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CO_2 Chemisorption to Characterize Calcium Catalysts in Carbon Gasification Reactions

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CO_2 chemisorption, at different temperatures, has been studied in CaO and in the CaO–carbon system by means of simultaneous TG–DTA, MS, and XRD techniques. As a whole the different techniques used show that CO_2 chemisorbs in an irreversible manner and is mainly restricted to the surface of the CaO particles, provided that the chemisorption temperature is lower than 573 K. CO_2 chemisorption at 573 K can be used as a tool to measure the external surface area of CaO particles. Selective CO_2 chemisorption at 573 K has been applied to the CaO–carbon system in the field of catalytic carbon gasification. Several examples are given to show the usefulness of the catalyst surface area determined by CO_2 chemisorption in interpreting the catalytic activity of calcium in carbon gasification.

I. INTRODUCTION

The importance of catalyst dispersion, that is, the concentration of catalyst sites, in the field of heterogeneous catalysis has been well documented (*1*). Extensive literature exists on the determination of the dispersion of a catalyst, which is usually measured by one or more of the following techniques: selective chemisorption, X-ray diffraction line broadening, electron microscopy, and small-angle X-ray scattering (*2*). However, in the field of catalyzed carbon gasification the extent of catalyst dispersion has not been sufficiently evaluated. A survey of the literature indicates that only in recent years have different research groups attempted to measure catalyst dispersion to prove its role in carbon gasification. By far the most frequently used technique is selective chemisorption and research has mainly been restricted to alkaline metal catalysts.

Ratcliffe and Vaughn (*3*) argued that chemisorption of CO_2 at 573 K in a TGA system provides a selective and rapid technique to measure the active site density of alkaline catalyst on coal. Hashimoto *et al.* (*4*), using a flash desorption method (Curie-point pyrolizer), determined the amount of oxygen trapped by the alkaline metal–carbon system. Gasification rates in steam were proportional to the chemisorbed oxygen. Cerfontain *et al.* (*5*), using a step-response experiment with labeled molecules, have also related gasification sites for the alkaline metal–carbon to the amount of CO_2 chemisorbed by the catalyst. Mims and Pabst (*6*) concluded that the relative reaction rates for alkaline salt-catalyzed carbon gasification by H_2O, D_2O, and CO_2 can be unified if the catalyst dispersion is known. They suggested the use of a surface alkylation technique to evaluate catalyst dispersion. However, little research has been conducted to determine the dispersion of alkaline-earth metals; in particular the important Ca–carbon system has not been sufficiently studied in this context.

Based on the well-known fact that CO_2 chemisorbs on alkaline and alkaline-earth

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oxides, two different approaches have been used to determine the dispersion of ion-exchanged calcium in lignites (*7, 8*). The results confirmed, in both cases, that CO_2 chemisorbs on the CaO particles. Two isotherms at 298 K were successively measured by Radovic *et al.* (*7*) in an attempt to differentiate between physical adsorption of CO_2 on the carbon and chemisorption on the Ca species. Linares *et al.* (*8*) observed that the surface area, as measured by CO_2 uptake at 298 K, increases monotonically with calcium loading. Assuming this increase is due to chemisorption on the CaO present in char, they deduced the CaO particle dispersion. However, in both cases the large amount of CO_2 physically adsorbed by the carbon matrix rendered difficult the quantification of the catalyst dispersion.

Physical adsorption of CO_2 is very often used in surface area determination of carbonaceous material (*9*). Therefore when CO_2 adsorption is used to characterize calcium loaded in carbon its adsorption in the carbon support should be minimized. Because CO_2 adsorption is an exothermic process, its uptake by the carbon surface can be avoided by increasing the adsorption temperature. However, because bulk $CaCO_3$ formation may occur, in addition to surface coverage of the catalyst, the chemisorption temperature must be studied to assume 1 : 1 stoichiometry. Recently, CO_2 chemisorption at 573 K has been used to interpret the calcium activity in the CO_2 and steam carbon gasification (*10*).

Taking into account that calcium is the most important *in situ* catalyst for the gasification of lignite chars (*11*), this paper, which is based on earlier results (*3, 7, 8, 10*), analyzes the CO_2 chemisorption method in both the bulk CaO and the CaO–carbon system. In this context, the paper examines in depth the experimental conditions of the chemisorption of CO_2 (with emphasis in the temperature) in (i) bulk CaO samples and (ii) CaO–carbon samples in order to assess the surface area, the average particle size, and the dispersion of the catalyst. The paper also shows examples of CO_2 chemisorption utility when it is applied to selected calcium–carbon samples in the field of catalyzed carbon gasification.

II. EXPERIMENTAL

In order to simplify the study and to seek the optimum experimental conditions for the CO_2 chemisorption method, this study has been first conducted using a calcium oxide sample from calcium acetate.

The calcium–carbon system has been studied using a pure carbon, to avoid HCl/HF acid treatment (used to demineralize impure carbon samples) which might affect the carbon–CO_2 gasification reaction catalyzed by calcium (*12*). The preparation procedure was as follows: a phenolformaldehyde polymer resin was pyrolyzed to yield carbon A, which had a calcium capacity of 0.4; carbon A-2 was obtained by nitric acid treatment of A which increased ion-exchange capacity to 3.2% Ca, from 1.5 *M* calcium acetate solution after 8 hr contact time (*10*). Other Ca samples have been prepared by impregnation with calcium acetate solution. Further experimental details of the Ca–carbon preparation and analysis are given elsewhere (*10, 13*). Table 1 presents some characteristics of these two carbons.

X-ray diffraction (XRD) patterns have been obtained in a Sheifert diffractometer (Cu*Kα* radiation) in order to identify calcium species, as a function of the temperature treatment.

Reactivity measurements in CO_2 (0.1 MPa), using experimental procedures similar to those described in Ref. (*10*), as well as CO_2 chemisorption uptakes, have been obtained gravimetrically in a simultaneous TG–DTA system (Stanton Redcroft 780). About 20 mg of sample is heated at 20 K/min to 1173 K for 10 min in flowing N_2. The sample temperature is then lowered to the reaction or chemisorption temperature and N_2 is switched to CO_2. Weight loss (in the reactivity experiment) and weight gain (in

TABLE 1

Some Characteristics of the Carbon Used

Carbon	Elemental analyses (%)				S_{N_2} BET (m^2/g)	Pore volume[b] (cm^3/g)		TPD ($\mu mol/g$)		% Ca
	C	H	N	O[a]		V_{micro}	V_{meso}	CO	CO_2	
A	96	0.56	0.26	3.30	615	0.254	0.339	300	178	0.4
A-2	83	1.43	0.37	15.20	668	0.265	0.271	2797	1968	3.2

[a] By difference.

[b] V_{micro} from CO_2 at 273 K (DR equation) and V_{meso} from mercury porosimetry ($7.5 < \phi < 50$ nm).

chemisorption) are analyzed as a function of reaction time. Reactivity data as well as CaO surface area are given per gram of original sample. Complementary techniques such as DTA and mass spectrometry have also been used.

III. RESULTS AND DISCUSSION

The CO_2 Chemisorption Method

Figure 1 shows, as an example, the different steps of a typical CO_2 chemisorption experiment carried out at 573 K on a calcium–carbon sample. Similar results are obtained for bulk CaO samples.

(i) Heating in N_2 flow (20 K/min) to 1173 K and 10 min soak time. Three endothermic weight losses, which correspond to H_2O, CO_2, and CO evolution from the oxidized carbon, are observed. During the treatment the calcium precursor will decompose to CaO.

(ii) Sample temperature is lowered in N_2 flow to the chemisorption temperature—573 K in this example—with a soak time of 10 min.

(iii) N_2 is switched to CO_2; a sharp exothermic heat and a weight gain related to the CO_2 chemisorption on the CaO is observed. The graph shows that the chemisorption process is very fast and is not significantly controlled by diffusion.

(iv) CO_2 is switched to N_2. At 573 K there is no weight change observed, indicating that CO_2 physisorption on the carbon surface may be neglected.

The difference in weight observed from

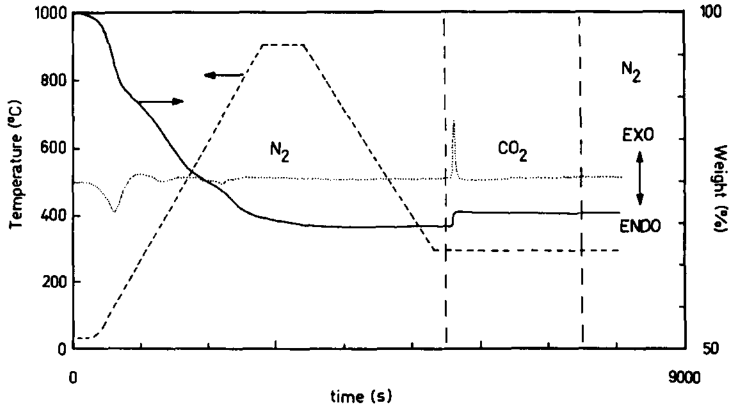

FIG. 1. Steps of a CO_2 chemisorption run on a CaO–carbon sample. (· · ·) DTA; full scale: +200 to −200 μv; (--- temperature); and (—) weight.

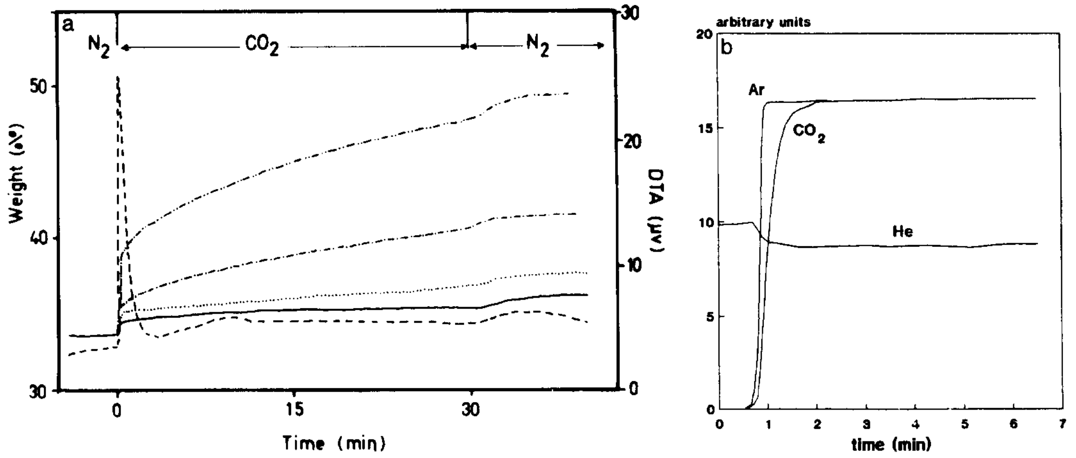

FIG. 2. CO_2 uptake on pure CaO. (a) TG curves at different temperatures: (—) 573 K; (· · ·) 623 K; (·-·) 673 K; (-···) 773 K; and (---) DTA at 573 K. (b) MS response for CO_2 chemisorption at 573 K.

step (ii) to step (iv) (both measured in N_2 flow) will be used in further calculations. The CO_2 uptake will correspond to chemisorption on the CaO and not to the carbon support.

Assuming that one CO_2 molecule chemisorbs on one CaO site, the number of Ca atoms on the surface of the catalyst, its dispersion (*d*), average particle size (*D*), and their available external surface area (*S*) can be estimated (*7*).

Some concern may exist about the 1 : 1 stoichiometry used because, since bulk carbonation is thermodynamically favorable, it may be present together with chemisorption. However, considering that kinetics plays an important role (see exothermic heat shape in Fig. 1), a long contact time will be necessary in order to have a noticeable contribution of bulk carbonation.

The effect of contact time at different temperatures is analyzed in Fig. 2a where TG curves (and DTA at 573 K) show the CO_2 uptake by a CaO sample prepared *in situ* by thermal treatment of calcium acetate. Important features of these curves are the following: (i) The CO_2 uptake increases with temperature. (ii) For low contact temperatures a stepped increase is found with a quasihorizontal plateau in contrast to the continuous increase found at higher contact temperatures. When CO_2 chemisorption at 573 K is studied after 4 h of contact time, CO_2 uptake increases less than 10% in respect to the amount reached after 30 min of contact. (iii) The DTA curve, associated with the chemisorption process, reaches baseline in less than 30 min. This is in agreement with experiments carried out in another experimental system where the reactor was coupled with a quadrupole mass spectrometer (*14*).

Figure 2b shows an isothermal chemisorption of CO_2 at 573 K on an outgassed CaO sample monitored by MS. After helium has been switched for a gas mixture of CO_2/He/Ar (10/88/2%), the expected CO_2 level is recovered much later than that with Ar because of CO_2 chemisorption on CaO. In this experiment less than 2 min is sufficient to recover the CO_2 level. Quantification of the CO_2 uptake, determined from the discrepancy between Ar and CO_2 curves, agrees well with those obtained from TG experiments.

From the above results it is thought that uncertainty about the contribution of the bulk carbonation on the CO_2 uptake may be avoided because this process is much slower than the chemisorption process. Of course, the higher the CO_2–CaO contact temperature, the higher the carbonation contribution will be. Thus, for contact temperatures <573 K the bulk carbonation is insignificant, whereas for $T > 573$ K its contribution may be more important. According to the curve shapes obtained upon CO_2 exposure, in both bulk CaO and CaO–carbon samples, we deduce that bulk carbonation at 573 K, if present, is not important. Thus, in all the TG experiments presented hereafter a contact time of 30 min has been used. This arbitrarily chosen time is justified because our TG system needs a stabilization time of about 2–5 min when CO_2 is switched to N_2, as can be observed in Fig. 2a.

Because these results may depend on the chemisorption temperature used, special attention is given to studying the CO_2–CaO interaction as a function of temperature with TG–DTA, XRD, and MS techniques. For this purpose the chemisorption of CO_2 has been investigated first on calcium oxides samples prepared by thermal decomposition of calcium acetate. The study has also been extended to a more complex calcium–carbon system in order to test the original work of Ratcliffe and Vaughn (*3*), where the chemisorption temperature was not studied.

Chemisorption Temperature

The temperature range covered in this study goes from 300 to 973 K. Figure 3 shows the CO_2 uptake by CaO, obtained from calcium acetate, using the above experimental procedure. CO_2 uptake increases with temperature in two different ways, probably due to two different chemical processes. At low temperatures (<573 K) a smooth slope is observed which could be related to the chemisorption of CO_2 on the external CaO particles. Recently (*14*), by analysis of the thermodynamics and kinetics of the CO_2–CaO surface and bulk reactions it has been shown that CO_2 chemisorbs on the CaO surface by an activated process which fits the Ellovich model. At a given temperature the CO_2 uptake is governed by the activation energy of a specific site and not by diffusion. At temperatures higher than 573 K the slope becomes very pronounced, reaching through extrapolation a CO_2/CaO ratio near unity. At 573 K the heat evolved is 105 ± 6 KJ/mol, whereas at the highest temperature studied the heat evolved is 150 ± 8 KJ/mol, a value which is relatively near to that published for calcium carbonate formation, 178 KJ/mol (*15*). This result is in agreement with the complete $CaCO_3$ bulk formation at this reaction temperature (973 K) after 30 min of contact time.

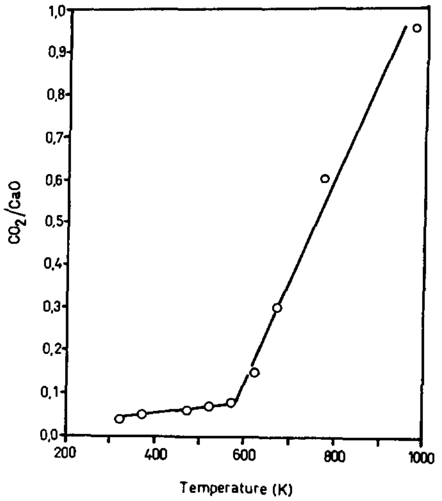

FIG. 3. CO_2/CaO ratio obtained on a pure CaO sample at different temperatures. CO_2 pressure, 1 atm; contact time, 30 min for each point.

XRD has been applied to a series of CaO samples from calcium acetate, prepared in a horizontal furnace and held for 30 min in contact with CO_2 at different temperatures. The experimental procedure used for this CaO–CO_2 sample series is similar to that described for the TG system. At temperatures lower than 573 K, XRD profiles show only peaks which correspond to CaO (even if CaO was in contact with 1 atm of CO_2 at 573 K for 30 min). Considering that XRD is a bulk technique, the absence of $CaCO_3$ peaks indicates that CO_2 uptake by CaO is

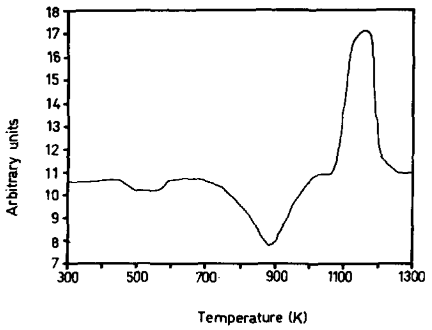

FIG. 4. CO_2 evolution profile of a TPR experiment of a pure CaO sample. Atmosphere: 88% He, 10% CO_2, and 2% Ar. Heating rate: 100 K/min.

mainly restricted to its external surface. At higher temperatures (i.e., 773 K) $CaCO_3$ formation by CO_2 diffusion through the interior of the CaO particles is observed. $CaCO_3$ XRD peaks increase as the reaction temperature increases. At 1023 K the results show only the $CaCO_3$ species. A heat treatment of $CaCO_3$ in CO_2 flow (in the TG system) shows, as expected, that decomposition is completed at 1243 K.

Figure 4 shows the CO_2 evolution profile of a CaO sample heated to 1250 K (100 K/min) in a flowing mixture of He (88%), Ar (2%), and CO_2 (10%). Details of the equipment and of the experimental procedure are given elsewhere (*16, 17*). The CO_2 level shows two well-defined minima; a small one in the region of 573 K (surface chemisorption) and a large one at 920 K (bulk carbonation), as well as a maximum at 1073 K (carbonate decomposition previously formed). The high heating rate used allows one to clearly differentiate chemisorption from bulk carbonation. Near 573 K there is a boundary region delimiting these two processes, in agreement with the results of Fig. 3. Figure 4 also shows that the temperature stability range of $CaCO_3$, under the experimental conditions used (10% CO_2 and 100 K/min) is from 1030 to 1080 K.

Figure 5 shows the effect of chemisorption temperature on a CaO–carbon system; a trend similar to that found in CaO particles is observed. The higher CO_2 uptake, with respect to that shown in Fig. 3, indicates that the CaO particles on the carbon matrix are smaller than those in the CaO sample. Chemisorption temperatures higher than 873 K cannot be studied due to catalytic gasification of the carbon matrix.

Taking into account that the CO_2 chemisorption method proposed will be applied to the CaO–carbon system in the field of catalytic carbon gasification, the highest chemisorption temperature possible (restricted to a surface coverage of the CaO particles) will be the most appropriate due to the lowest CO_2 physisorption uptake by the carbon matrix. We conclude that to assess the average particle size of calcium oxide supported in carbon (or its surface area) the chemisorption temperature can be fixed at 573 K (lower temperatures will allow CO_2 adsorption in the carbon surface whereas higher temperatures should be avoided because of bulk carbonation). Examples of selected applications are given below.

Calcium Activity in Carbon Gasification Reactions

X-ray diffraction technique is severely limited to interpreting reactivity data as well as to following loss in catalytic activity of

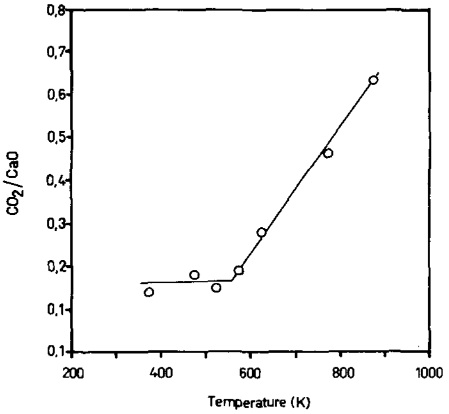

FIG. 5. CO_2/CaO ratio obtained on a CaO–carbon sample (3.2% Ca) at different temperatures. CO_2 pressure, 1 atm; contact time, 30 min for each point.

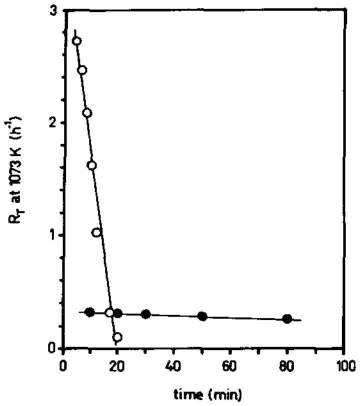

FIG. 6. Reactivity in CO_2 (O) and steam (●) at 1073 K versus reaction time for sample with 3.2% Ca.

well-dispersed calcium during carbon gasification (*18*). Very small calcium particles (<5 nm), which are mainly responsible for the catalytic activity, are not detected by this technique. Furthermore, neither the small amounts of calcium loading in carbon—frequently used in catalytic carbon gasification—nor the small amounts of Ca–carbon samples can be measured by XRD techniques. As will be shown below, CO_2 chemisorption could be a useful tool for studying *in situ* calcium activity in carbon gasification reactions.

Figure 6 shows reactivity data in CO_2 (0.1 MPa) and in steam (19.7 KPa) at 1073 K plotted versus reaction time (*18*). The graph reveals that calcium activity is much higher in CO_2 than in steam. It is noteworthy that during gasification in CO_2, reactivity decreases noticeably in contrast to the behavior found in steam where the catalyst maintains a constant level of activity. The external surface of the catalyst (after CO_2 and steam gasifications) has been determined by measuring the CO_2 uptake by the CaO, which is expected to be formed after heat treatment in N_2 (at 1173 K) of the calcium–carbon sample. Figure 7 presents the external CaO surface area from CO_2 chemisorption versus reaction time. From Figs. 6 and 7 it is evident that, for a given reaction atmosphere, reactivity is related to CaO surface area. In CO_2 gasification the reactivity decreases with time, whereas in steam gasification the reactivity is almost constant over the reaction time studied. Interestingly, CO_2 gasification causes an important enlargement of the catalyst particle size (as is shown by the CaO surface area decrease in Fig. 7), which leads to a marked loss in catalytic activity during reaction time. On the other hand, in steam no appreciable change in the catalyst surface area is found, as is also the case with reactivity data.

Considering that both reactions have been studied at the same temperature, it is evident that the gas-phase atmosphere affects the chemical composition of the catalyst and its sintering behavior. In CO_2 atmosphere (0.1 MPa) the catalyst is very active and the reaction mechanism involves a transformation of the active species (probably CaO) to $CaCO_3$, as has been demonstrated by XRD. However, in steam (19.7 KPa), where the catalyst activity is lower, there is no evidence of a transformation of the active phase to carbonate because of the low CO_2 partial pressure. The calcium species present under steam gasification will be mainly CaO ($Ca(OH)_2$ if presents will immediately decompose to CaO) and a small amount of $CaCO_3$. The lower tendency of CaO with

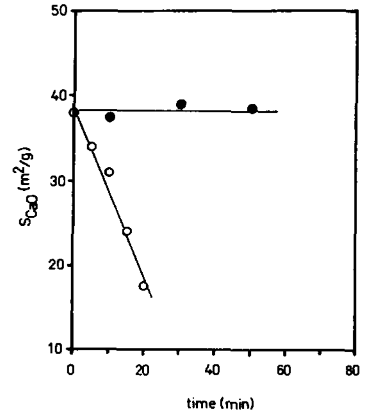

FIG. 7. Changes in the CaO surface area as a function of the reaction time in CO_2 (O) and in steam (●) at 1073 K for sample with 3.2% Ca.

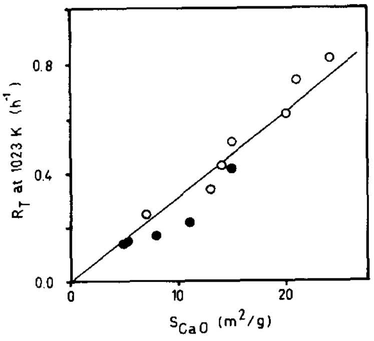

FIG. 8. CO_2 reactivity at 1023 K versus CaO surface area. (○) original CaO carbon sample with 3.2% Ca; (●) heat-treated sample.

respect to $CaCO_3$ to sinter is evident from Fig. 7, as is also expected from the Tamman temperature (1501 and 838 K, respectively).

CO_2 reactivities at 1023 K (0.1 MPa) of two calcium–carbon samples with different initial catalyst dispersions have been studied. The different initial catalyst dispersions have been obtained by submitting one of the samples to an additional heat treatment in N_2 at 1223 K for 2 hours. In agreement with earlier results (*7, 19*) it is observed that heat treatment produces an important decrease in reactivity, from 0.82 to 0.42 h^{-1} for the untreated and treated samples, respectively. In both samples the CO_2 reactivity decreases noticeably with burn-off. The decrease in reactivity due to heat treatment is comparable to that obtained in the untreated sample after 40% burn-off.

Interestingly, the CaO surface area of these samples at different percentages of burn-off decreases in a manner similar to that of CO_2 reactivity, indicating again the close relationship between catalytic reactivity and available surface area of the catalyst. Thus, it is important to point out that the heat treatment causes a 50% reduction in both the initial reactivity and the CaO surface area.

In Fig. 8 reactivities for these two samples are plotted versus surface area of CaO for different burn-off levels. The relationship found indicates that the remaining surface area of the catalyst is a key factor controlling its catalytic activity; the higher the available CaO surface, the higher will be the contact CaO–carbon and therefore its catalytic activity. Another example showing a linear relationship between surface area of CaO and reactivity is given elsewhere (*10*), where it was found that for calcium contents lower than the maximum ion exchange capacity of the carbon support, the CO_2 and steam reactivities increased linearly with the available surface area of the catalyst.

From CO_2 reactivity data and CaO surface area, the rate/m^2 values have been calculated and plotted in Fig. 9. The rate/m^2, which is related to the turn-over rate, varies with the degree of burn-off, depending on the reaction temperature used. For the two samples reacted at 1023 K we observe, over a wide range of burn-off, that the areal rate is almost constant (with an average value of $\approx 0.03\ h^{-1}\ m^{-2}$), which confirms the importance of the available surface area of the catalyst as a key factor controlling its catalytic activity. However, at a reaction temperature of 1073 K the areal rate decreases noticeably with burn-off, despite the fact that CaO surface area at this temperature decreases more than at 1023 K. At a 10%

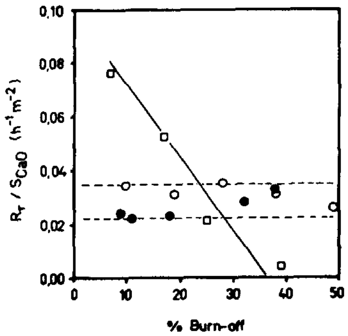

FIG. 9. Reactivity per unit surface area of CaO versus degree of activation. Reaction temperature, 1023 K: (○) Sample with 3.2% Ca; (●) heat-treated sample. Reaction temperature, 1073 K: (□) sample with 3.2% Ca.

TABLE 2

CO_2 Reactivity (1073 K) and CaO Characteristics

Sample	% Ca	Reactivity (g/g h)	d	D (nm)	S_{CaO} (m^2/g of sample)
A-2-0.5	0.5	0.80	0.28	4.42	2.2
A-2-6.0	6.0	3.60	0.56	2.21	61.6
A-2-6.7	6.7	3.60	0.51	2.43	63.7
A-2-7.2	7.2	3.60	0.48	2.58	65.1
A-2-8.0	8.0	3.60	0.41	3.02	62.3
A-2-9.4	9.4	3.54	0.35	3.54	61.6

burn-off level the areal rate is much higher at 1073 K than at 1023 K, as expected. The striking fact is the strong influence that the reaction temperature has on these results. As has been analyzed elsewhere (*18*), in addition to the importance of the catalyst dispersion, there should be an additional effect caused by the different chemical changes in the catalyst due to the different reaction temperatures used.

A series of calcium acetate-impregnated carbons with different calcium loadings has also been studied. In Table 2 CO_2 reactivities (0.1 MPa and 1073 K) together with CaO particle characteristics deduced from CO_2 chemisorption (dispersion, average particle size, and CaO external surface area per gram of sample) are compiled. A sample with 0.5% Ca prepared by ion exchange is also included.

Reactivities for the impregnated samples are constant ($\approx 3.6\ h^{-1}$) in spite of increasing calcium loading from 6.0 to 9.4 wt%. CO_2 chemisorption data allow interpretation of this unexpected reactivity behavior since, upon increasing the calcium content, there is a continuous decrease in dispersion (from 0.56 to 0.35; see Table 2) and a constant external surface area of CaO is found. The results show that reactivity and external surface of the catalyst are closely related by an areal rate constant equal to 0.057 for these impregnated samples. For samples with lower loadings of Ca, the areal values are 0.078 for a sample with 3.2% Ca (as deduced from Fig. 9) and 0.36 for a sample with 0.5% Ca. These results show that the specific activity of calcium decreases as its concentration in char increases, and is constant for higher loading. These different activities indicate that the available surface areas of the calcium particles have different effectivities, probably due to different carbon contacts.

The activity of a catalyst in the gasification of a given carbon depends mainly on its nature, its concentration, and its dispersion in the carbon matrix as well as in the catalyst–carbon contact. All of the above CO_2 chemisorption–reactivity results demonstrate that CaO particle size or its available surface area is one of the key factors (but not ultimately responsible) in understanding its catalytic activity and is much more relevant than its concentration. Consequently, catalyst concentration should not be used to compare catalytic activity of different catalysts or different carbons. The concept of dispersion or external surface area of the catalyst (even if not absolute) seems much more relevant and reliable. In this context it should be pointed out that, even if some uncertainty about the 1 : 1 stoichiometry used may persist, the results show the utility of the available surface area of the catalyst, which has not been studied before for the calcium–carbon system. However, for a quantitative assessment of the catalytic activity of calcium in carbon–gas reactions, the catalyst–carbon contact (or the effective active sites of the catalyst) is of much more importance than its available external surface area. Of course, these two parameters, active sites and surface area, must be more or less related. By selective chemisorption, the surface area can be determined, but not the active sites. Most of the results presented here indicate that CaO surface area is closely related to activity and therefore to catalyst–carbon contact. TPD obtained after CO_2 chemisorption clearly shows that not all the measured external surface area of CaO is in contact with the carbon. New insights into the catalyst–carbon contact, obtained by interpretation of these TPD experiments, will be published elsewhere (*20*).

IV. CONCLUSIONS

Results obtained by different techniques (TG–DTA, MS, and XRD) show that CO_2 chemisorbs in an irreversible manner and is mainly restricted to the surface of the CaO particles if the chemisorption temperature is lower than 573 K.

The purpose of this paper is to analyze selective CO_2 chemisorption applied to the characterization of calcium catalyst for gasification reactions. The results show that CO_2 chemisorption is a suitable technique to study *in situ* calcium activity in carbon gasification. Reactivity in CO_2 and steam shows a close relationship with external surface area of CaO particles.

The characterization of several CaO–carbon samples in the field of catalyzed carbon gasification by selective CO_2 chemisorption demonstrates the usefulness of this technique in determining CaO dispersion and hence in understanding the catalytic activity of calcium in these reactions.

This paper confirms previous publications in which the dispersion of the catalyst has been the object of study and its relevant contribution to carbon gasification reaction has been pointed out.

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