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The Heats of Chemisorption of Carbon Dioxide on Zinc Oxide

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The heats of chemisorption of carbon dioxide on oxygen-deficient zinc oxide were determined by a gas chromatographic technique, and calculated from the change with temperature in the retention time. These heats were found to vary linarly with the concentration of "free zinc." It is suggested that the free electron concentration of the zinc influences the heat of adsorption.

The chemisorption of carbon dioxide on zinc oxide was studied by various methods (*1–4*). These chemisorptions are of importance in industrial processes where information on chemisorbed gases under flow conditions are needed. Conventional techniques used for heat adsorption measurements, such as the calorimetric method, although eliminating many uncontrollable interfering parameters, are not quick and relevant to industrial processes. Catalysts are used mostly in conditions where high vacuum is not applied. On the other hand, flow methods are used in practice.

Heats of chemisorption of carbon dioxide were determined in this study, using the Transient Response Technique (TRT) (*5*), i.e., under flow conditions, at temperatures of 300–365°C. Heats of chemisorption were calculated by plotting the logarithm of the corrected retention time (t_m) versus the reciprocal of the absolute temperature (*5*).

METHODS

Materials. Five different samples of zinc oxide, prepared by boiling zinc metal and oxidizing the vapor (French Process), were obtained from the New Jersey Co., Palmerton, Pennsylvania. Their specific surface areas were 2.85, 3.64, 6.2, 7.3, and 8.8 m^2/g. Silica gel was of analytical grade as supplied by Wilkens Instruments Co. Gases used in this study were Air Reduction Co. helium (99.9%), Matheson Co. prepurified nitrogen, and Chemical and Phosphates (Haifa, Israel) carbon dioxide (99.9%).

Apparatus. The gas chromatograph used was Aerograph A-90-P with a hot wire detector. The instrument was connected to a Honeywell recorder with a 1-mV full span and a balancing speed of 1.2-sec full scale. The columns were made of copper tubing of 4-mm ID and 50-cm length, wound into compact spirals. Zinc oxide was filled into the columns, even packing being ensured by tapping with a piece of rubber tubing. Quartz wool was inserted at both ends of the filled column. The temperatures of the column and of the hot wire detector were kept constant at ±2°C. A six-port sampling valve having a 0.25-ml calibrated sample loop (XA-204 supplied by Wilkens Instrument Co.) was used for the injection of gas pulses into the helium stream passing over the zinc oxide filled in the column. The flow rate was measured by a soap bubble flow meter and was kept constant within ±1%. A Cary 14 recording spectrophotometer and an Optica CF 4 spectrophotometer were used for the determination of chromium.

Measurements. The flow rate was maintained at 10 ml/min. The "dead time" of the zinc-oxide-packed column was determined under the same conditions of adsorption, by injecting a nitrogen 0.25-ml pulse into the stream of helium.

The gas sample loop of the six-port

sampling valve was filled with carbon dioxide taken from a gas burette, where it was kept at constant temperature and pressure. The carbon dioxide was dried by passing it over anhydrous magnesium perchlorate. The retention times of the carbon dioxide were corrected (*6*) and the logarithms of t_m were plotted versus $1/T$ (Fig. 1).

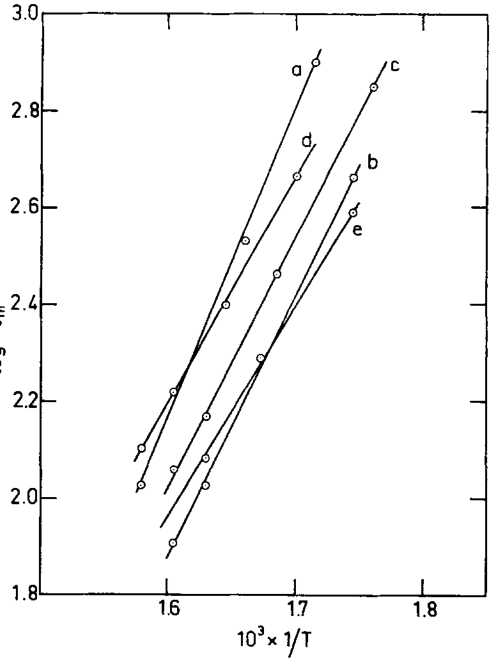

FIG. 1. Plot of log t_m vs. $1/T$ for 0.25-ml samples of carbon dioxide. The zinc oxide specific areas: (a) 8.8; (b) 7.8; (c) 6.2; (d) 3.64; (e) 2.85 g/m^2.

The reversibility of adsorption–desorption was checked by comparing the peak areas obtained by desorption of carbon dioxide from the zinc oxide column to the areas obtained by the desorption of the same volume of carbon dioxide under the same condition, emerging from a silica gel filled column (ID 4 mm, 20 ft long). The areas obtained were in good agreement.

The columns were flushed with helium for about 10 hr before each experiment at 370°C.

Analytical. The excess of zinc on the surface of the five different samples was determined by a modified (*7*) procedure based on that described by Norman (*8*). The acids mixture was kept at 0°C. Five grams of each zinc oxide sample was added to the cooled mixture and stirred for 2 minutes. The solution was decanted from the solid and the amount of excess zinc was determined spectrophotometrically (*8*) by a Cary 14 recording spectrophotometer and Optica CF 4 spectrophotometer. The amount of excess zinc was calculated as the fraction of total zinc in the sample.

RESULTS AND DISCUSSION

The adsorption of carbon dioxide on zinc oxide was rapid at room temperature, as has been observed previously (*3*).

The desorption at this temperature region was activated. By continuous heating the desorption of the gas adsorbed at room temperature commenced at 260°C. Runs carried out by isothermal injection of 0.25 ml of carbon dioxide at this temperature were discontinued because the adsorptions were irreversible.

At 280–290°C the recovery was quantitative but too slow to be suitable for the gas-solid chromatography method. From 300°C the recovery of carbon dioxide was fairly fast and quantitative. The heats of chemisorption were calculated from the curves in Fig. 1, and are presented in Table 1.

TABLE 1
WEIGHTS, SPECIFIC AREAS, EXCESS OF "FREE ZINC," AND HEATS OF ADSORPTION FOR ZINC OXIDE

Column	Weight (gm)	Specific area (m^2/gm)	Excess Zn (ppm)	ΔH (kcal/mole)
a	4.0	8.8	13	29.6
b	5.0	7.3	9	24.8
c	5.6	6.2	8.3	23.3
d	7.2	3.64	6.5	21.4
e	7.6	2.85	6.1	20.7

There is no linear relationship between the specific areas of the zinc oxide samples, and the respective heats of absorption of carbon dioxide (Fig. 2). This relationship has been observed previously (*1, 2, 9*) with various coverages on the same sample of zinc oxide. On the other hand, the relation-

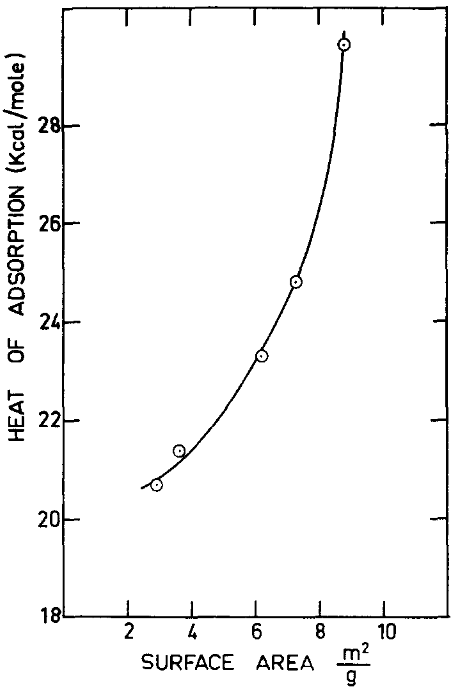

FIG. 2. Heats of adsorption of carbon dioxide vs. surface area of zinc oxide samples.

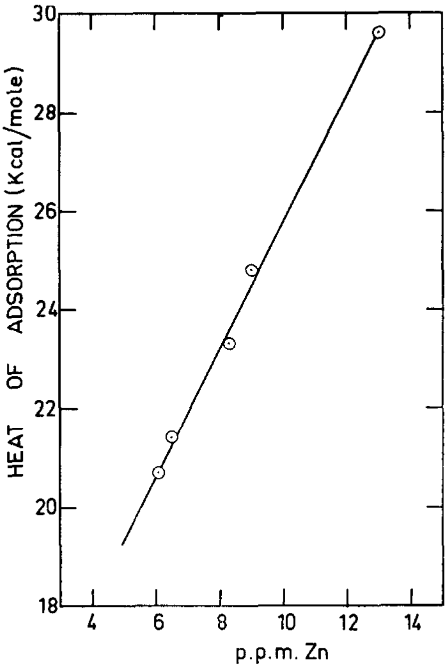

FIG. 3. Heats of adsorption of carbon dioxide vs. excess of "free zinc" on the zinc oxide surfaces.

ship between the excess of "free zinc" ("fz") on the surface and the heat of adsorption (Fig. 3) might suggest the exclusive participation of "fz" sites on the chemisorption of carbon dioxide on zinc oxide.

The relationship between the heat of adsorption and the concentration of "free electrons" is clearly shown by the adsorption of carbon dioxide on gallium-doped zinc oxide. The heat of adsorption obtained by TRT was about 36 kcal/mole (*7*). It is difficult to assume that at this range of temperatures there is an exclusive formation of surface carbonate (3) or a CO_2^- species (*4*b). However, electron trapping by CO_2 molecules at higher temperatures is more pronounced and the free electron concentration of the zinc oxide may therefore be expected to influence the heat adsorption. Comparison of the results obtained by the TRT with results obtained recently (*2*) by conventional methods showed good agreement. Hart and Sebba (*2*) obtained heats of chemisorption of 20 kcal/mole for their lowest coverage. The higher results observed in this work might be the result of the change of heat of adsorption with coverage.

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