

**LOW TEMPERATURE SO₂ CAPTURE BY CALCIUM BASED SORBENTS:
CHARACTERIZATION OF THE ACTIVE CALCIUM.**

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INTRODUCTION

Well dispersed CaO particles play an important role in some heterogeneous solid-gas reactions. Examples are the carbon-gas reactions catalyzed by calcium and the SO₂ retention by calcium-based sorbents. In these solid-gas reactions the characteristics of the CaO particles (i.e., dispersion, available surface area, etc.) have to be known to understand their behavior and their catalytic activity. Unfortunately, the characterization of well dispersed CaO particles by XRD does not give valuable information¹⁻³.

Selective CO₂ chemisorption has been deeply analyzed to characterize both CaO and CaO-carbon samples; thermodynamic arguments and details of the method have been discussed elsewhere³⁻⁵. The results show that CO₂ chemisorbs on CaO in an irreversible manner, and is restricted to the surface of the CaO particles, provided that the chemisorption temperature is lower than 573K. Therefore, this technique allows to assess the available surface area of the particles (active calcium) and consequently CaO dispersion. These two parameters were used to interpret the catalytic activity of calcium in different carbon-gas reactions. The usefulness of the method has been shown, gasification rate shows a close relationship with the area of the CaO particles^{3,6,7}. Based on the above results, and considering that the SO₂-CaO interaction might depend on the surface of CaO, the CO₂ chemisorption has been used to characterize the SO₂ retention by CaO prepared from thermal decomposition of several limestones⁸⁻¹⁰. The observation that SO₂ retention at 573K depends strongly on the dispersion and surface area of the CaO particles leads us to propose the use of carbon supports to improve the dispersion of the CaO particles^{11,12}. In this context, this paper extends and analyzes the usefulness of the CO₂ chemisorption method to characterize the active calcium in a wide variety of CaO-carbon samples. Several parameters, preparation conditions, nature of the calcium compounds, porosity of the carbons, etc. have been used to vary the available surface of the CaO particles.

EXPERIMENTAL

CaO samples. CaO samples were prepared by thermal decomposition of commercially available CaCO₃ and several limestones of very different origins. Decomposition was carried out in a thermobalance (Stanton-Redcroft) as described elsewhere¹⁰.

CaO-carbon samples. A large number of samples of calcium containing carbon have been selected for this study. The samples have been prepared varying calcium precursors, calcium content, carbon support properties (porosity, surface area, surface chemistry, etc.), and preparation methods (impregnation, ion-exchange).

CO₂ chemisorption. As described elsewhere^{3,4} the sample (CaO or CaO-carbon) is heated in N₂, at 20K/min, up to 1173K, subsequently it is cooled to 573K and then N₂ is switched to CO₂. From the CO₂ uptake, and assuming that one CO₂ molecule chemisorbs on one CaO site (1:1 stoichiometry), the number of calcium atoms, the available surface area and dispersion can be estimated^{3,4}.

SO₂ retention experiments. Isothermal SO₂ retention measurements of calcium-based samples were mainly performed by TG at 573K (other temperatures have also been tested). Details of the procedure are described elsewhere^{10,12}. Prior the retention run, the sample was heated, at 20K/min, up to 1173K, in a N₂ flow (60 mL/min), for 10 min. Subsequently, the sample was cooled to 573K and N₂ flow was changed to a gas mixture containing 0.3 vol% SO₂ in He. The amount of SO₂ retained by the sample, after 1.5-2 h of reaction, was determined by the increase in weight.

RESULTS AND DISCUSSION

The retention of SO₂ by CaO has been analyzed in our laboratory in a wide range of reaction temperatures (298-1173K)⁸⁻¹⁰. At temperatures lower than 673K the interaction of SO₂ with CaO forms CaSO₃^{8-10,13,14}, being this compound an intermediate of the formation of CaSO₄ at higher temperatures^{8-10,14,15}. Depending on the reaction temperature considered (T < 673K) two processes are distinguished during the formation of CaSO₃. For higher temperatures than 573K the formation of CaSO₃ occurs through a bulk process, however at temperatures below 573K, the SO₂ retained produces surface CaSO₃¹⁰, both in presence and in the absence of O₂, through the reaction⁹:

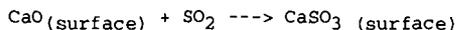


Figure 1 presents the isothermal retention of SO₂ at 573K, expressed as mol of SO₂ retained per gram of sample, versus time. After a period slightly over 1h, the uptake of SO₂ is practically constant. The SO₂-CaO surface reaction is confirmed on a large number of CaO by the observation that the ratio between mol of SO₂ (obtained from runs like that of Figure 1) per mol of CaO on the surface (determined from CO₂ chemisorption) is very close to one (see Figure 2). The extend of this surface reaction can not be explained by referring to any "classical" textural parameter of the limestones (N₂ (BET) surface area, pore volume, etc.) or those of CaO¹⁰. On the contrary, an interesting correlation between the SO₂ retention degree and the surface CaO is obtained, as shown in Figure 2. From this correlation, that shows the importance of the CaO surface area, it follows that the higher the dispersion of CaO, the higher the retention of SO₂. By selecting systems with high CaO dispersion¹², the efficiency to retain SO₂ can be increased. Activated carbons can act as dispersing agent as it is shown next.

A large number of CaO containing activated carbons prepared with different type of activated carbons, calcium compounds, calcium loadings and method of preparation have been selected for this study. Figure 3 compiles the SO₂ retention by these CaO-carbon samples which have been determined at 573K from runs similar to

that of Figure 1. It is interesting to note that samples containing less than 15% in weight of calcium exhibit retentions similar to those of bulk CaO (Figures 2 and 3).

The SO₂ retention (Figure 3) shows a marked dependence on the calcium content. Increasing the calcium content, the available CaO surface will increase, if there is not an important loss of dispersion. Figure 4 presents the CO₂ chemisorption data plotted versus calcium content of the supported samples. The results show that activated carbons act as good dispersing agents, they allow to increase the available CaO surface in respect to unsupported CaO.

Despite some data dispersion, both Figures 3 and 4 indicate that correlations between the calcium content and the CaO surface or the SO₂ retention exist. Figure 5, that presents the SO₂ retention per gram of sample versus the CaO surface, confirms the existence of a correlation among SO₂ retention and CaO surface as observed for unsupported CaO (Figure 2). Nevertheless, two aspects of Figure 5 need to be pointed out: 1) the ratio mol SO₂/mol CaO_S is usually higher than unity, contrary to that found on Figure 2 for unsupported CaO. It means that the SO₂ retention by CaO-carbon is not restricted to the CaO surface and that some bulk CaSO₃ occurs. 2) this behaviour is more pronounced in highly dispersed CaO (high CaOs values).

To prove the formation of bulk CaSO₃, SO₂ retentions have been conducted at different temperatures. Figure 6 presents the results obtained on two CaO samples (unsupported and supported one). An important shift to lower temperatures (about 200K) is observed in the transition from surface to bulk CaSO₃ formation, in the case of carbon supported CaO. For practical applications of these supported CaO samples to remove SO₂, the observation that in the temperature range of 573-673K the CaO conversion is almost 100% is very interesting. It has to be noted that the application of these results is based on the fact that CaO can be regenerated, and hence reused for SO₂ removal, by thermal decomposition (873-973K) of CaSO₃^{9,10,16,17}.

The most serious challenge at this moment is to be able to increase the amount of CaO supported on a given activated carbon. In fact, the maximum SO₂ retention reached with these supported CaO, expressed per gram of sample, is comparable to those obtained with some bulk CaO, as can be seen comparing Figures 2 and 5.

CONCLUSIONS

SO₂ retention by CaO and CaO-carbon depends very much on the CaO surface area which can be determined by CO₂ chemisorption. For unsupported CaO the retention is a surface process whereas for carbon supported CaO both surface and bulk reaction take place. Activated carbons act as good dispersing agent enhancing the SO₂ retention. The usefulness of the SO₂ removal at low temperatures by CaO supported on carbon appears to be limited by the amount of CaO that can be loaded on the carbon. This point needs further studies.

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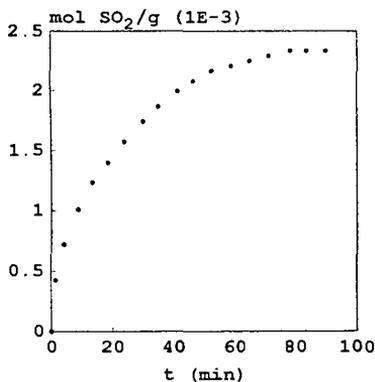


Figure 1. Sulfur dioxide retention by CaO at 573K versus time.

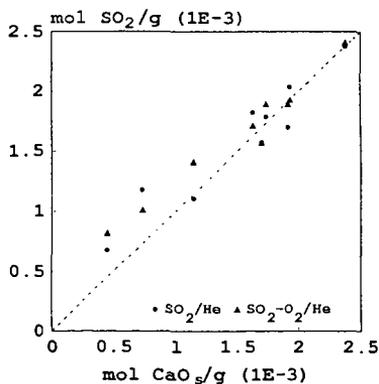


Figure 2. SO₂ retention versus surface CaO (un-supported CaO).

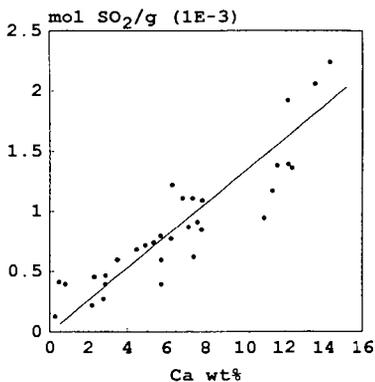


Figure 3. SO₂ retention versus Ca wt% (CaO/activated carbon samples).

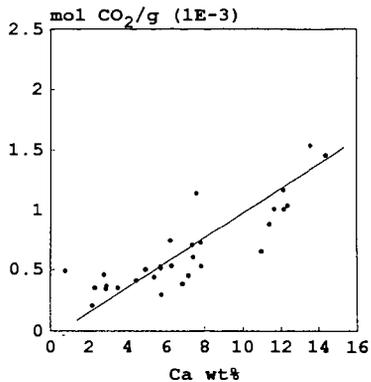


Figure 4. Chemisorbed CO₂ versus Ca wt% (CaO/activated carbon samples).

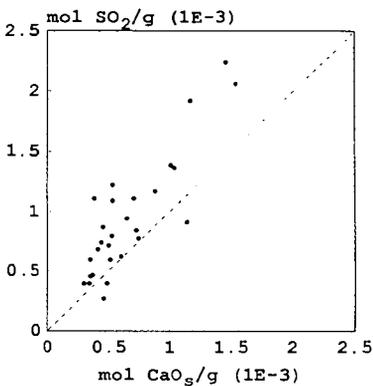


Figure 5. SO₂ retention versus surface CaO (CaO/activated carbon samples).

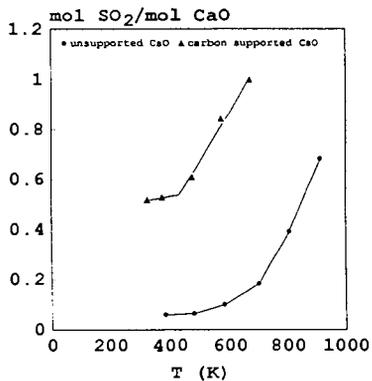


Figure 6. SO₂ molar conversion versus temperature.