CO, O₂, and CO₂ Adsorption on Scandium Oxide

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The adsorption of O_2, CO, and CO_2 on Sc_2O_3 was studied in the temperature range -195 to 550°C. Isobars and isosteric heats were calculated, and ir spectra were measured for the identification of surface species. Oxygen is physically adsorbed at low temperatures. A slow chemisorption of oxygen begins about 100°C, while above 350–400°C there appears to be incorporation of oxygen into the lattice. Carbon monoxide is physically and reversibly adsorbed at temperatures up to 25°C; however, chemisorption sets in above 100°C and the ir spectrum shows the presence of surface carbonate at 210°C. The adsorption of carbon dioxide is fast, giving high surface coverage; the spectra show the presence of both symmetric and bidentate surface carbonate. The slow oxygen chemisorption obeys a pseudo-Langmuirian isotherm. The large CO_2 chemisorption and the CO physical adsorption are better fit by a Freundlich model.

INTRODUCTION

Adsorption of CO, O_2, and CO_2 on Sc_2O_3 has been studied over a wide interval of temperatures. IR spectra were made for the identification of adsorbed species. Previous work on this subject (*1–3*) has been carried out in this laboratory.

EXPERIMENTAL

Materials

Sc_2O_3 with a purity of 99.9 wt%, obtained from Fluka AG, was used. The impurities are stated to be 0.02% Y_2O_3, 0.01% Yb_2O_3, and traces of Bi_2O_3, PbO, and SiO_2. The mean grain size, as determined by electron microscopy, is less than 2 μm with an apparent density of 0.518 g·cm⁻³. SEM photographs, at a magnification of 9000, show a high surface heterogeneity. The type C crystalline structure has been

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verified by X-ray diffraction. BET specific surface was 16.8 m²·g⁻¹. Differential thermal analysis, up to 1050°C, did not show any thermal peak.

The starting powder was pressed into tablets and thermally stabilized by heating in a tubular furnace for 4 hr at 700°C in flowing air. The BET specific surface of the powder so treated was 16.0 m²·g⁻¹ with a pore volume, $V_p = 0.06$ cm³·g⁻¹, as determined by nitrogen adsorption. The calculated average pore radius is $r \simeq 75$ Å.

IR spectra in the 3000–4000 cm⁻¹ region, for the outgassed material at room temperature, show a wide band between 3000 and 3500 cm⁻¹ due to adsorbed water. The relative intensity of this band decreases sharply when the sample is outgassed at 250°C. On outgassing at 500°C, a band at 3665 cm⁻¹ develops, whose position does not change by further outgassing at 600 and 710°C, although at the latter temperature a narrow shoulder on the high frequency side was observed. Heating in
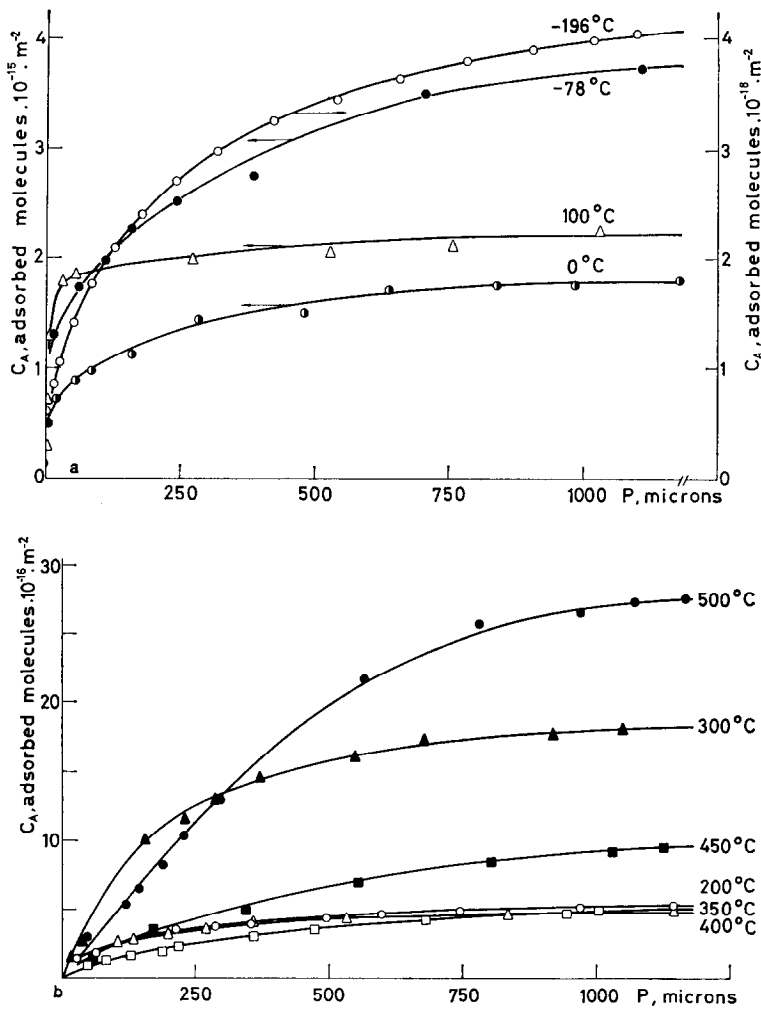
FIG. 1. (a) and (b). Adsorption isotherms of oxygen.

flowing helium up to 500°C gave a loss in weight of 0.17%; when the sample was previously hydroxylated, the loss in weight under the same condition was 0.24%.

CO, 99.97% pure from Societe de L'Air

TABLE 1

Experimental Coverages

(P_{O_2}, P_{CO} = 1 Torr; P_{CO_2} = 100 Torr)

	Temperature (°C)					
	−196	−78	0	200	300	500
O_2	0.56	0.0005	0.0002	0.0074	0.026	0.039
CO	1.00	0.061	0.011	0.047	0.0028	0.0005
CO_2	—	—	0.53	0.22	0.18	—

(S_{O_2} = 14 Å², S_{CO} = 16 Å², S_{CO_2} = 17 Å²)

Liquide, O_2, 99.9%, and CO_2, 99.95%, from Sociedad Española del Oxigeno (SEO), were let into the storage bulbs after passing through a purification train and then condensation in a trap cooled to liquid nitrogen temperature, only the middle fraction being taken. Helium, 99.995% pure, also from SEO, was used in volume calibration.

Apparatus

Adsorption isotherms of O_2 and CO were carried out in a volumetric apparatus by means of a set of thermistors, Veco A-58, as pressure transducer, with a higher measuring limit in the range of 1.5 Torr; details
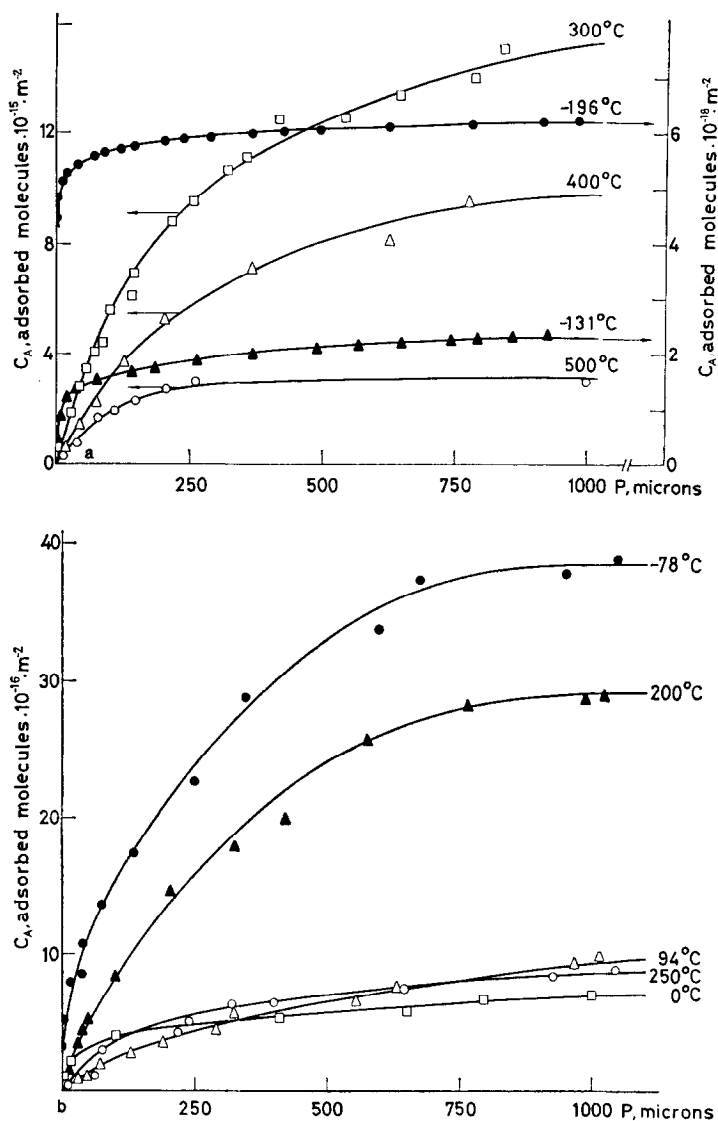
Fig. 2. (a) and (b). Adsorption isotherms of carbon monoxide.

on the method of operation have been de-
scribed elsewhere (4). Corrections for
thermal transpiration effect were made
following the absolute method as described
by Tompkins and Wheeler (5). The de-
termination of adsorption isotherms of
CO_2 were made by the gravimetric method
with a Cahn RG Electrobalance.

IR spectra were obtained with a Perkin
Elmer 125 spectrometer. Cells made of
Pyrex glass or quartz with sodium chloride
and potassium bromide windows and

greaseless stopcocks were used. An electric
furnace was used for the necessary thermal
treatments. All measurements of ir spectra
were made at room temperature after the
indicated pretreatments.

RESULTS AND DISCUSSION

Isotherms

In Figs. 1 and 2, adsorption isotherms are
shown for oxygen and carbon monoxide on
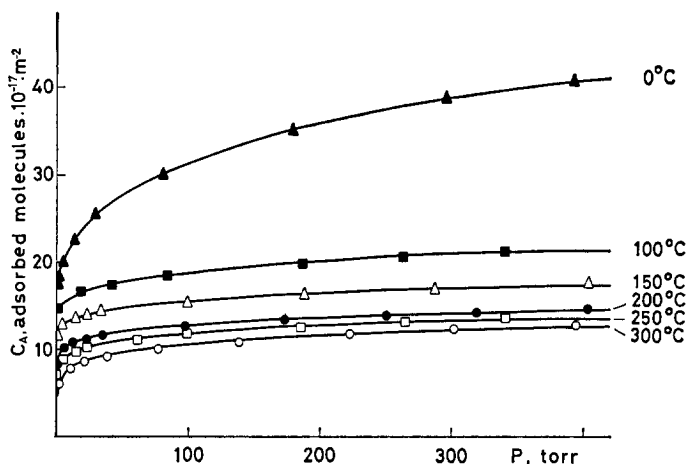scandium oxide, in the temperature interval

FIG. 3. Adsorption isotherms of carbon dioxide.

−196 to 500°C. Before an experiment was started, the sample was treated at 550°C for 24 hr at about 10 Torr pressure of oxygen or carbon monoxide, respectively, and then pumped at 10^{-6} Torr at the same temperature for 24 hr. The adsorptions of both oxygen and carbon monoxide are very slow, that of oxygen particularly so.

FIG. 4. Adsorption isobars of carbon monoxide at 1 Torr; Δ, oxygen at 1 Torr.

Equilibration times were sometimes about 24 hr for temperatures above 100°C. For this reason, in some runs only the ascending branch of the isotherm was determined. In Table 1, experimental coverages at 1 Torr pressure are given for several temperatures; these are expressed as the fraction of BET area occupied by the adsorbed gas. For these calculations, values of $S_{CO} = 16$ Å²/molecule and $S_{O_2} = 14$ Å²/molecule were assumed.

Figure 3 shows the adsorption isotherms of carbon dioxide on scandium oxide, as determined by the gravimetric method. Before starting an experiment, the sample was first treated at 500°C for 24 hr with 100 Torr of carbon dioxide and then pumped at 10^{-6} Torr at 500°C for 24 hr. These results differ very little from those obtained by the volumetric method in previous work (*3*). In Table 1, coverages are given for a pressure $P_{CO_2} = 100$ Torr, computed on the basis that $S_{CO_2} = 17$ Å²/molecule.

Isobars

In Fig. 4, adsorption isobars for oxygen and carbon monoxide at 1 Torr pressure are represented. These curves, presenting sharp maxima at 300 and 200°C, respectively, suggest the existence of two different
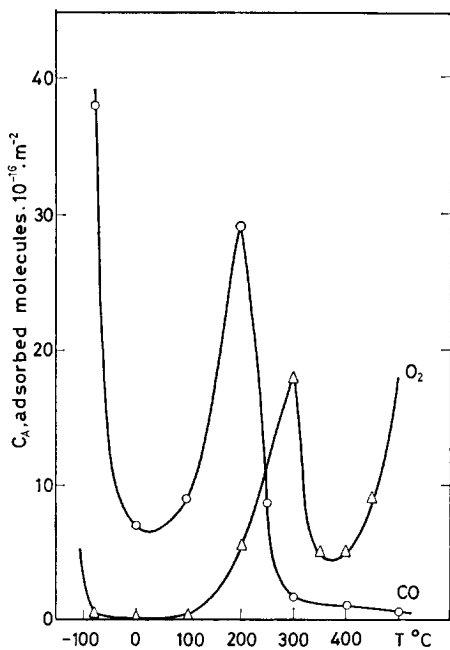
processes of adsorption, corresponding to the two descending branches for each gas. The second ascending branch shown by oxygen above 350°C is presumably related to an incorporation of oxygen into the scandium oxide lattice. The adsorption at these temperatures is extremely slow. Oxygen incorporation could result from (a) a slight stoichiometric excess of cationic component introduced by the thermal pretreatment or the treatments in vacuum at high temperatures (6), allowing oxygen incorporation as O^{2-}, or (b) the diffusion of oxygen anions or molecules into the very open defective structure characteristic of oxide with type C cubic structure.

In Fig. 5, isobars are shown for carbon dioxide at the two pressures $P_{CO_2} = 100$ Torr and $P_{CO_2} = 1$ Torr. The curves exhibit a sort of shoulder, whose existence was also confirmed by direct determination of the isobar, via the gravimetric method, at a pressure $P_{CO_2} = 4.5$ Torr.

FIG. 5. Adsorption isobars of carbon dioxide at 1 Torr; Δ, carbon dioxide at 100 Torr.

IR Spectra

The spectrum of scandium oxide in the low frequency region (700–240 cm^{-1}) has been studied by McDevitt and Baun (8). In this work, bands of difficult in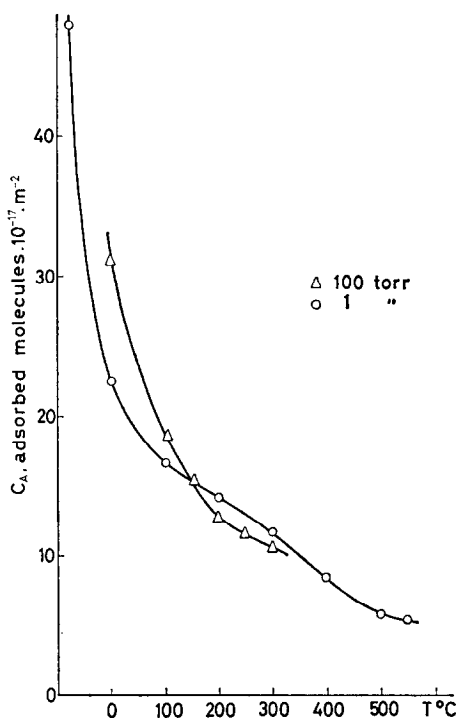terpretation were found at frequencies of 935, 960, 1030, 1115, and 1320 cm^{-1}, for samples previously outgassed. In the present work, adsorption of oxygen at 300°C yields a weak band at 1385 cm^{-1} and a shoulder at 1105 cm^{-1}, both of them remaining
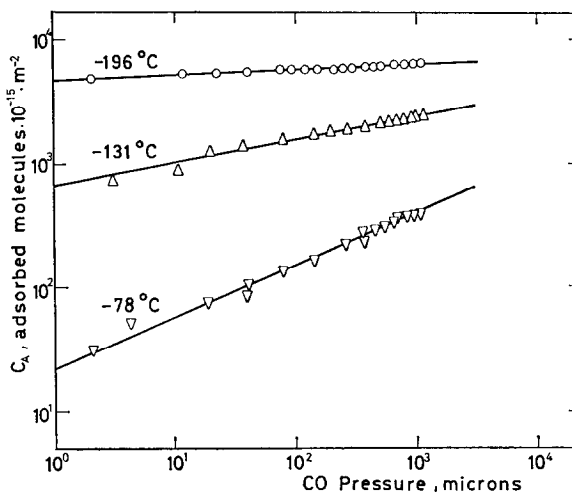

FIG. 6. Adsorption isotherms of carbon monoxide according to Freundlich model.
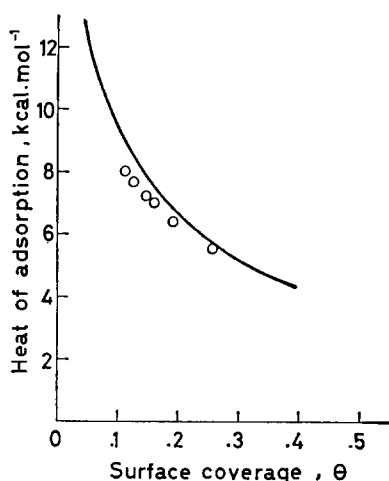
FIG. 7. Variation of isosteric heats of adsorption with coverage for carbon monoxide.

after prolonged pumping (12 hr) at room temperature, but disappearing after pumping at 500°C. Oxygen adsorption does not cause any shift in the hydroxyl band.

Although a progressive hydroxylation of scandium oxide results in a decrease in the amount of carbon dioxide subsequently adsorbed, IR spectra do not indicate any interaction between CO_2 and hydroxyl groups.

Carbon dioxide adsorption at 300°C yields three bands, at 1220, 1440, and 1635 cm^{-1}. The spectra of scandium oxide with and without adsorbed carbon dioxide are shown in Fig. 10. According to Hair (8),

the 1440 cm^{-1} band is characteristic of a symmetric surface carbonate; weaker bands at 1635 and 1220 cm^{-1} are attributed to the formation of a carbonate by linkage to two adjacent actions on the surface. A monodentate carbonate may be ruled out because the splitting in the 1440 cm^{-1} band of the symmetrical carbonate would be much less (ca. 100 cm^{-1}) than the observed splitting to 1635 and 1220 cm^{-1}. Both carbonate species disappear after outgassing at room temperature for 1 hr. In the low frequency region of the spectrum of scandium oxide, CO_2 adsorption causes a band shift from 1320 to 1130 cm^{-1} and a similar shift in the 1115 cm^{-1} band toward lower frequencies.

IR spectra of adsorbed CO at room temperature show bands at 2100 and 2160 cm^{-1}. Both disappear after evacuation, indicating the presence of weakly adsorbed CO. Adsorption at 210°C, by contrast, does not yield bands due to CO itself; instead, weak bands appear at 1640, 1455, 1430, and 1220 cm^{-1}, characteristic of the formation of surface carbonates, as indicated above. The hydroxyl band does not undergo any shift. The Sc_2O_3 spectrum shows a clear shift of the 1320 and 1115 cm^{-1} bands in the opposite direction to those observed for CO_2 adsorption.
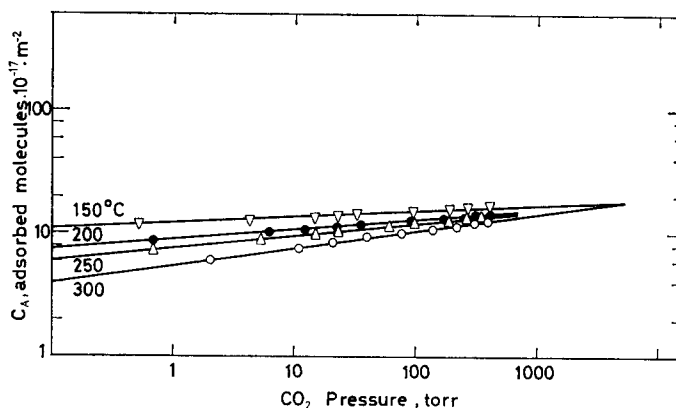

FIG. 8. Adsorption isotherms of carbon dioxide according to Freundlich model.

Heats of Adsorption; Analysis of Adsorption Models

By application of Clapeyron–Clausius equation to the first descending branch (low temperatures) of the oxygen isobar, a value of $Q_{O_2} = 3.3$ kcal·mol^{-1} for the heat of adsorption of oxygen was calculated. This value, scarcely changing with coverage, confirms the physical adsorption characteristics of the process.

Between 300 and 350°C, the isosteric heat of adsorption of oxygen is calculated to be 34.2 kcal·mol^{-1}. In this case the coverages are too small to permit study of the variation of heat of adsorption with coverage. The isotherms at each temperature satisfy a Langmuir-type equation. However since the calculated monolayer amount, v_m, decreases with increasing temperature, this "pseudo-Langmuirian" behavior is not considered significant.

The adsorption heat of CO at low temperatures has a value $Q_{CO} = 8.0$ kcal·mol^{-1}, and the value decreases exponentially with coverage. The experimental results of isotherms at −196, −131, and −78°C fit very well a Freundlich isotherm, as shown in Fig. 6. The mean heat of adsorption Q_{CO}, is 4.6 kcal·mol^{-1} for a coverage of $\theta = 0.37$.
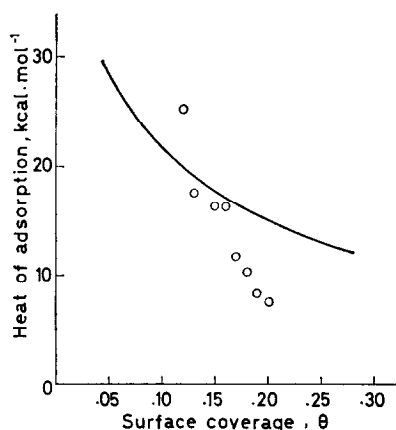

FIG. 9. Variation of isosteric heats of adsorption with coverage for carbon dioxide.

In Fig. 7 the experimental data of the isosteric heats, as compared to the theoretical curve $Q - \theta$, obtained from the mean value of Q_{CO} are given (9). The constant r has a value $r = 3.5 \times 10^{-3}$ K^{-1}. The log θ–log p family of straight lines in Fig. 6 meets at a common point corresponding to the value of 9×10^{18} molecules m^{-2} for the monolayer.

As deduced from the ir spectra, CO adsorption at high temperatures results in the formation of surface carbonate with the consequent appearance of CO_2 in the gaseous phase. For this reason, an analytical
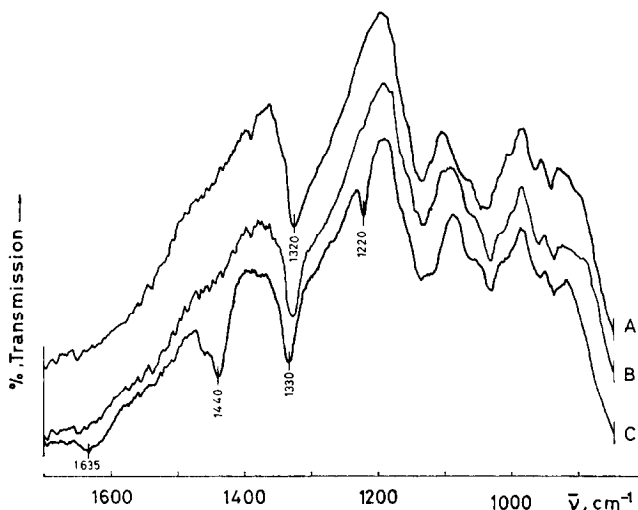

FIG. 10. IR spectra: (A) base spectrum of Sc_2O_3; (B) after outgassing; (C) after CO_2 adsorption above 200°C.

study of the isotherms for these temperatures has not been made.

Carbon dioxide adsorbs at low temperatures with an adsorption heat $Q_{CO_2} = 5.7$ kcal·mol^{-1}, also characteristic of physical adsorption. At temperatures above 200°C, the adsorption heat is higher, $Q_{CO_2} = 25.3$ kcal·mol^{-1}, for $\theta = 0.12$, and it decreases with increasing coverage. The isotherms at these higher temperatures fit a Freundlich model, as Fig. 8 shows, with a value of $C_M = 2 \times 10^{18}$ molecules m^{-2} for the monolayer. The values of isosteric heats obtained for different coverages (Fig. 9) deviate from the theoretical curve calculated from a mean heat $Q_{CO_2} = 9.5$ kcal·mol^{-1} (9).

The formation of carbon dioxide after the high temperature adsorption of carbon monoxide (1) and the very slow adsorption and incorporation of oxygen, together with the ease of the adsorption–desorption of carbon dioxide, point toward the following schematic mechanism for the catalytic oxidation of carbon monoxide on scandium oxide:

$$CO + 2O_s \rightarrow (CO_3)_s \rightarrow CO_2 + cat_{red}$$
$$O_2 + cat_{red} \rightarrow cat_{ox},$$
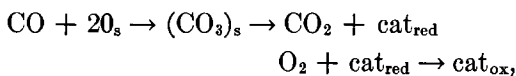
in which the second step is rate-limiting. Further studies on this subject are being conducted.

Note. Subsequent to completion of this paper, the recent publication of Rosynek (10) on the adsorption of CO_2 on Al_2O_3 came to our attention. Rosynek's results for CO_2 adsorption isotherms, isosteric heats, and ir spectra resemble rather closely those reported here for Sc_2O_3. One significant difference is his report that an ir band at 1480 cm^{-1}, attributed to a unidentate carbonato complex on the Al_2O_3, is only slightly reduced by heating under vacuum to 150°C.

REFERENCES

1. González de Prado, J. E. González Tejuca, L., Pajares, J. A., and Soria, J. A., *Acta Cient. Venez.* **24**, (Supp. 2), 189 (1973).
2. González de Prado, J. E., González Tejuca, L., Pajares, J. A., and Soria, J. A., *Ann. Quim.* **69**, 1083 (1973).
3. González de Prado, J. E., González Tejuca, L., Pajares, J. A., and Soria, J. A., *Ann. Quim.* **69**, 1239 (1973).
4. González Tejuca, L., Doctoral Thesis, Universidad Complutense, Madrid, 1970.
5. Tompkins, F. C., and Wheeler, D. E., *Trans. Faraday Soc.* **29**, 1248 (1933).
6. Berard, M. F., Wirkus, C. D., and Wilder, D. R., *J. Amer. Ceram. Soc.* **51**, 643 (1968).
7. McDevitt, N. T., and Baun, W. L., *Spectrochim. Acta* **20**, 799 (1964).
8. Hair, M. L., "Infrared Spectroscopy in Surface Chemistry." M. Dekker, New York, 1967.
9. Halsey, G., and Taylor, H. S., *J. Chem. Phys.* **15**, 634 (1947).
10. Rosynek, M. P., *J. Phys. Chem.* **79**, 1280 (1975).