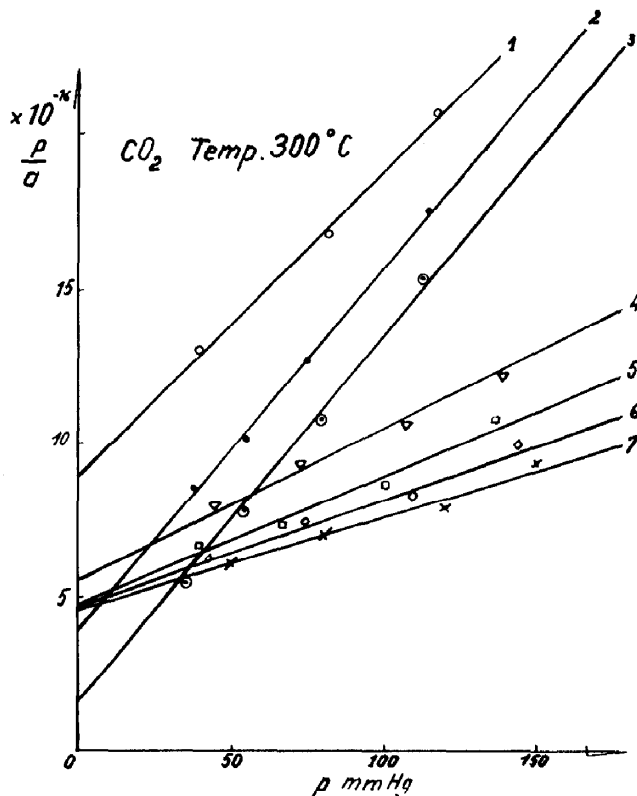


FIG. 4. Carbon dioxide adsorption isotherms at 300°C as Langmuir plots of p/a vs p .

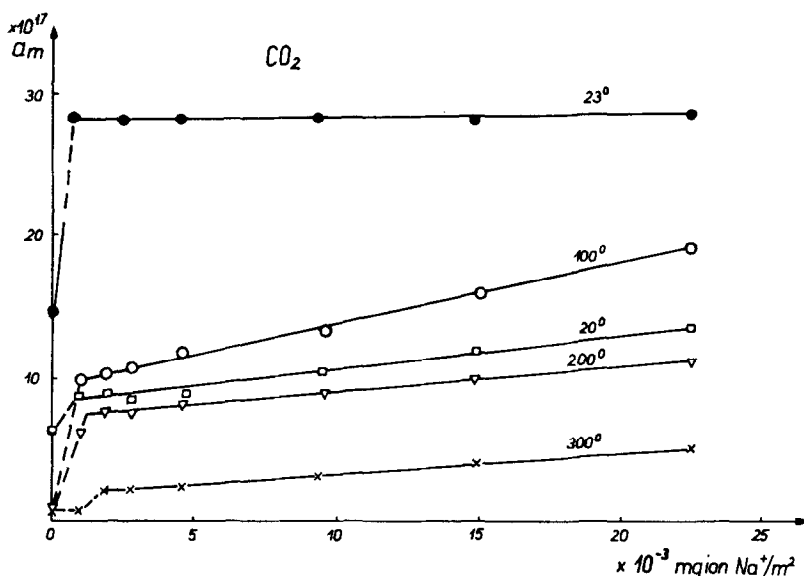
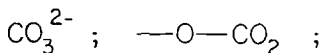


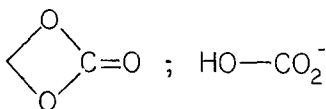
Fig. 5. The maximum number of CO_2 adsorption centers/ m^2 as a function of $\text{mg-ions Na}^+/\text{m}^2$.

by Stuart and Whateley (4) and Whateley and Evans (5) revealed the formation of the following groupings during adsorption:



I

II



III

IV

These and the present results have certain points in common which, in spite of some reservations, allow us to assume the existence of similar adsorbed carbon dioxide forms on the surface of sodium-silica catalysts. They observed a maximum for the second form at 100°C and for the third form at 300°C , which are the same temperatures where we found the maxima of the isobaric curves of CO_2 adsorption on the surface of the sodium-silica catalysts.

The straight-line plots of (p/a) vs p were used for calculation of the coefficient a_m ,

i.e., the maximum number of carbon dioxide adsorption centers, and coefficient λ , and subsequently, from the equation $\lambda = \lambda_0 \exp(Q/RT)$, of the heat (Q) of adsorption.

The a_m values are presented in Fig. 5 as a function of the amount of Na^+ ions per square meter of catalyst surface.

Similarly as with ammonia (3), the carbon dioxide adsorption curves also exhibit stepwise changes within the sodium content range 0.5 to 1.5×10^{-3} $\text{mg-ions Na}^+/\text{m}^2$. The a_m values are directly related to the sodium content in the catalyst surface.

In Fig. 6, the maximum number of carbon dioxide adsorption centers is plotted against adsorption temperature. The a_m values were determined for three catalysts differing in surface sodium content. At 100°C the sodium-silica catalysts exhibit maximum a_m values, which are close to the number of sodium ions deposited on the catalyst surface. Therefore, to a certain approximation, it could be assumed that at 100°C the maximum number of carbon dioxide adsorption centers is a measure of the surface basic centers combined with sodium ions. The sodium-deficient gel surface exhibits an initially rapid fall in a_m and subsequently a_m becomes independent of adsorption temperature.

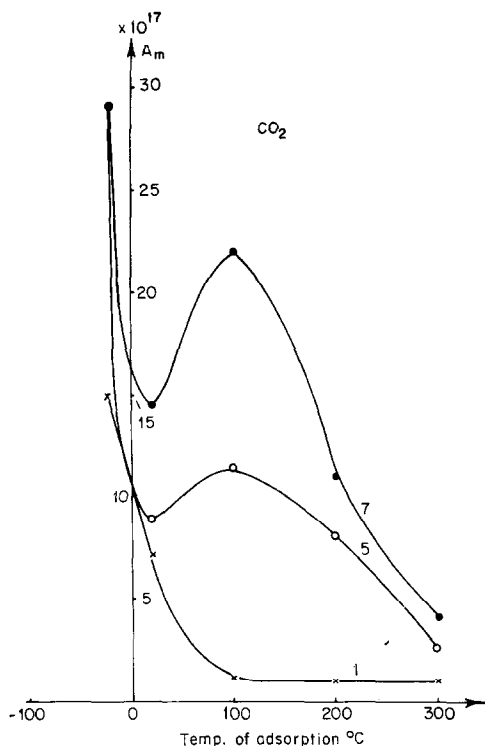


FIG. 6. The maximum number of CO_2 adsorption centers/ m^2 as a function of adsorption temperature.

The last quantity studied as a function of sodium content in the catalyst surface is the isosteric heat of carbon dioxide adsorption (Fig. 7). If the region of stepwise

changes is ignored, then the heat of adsorption at temperature from -23 to 300°C is constant, irrespective of the surface sodium content. Physical adsorption prevails in the former case, and uniform chemisorption predominates in the latter. At intermediate temperatures the isosteric heat of adsorption diminishes as the sodium content is increased.

IV. CONCLUSIONS

Summarizing, it appears from a comparison of the present results with those of the earlier study (3) with ammonia on sodium-silica catalysts that, despite the increase of adsorption of both CO_2 and NH_3 with rise in sodium content, the centers responsible for the adsorption of each compound are different. This suggestion is supported by the following experimental facts:

1. In strictly similar conditions the number of carbon dioxide molecules adsorbed is nearly one-tenth that of ammonia molecules adsorbed per unit catalyst surface area.
2. The number of carbon dioxide adsorption centers is independent of catalyst degassing temperature, whereas that ammonia adsorption centers decreases with rise in the temperature.
3. The diagrams representing adsorptions

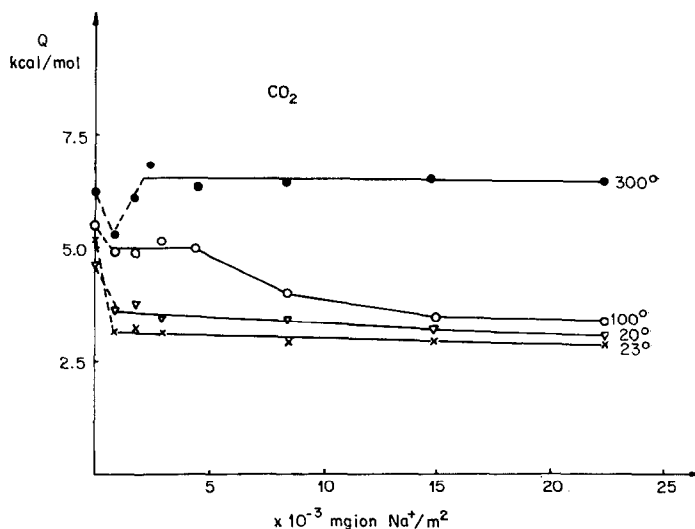


FIG. 7. The heat of carbon dioxide adsorption as a function of $\text{mg-ions Na}^+/\text{m}^2$.

of carbon dioxide and ammonia as functions of the same variables differ from each other in an essential manner. With ammonia, the extrema in the adsorption curves are seen to occur invariably at the same Na^+ content in the catalyst.

It was assumed that ammonia molecules are adsorbed on acidic centers. The present data confirm also the other assumption that carbon dioxide molecules are adsorbed on basic centers associated with sodium ions. However, particularly at elevated temperatures, participation of acidic centers in adsorption of carbon dioxide cannot be ruled out as a possibility.

When considered from a more general point of view, the present data demonstrate that poisoning of acidic catalysts with alkali-metal ions represents a very complicated process. While poisoning acidic centers of one type, the alkali-metal ions give rise to the formation of other types of

acidic centers. The new centers are very likely to exhibit a catalytic activity different from that of the centers in the unalkalized catalysts. Such an alteration is indicated by the changes of the quantities associated with the thermodynamics and kinetics of ammonia adsorption on sodium-silica catalysts compared with the values of these quantities determined for the pure silica gel.

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