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The Thermodynamics and Kinetics of CO\textsubscript{2} Chemisorption on CaO

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Abstract

Equilibrium chemisorption of CO\textsubscript{2} on CaO was measured at 923 K to 1013 K, and the kinetics of adsorption were measured in 1333 Pa pressure of CO\textsubscript{2} at 983 to 1033 K. Surface areas were measured by the BET method. From the assumptions that only (100) surfaces of the CaO were exposed, and that CO\textsubscript{2} reacted with surface O\textsuperscript{=} ions to form CO\textsubscript{3}\textsuperscript{=} ions, coverage was calculated to approach a complete monolayer. The equilibrium data fit Langmuir isotherms, except at >80% monolayer coverage. The enthalpy of adsorption was \(-199 \pm 8\) kJ per mole for <80% coverage and somewhat less at >80% coverage. The apparent activation enthalpy for adsorption was \(40 \pm 10\) kJ per mole. CO\textsubscript{2} was dissolved in the CaO grain boundaries or crystals by a process with an apparent activation enthalpy of \(303 \pm 15\) kJ/mole CaO.
Studies of the thermodynamics and kinetics of chemisorption of gases on metal surfaces have long been, and remain, an active area of investigation [1]. In contrast, very few quantitative studies have been made of chemisorption on oxide surfaces. We became interested in the chemisorption of CO$_2$ on CaO because of observations that CO$_2$ catalyzes the rapid reduction in CaO surface areas at temperatures as low as 900 K and pressures as low as 660 Pa [2,3].

Busca and Lorenzelli [4] have recently reviewed infrared studies of carbon oxides on metal oxide surfaces. These studies are in general agreement that at the temperatures of our interest—800 K and above—the CO$_2$ is chemisorbed as carbonate ions, coordinated in any of a number of possible ways with the metal ions of the surface. Fukuda and Tanabe [5] concluded that carbonate ions may be present on CaO surfaces in two different coordinations.

On Sc$_2$O$_3$, CO$_2$ is reported [6] to be only weakly chemisorbed (the measured heat of adsorption is -7.2 kilocalories per mole). The kinetics of desorption of CO$_2$ from silica surfaces have been studied [7], but the reported activation energies are a function of the heating programs used in the study. In the present study, the thermodynamics and kinetics of adsorption of CO$_2$ on CaO have been measured as functions of temperature, pressure, and surface coverage. The results are shown to be consistent with expectations from observations of chemisorption on metals [1].

EXPERIMENTAL

Samples preparation. Single crystals of high purity calcite [8] were cut along the natural cleavage planes into slices with average
dimensions of 3.8 mm x 4.5 mm x 0.8 mm. Four such pieces were placed in a Pt crucible. It was hung from a symmetrical microbalance into a quartz resistance furnace [9]. A chromel-alumel thermocouple tip was placed 5 mm from the bottom of the crucible. Calibration with another thermocouple introduced from the top of the furnace showed the temperature to remain constant within ±1°C over a length of 5 cm. Double-wound resistance wires were designed to minimize the temperature gradient along the furnace cross section. Pressure was controlled by a single-sided absolute sensor head plus a control system placed at the top of the thermobalance. Vacuum decompositions of the calcite crystals to CaO were carried out at 959 K, while the recorded pressure at the ion gauge was 5 x 10⁻³ Pa. Two sets of calcite crystals were used for these experiments. The total initial weights were 160.8 mg and 156.5 mg. The specific surface area of the porous CaO obtained was in both cases 118 ± 2 m²/g-CaO.

These high surface area samples of CaO are stable in vacuum, but sinter when exposed to CO₂ at 900 K or higher [2,3]. The rate decreases as the surface area is reduced and becomes slow enough when the area is reduced below 20 m²/g-CaO to permit adsorption isotherm measurements. Accordingly, one sample was sintered at 959 K in CO₂ at 1333 Pa pressure for 100 h. After the CO₂ was desorbed at the same temperature in vacuum, N₂ adsorption measurements at 78 K showed the sample specific surface area to be 19 m²/g-CaO and its volume of mesopores to be 0.034 cm³/g-CaO. The surface area of this sample decreased over the total time of the adsorption measurements to 15 m²/g. For the other sample the CO₂ treatment was carried out at 959 K and 1333 Pa for 50 h, and then at 973 K and 2000 Pa for an additional 50 h. This yielded CaO
samples of 12.5 m$^2$/g specific surface area and 0.028 cm$^3$/g mesopore volumes. This area did not change significantly during adsorption studies.

Adsorption measurements. Tests showed that at 973 K the measured CO$_2$ pressure at which calcite formation started was 5% below the reported equilibrium value [13]. Isothermal adsorption of CO$_2$ was studied at 923 K to 1013 K and in the pressure range from 65 Pa to 70-80% of the reported equilibrium pressure. For each temperature, weight variations were recorded continuously using the microbalance with a sensitivity of 2x10$^{-5}$ g/cm. In an external vessel a fixed amount of CO$_2$ was stored at a preselected pressure and at room temperature. As soon as the reaction chamber reached the desired temperature, a valve between the vessel and reaction chamber was opened. Constant pressure was established without observable delay. Runs with CO$_2$, but without samples, were made to calibrate the system. The sample volume was too small to affect the pressure significantly. The pressure control system was used to maintain constant CO$_2$ pressure during adsorption. Blank runs with N$_2$ gave buoyancy corrections of 10$^{-4}$ g when the pressure was 65 Pa, and less than 2x10$^{-5}$ g when the pressure was greater than 150 Pa. In an adsorption run, enough CO$_2$ was introduced as soon as the isothermal conditions were reached to give a pressure equal to 70-80% of the equilibrium pressure for the carbonate formation reaction. Pressure and temperature were held constant until the thermogravimetric trace was constant to within its sensitivity. Weight changes were than less than 1.5x10$^{-9}$ g/min. The weight gain was reproducible to within 3% even if the CO$_2$ was introduced step by step. The pressure was then decreased
step by step, and the points where the TG trace showed the weight changes to be no more than $10^{-9}$ g/min were taken as equilibrium points.

Adsorption isotherms were then determined by increasing the CO$_2$ pressure step by step. No hysteresis was observed, but the times required to reach constant weights of CO$_2$ absorbed were much longer during adsorption than during desorption. After each isotherm, the residual CO$_2$ was pumped off in high vacuum and the temperature was reset for another isothermal run. This process required at least 4 hours heating at the run temperature.

Adsorption kinetics measurements were made on the samples of 12.5 m$^2$/g surface area in the temperature range 983-1033 K, and at the constant CO$_2$ pressure of 1333 Pa. The adsorption rates depended strongly upon the starting surface state. Reproducible runs were obtained by introducing initially an arbitrary small quantity of CO$_2$, $7 \times 10^{-5}$ g, a quantity equivalent to 0.09% of the amount of CO$_2$ required to transform all the CaO to CaCO$_3$. At each temperature, the weight was recorded from the initial time when CO$_2$ was introduced to the time when the weight change was less than $10^{-9}$ g/min. Time was allowed to reach the equilibrium point at each temperature, and at that moment the CO$_2$ pressure was raised to 1333 Pa. Weight increases were followed with the thermobalance sensitivity at $2 \times 10^{-5}$ g/cm. The initial chart speed was 30 cm/min and the final speed was 2 cm/h.

RESULTS AND DISCUSSION

The isobar measurements (Figs. 1 and 2) were initiated by holding a sample in a CO$_2$ pressure of the order of 70-80% of the pressure at
which calcite formation would begin. Constant weights were achieved in periods of 4 to 6 hours. Pressures were decreased in steps indicated on the curves. Equilibration at each step was rapid. Periods of the order of 4 hours heating at the temperature of the experiment in vacuum were required to remove about the final 20% of the CO$_2$ that was taken up by the CaO when equilibrated at pressures just below the pressure of calcite formation.

When pressures of CO$_2$ were reintroduced in steps to obtain the adsorption isotherms, the initial approach to equilibrium was slow, but once the CO$_2$ concentration in the sample reached the level characteristic of the desorption isotherm the adsorption curve followed the desorption curve to within a 2 or 3% scatter in the data.

These observations are consistent with the assumption that some 80% of the maximum CO$_2$ content of a sample is adsorbed or desorbed rapidly in response to changes in pressure, and that the remaining ~20% is absorbed in the sample, probably at grain boundaries but perhaps in solution in the bulk CaO lattice. Figure 3 shows how well the rapidly exchanged portion of the CO$_2$ in a sample can be fit to a Langmuir isotherm [10,11].

The Langmuir adsorption model assumes fixed adsorption sites. Infrared measurements indicate CO$_2$ to chemisorb as CO$_3$$^-$ ions [4,5]. To plot the data, the concentration of surface oxide ion sites was calculated from the surface areas measured by the BET method [11,12] on the assumption that the total area is accounted for by faces formed of 100 planes of the NaCl-type structure. We calculated that from 80 to 95% of the surface oxide sites are converted to CO$_3$$^-$ at the highest pressures of these isotherms. The fit to the linear plot has a
confidence of 0.995. Equally good fits were obtained at five other
temperatures ranging from 923 K to 1013 K. Slightly better fits can be
obtained by plotting only data taken at pressures below the point of
upward curvature found in some of the plots of Figs. 1 and 2. We cannot
identify the cause of this curvature. The Langmuir model predicts that
plots like those of Figs. 1 and 2 should become horizontal as coverage
reaches one monolayer.

The enthalpies of adsorption which are calculated from variations
in the logarithm of the pressure of CO₂ with the reciprocal of the
temperature at constant concentrations of CO₂ adsorption (Table I) are
constant at 199 ± 2 kJ/mole for surface coverages of 55-80%. The slow
change in surface area during measurements with the first sample
introduces less than 2% uncertainty into the calculated enthalpies.
From consideration of all probable errors, the uncertainty is set at
8 kJ. Lower enthalpies are calculated when measurements above the
upward curvature in Figs. 1 and 2 are included. This result is
consistent with repulsive interactions between surface CO₃⁻ ions.

The enthalpies of adsorption measured in this study can be
compared to the enthalpy of formation of calcite from CaO at the same
average temperature, 181 kJ/mole [13]. The enthalpy of adsorption of
CO₂ on CaO is, like the heats of adsorption of sulfur on metal
surfaces [19], more negative than the enthalpies of the corresponding
reactions of sulfur with the metals to form bulk sulfides. It is
interesting that the strongly adsorbed CO₂ greatly increases the rate of
sintering of CaO [2,3]. Perhaps diffusion of Ca^{++}--CO_{3}⁻ ion pairs is
responsible.
Figure 4 shows, in the insert, the very rapid uptake of CO$_2$ by CaO when CaO is first exposed to CO$_2$ at a constant pressure at various temperatures. The much slower later pickup of CO$_2$ is shown by the other part of the same figure. The rates of adsorption were calculated from the expression $J_{CO_2} = kP_{CO_2}$, where $J_{CO_2}$ is the moles of CO$_2$ reacted per second and $k$ is the rate constant from the initial, essentially linear portions of each plot. In the linear range, back reaction must be negligible, and the rate of the forward reaction must be little affected by the fraction of surface sites already occupied by CO$_3^-$ ions. From the temperature dependence of the adsorption rates, the apparent enthalpy of activation for the desorption reaction was calculated to be 40 kJ/moles ± 10 kJ/moles. This activation enthalpy lies within the range of values found for CO$_2$ adsorption on Sc$_2$O$_3$, from 35 kJ to 105 kJ, depending on treatment of the Sc$_2$O$_3$ adsorption data. From the temperature dependence of the slow absorption of CO$_2$ into the CaO, an apparent activation enthalpy of 303 kJ/moles ± 15 kJ/moles is calculated for the unidentified rate-limiting step of this slow process.

ACKNOWLEDGMENT

U. Auselmi Tamburini kindly provided computer calculations of data in the early part of this work.

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REFERENCES


Table I. Adsorption thermodynamic data.

<table>
<thead>
<tr>
<th>No. of isotherms used for enthalpy derivation (x 10&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Moles of CO&lt;sub&gt;2&lt;/sub&gt; per mole of CaO</th>
<th>Mole fraction of surface sites occupied by CO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Correlation coefficient</th>
<th>Adsorption enthalpy (kJ/moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample 1 (at 923-1000 K)</strong></td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>3.0</td>
<td>0.56-0.70&lt;sup&gt;†&lt;/sup&gt;</td>
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<td>0.99</td>
<td>0.998</td>
<td>-180*</td>
</tr>
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</table>

*These values used some data points above the deflection point.

†Range of values reflects range of total surface area 19 m<sup>2</sup>/g initially to 15 m<sup>2</sup>/g finally.
FIGURE CAPTIONS

Fig. 1. $\text{CO}_2$ adsorption isotherms obtained with CaO of 19 to 15 m$^2$/g surface area.

Fig. 2. $\text{CO}_2$ adsorption isotherms obtained with CaO of 12.5 m$^2$/g surface area.

Fig. 3. Illustration of fit to Langmuir model for adsorption.

Fig. 4. Ratios of $\text{CO}_2$ uptake by CaO to the maximum $\text{CO}_2$ uptake as function of time when $P_{\text{CO}_2} = 1333$ Pa.
Figure 1

- $S_{CaO}$: $m^2/g$
  - at $t = t_0$: 19
  - at $t = t_f$: 15.5

- $T (K)$:
  - 1: 923
  - 2: 943
  - 3: 973
  - 4: 988
  - 5: 998
  - 6: 1008

- $P_{CO2} (Pa)$
- $W_{CO2} / W_{CO2}^{t}$
Figure 2

\[ \alpha = \frac{W_{CO_2}}{W_{CO_2}^t} \times 10^2 \]

\[ \frac{n_{CO_2}}{gr_{CaO}} \times 10^5 \]

\[ S_{CaO} = 12.5 \text{ m}^2 / \text{g} \]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1'</th>
<th>953</th>
</tr>
</thead>
<tbody>
<tr>
<td>2'</td>
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</tr>
<tr>
<td>3'</td>
<td>993</td>
<td></td>
</tr>
<tr>
<td>4'</td>
<td>1013</td>
<td></td>
</tr>
</tbody>
</table>
\[ T = 923 \, K \]

\[ \frac{n_{\text{CO}_2}}{gr(\text{CaO})} \times 10^5 \]

\[ \frac{P_{\text{CO}_2}}{n_{\text{CO}_2}} = \frac{1}{b} \frac{1}{(n_{\text{CO}_2})_m} + \frac{P}{(n_{\text{CO}_2})_m} \]

Figure 3
Figure 4

\[ \alpha' = \frac{n_{CO_2}}{n_{CO_2, T}} \]

\( \text{FRACTION ADSORBED} \)

\( \text{TIME (sec)} \)

- O 983 K
- ▲ 1003 K
- □ 1023 K
- ▼ 1033 K

Figure 4
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