CO_2 Gasification of Activated Carbon Catalyzed by Earth Alkaline Elements

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Introduction

Apart from the well-known activity of the alkaline elements for the gasification of carbon, the earth alkaline elements also show a considerable activity for this reaction. In the literature conflicting results have been reported. For the CO_2 and H_2O gasification of physical mixtures of earth alkaline carbonate and carbon substrates, such as graphite and coal char (McKee, 1979, 1980; Spiro et al., 1983) a periodically increasing catalytic effect from Be to Ba was found. Moreover, above catalyst loadings of 5 wt. % the activity did not increase (Spiro et al.). This is in contrast with other studies, where ion exchange or impregnation had been applied, that show a gasification activity dependent on the catalyst concentration (Otto et al., 1979; Walker et al., 1979; Lang and Neavel, 1982; Hippo and Walker 1975. Sears et al. 1980; Agarwal and Sears 1980). Clearly, the results reported in the literature strongly depend on the preparation method of the samples, i.e., the catalyst dispersion.

Here we present results of a comparative study of the activity of the different earth alkaline elements for the CO_2 gasification of an activated carbon. Special attention will be given to the catalyst dispersion.

Experimental

The samples used in this study were prepared by pore volume impregnation of Norit RX extra, an acid-washed, steam-activated peat char, with an aqueous solution of the earth alkaline nitrates (Merck analytical grade), according to a procedure reported by Kapteijn et al. (1984). The carbon to metal ratio was 51.8. The influence of the catalyst concentration was studied for Ca using samples with C/Ca ratios of 108, 51.8, and 25.3.

The reactivity was determined isothermally by a gravimetric method (PBBR, Kapteijn and Moulijn 1983), and by temperature programming using a quartz fixed-bed flow reactor (Kapteijn et al., 1984). The products were analyzed by gas chromatography.

The procedures for the isothermal and the thermal cycling CO_2 gasification experiments are described elsewhere (Kapteijn et al., 1984). The upper temperature in the latter experiments was dictated by the activity of the catalyst; the CO_2 conversion never exceeded 2%. After the temperature-programmed CO_2 gasification, the samples were outgassed in a stream of helium (starting temperature 473 K; heating rate 10 K/min; endpoint temperature 1,200 K) followed by an isothermal period of 10 min.

The residues of the isothermal gasification experiments were, after cooling in CO_2, investigated by X-ray diffraction using Cu$K\alpha$ radiation.

Results

The results of the isothermal gasification at 1,050 K and a CO_2 pressure of 0.15 MPa are given in Figure 1. The gasification experiments were stopped before a complete burn-off was obtained. Especially in the initial gasification stages the activity of all samples decreased with increasing burn-off. The samples containing Be and Mg show hardly any catalytic activity and finally attain the gasification level of the pure activated carbon.

In Figure 2 the temperature dependency of the different earth alkaline elements for the CO_2 gasification is shown for the second temperature cycle. These data represent the activity at low burn-off levels. For comparison the activity of potassium carbonate at the same carbon to metal ratio is included (Kapteijn et al., 1984). It can be concluded that for both types of experiments the activity of the earth alkaline elements increases in the order: Activated carbon $\approx$ Be $\approx$ Mg $<$ Ba $\approx$ Sr $<$ Ca. The activity of Ca turns out to be equal to that of K at temperatures around 1,000 K. Table 1 gives values of the apparent preexponential factor, k_o, and activation energy. E_a, together with the normalized reaction rate, r_n, at 1,000 K.

The effect of the Ca concentration is shown in Figure 3. The activity increases with increasing catalyst concentration. The

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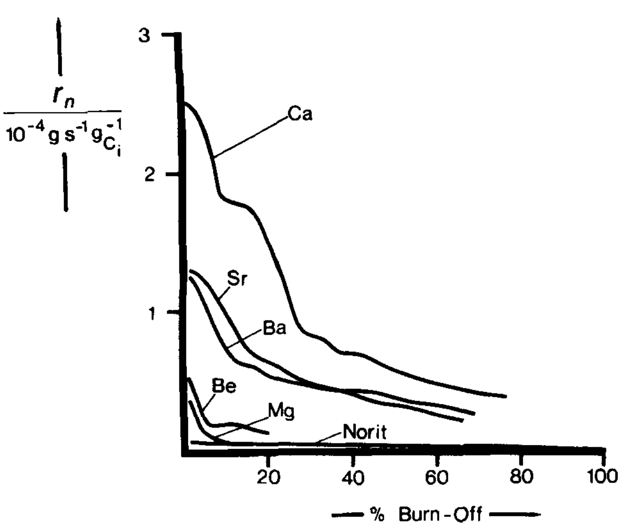

Figure 1. Normalized reaction rate r_n as a function of burn-off for isothermal CO_2 gasification of earth alkaline nitrate/Norit RX extra samples.

Temp., 1,050 K; CO_2 press., 0.15 MPa; CO_2 flow, 100 μmol/s; carbon to metal ratio, 51.8.

numerical results are included in Table 1. Within the experimental error (20 kJ/mol) the activation energy is hardly affected, or slightly increased, by addition of the catalyst.

Outgassing patterns of Be, Ca, Sr, and Ba are given in Figure 4. The patterns of Mg (not shown) and Be resemble that of the carbon itself, for which only a minor CO evolution at high temperature is observed. It can be seen from Figure 4 that the CO release in the case of the Ca sample starts at the lowest temperature, followed by Sr and Ba, in that order. The total amount of oxygen released (CO + $2CO_2$) per metal atom is about 2.0 for these three metals. This value is corrected for the CO evolution at the highest temperature, which is a contribution of the carbon itself.

Table 1. Apparent Preexponential Factors k_o, Activation Energies E_a, and Normalized Reaction Rates r_n for CO_2 Gasification of Earth Alkaline Nitrate/Norit RX Extra Samples at Different C/M Ratios

Sample	C/M	k_o 10^{10}mol(mol $C_i)^{-1}s^{-1}$	E_a kJ · mol^{-1}	r_n (1,000 K) μmol(mol $C_i)^{-1}s^{-1}$
Norit	—	$(0.16–1.8)*10^{-3}$	240–260	0.46
Be	51.8	$3.2*10^{-3}$	256	1.4
Mg	51.8	$2.4*10^{-3}$	246	3.2
Ca	107.0	1.6	287	16.0
	51.8	4.3	282	79.0
	25.3	20.0	284	280.0
Sr	51.8	11.8	295	44.0
Ba	51.8	0.2	265	28.0

In Figure 5 outgassing patterns are given for the different Ca samples used in Figure 3. The amounts CO and CO_2 released are plotted per mole Ca initially present. The total amount of oxygen released up to 1,100 K is for all samples about 2.0 mol/mol Ca. In the case of the Ca samples it is clearly seen that the CO and CO_2 evolution drop simultaneously between 1,050 and 1,100 K. The sample with the lowest Ca content gives relatively the highest CO_2 evolution.

X-ray diffraction (XRD) of the earth alkaline nitrate/Norit RX extra samples reveals that no crystallites are present, indicating highly dispersed systems. The X-ray diffraction patterns of several Ca-containing samples are given in Figure 6. Even after a 10 min heat treatment of the impregnated sample at 1,200 K in He, no crystallinity was observed. Gasification in CO_2, however, resulted in appreciable sintering of the catalyst. With increasing gasification level the reflection peaks of calcium carbonate (calcite) sharpen, indicating an increase in crystallite size during gasification. Also for Ba carbonate (witherite) and Sr carbonate, reflections were observed after gasification, whereas for Mg and Be only the reflections of the oxides were present. In Table 2 the average crystallite sizes for the different

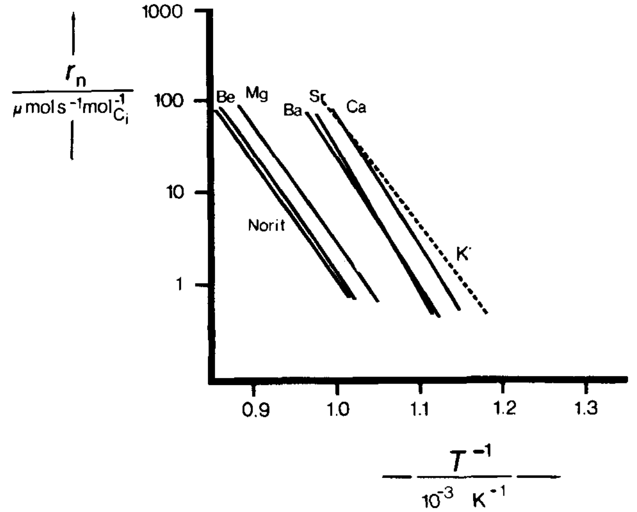

Figure 2. Normalized reaction rate r_n as a function of T^{-1} for temperature-programmed CO_2 gasification of earth alkaline nitrate/Norit RX extra samples.

CO_2 press., 0.15 MPa; CO_2 flow, 100 μmol/s; 360 mg C; carbon to metal ratio, 51.8. Line thickness indicates data scatter.

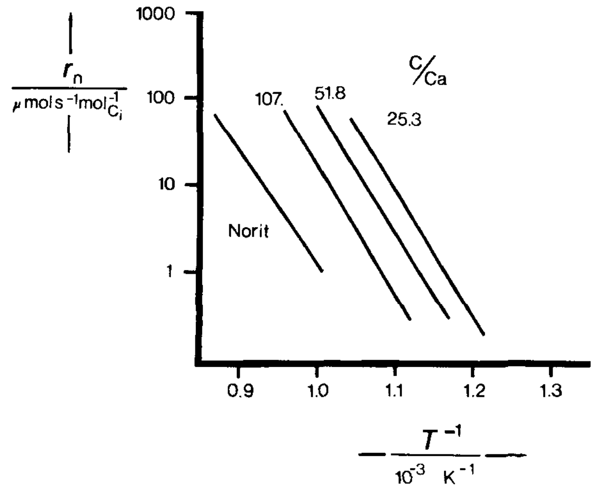

Figure 3. Normalized reaction rate r_n as a function of T^{-1} for the temperature-programmed CO_2 gasification of calcium nitrate/Norit RX extra samples with different C/Ca ratio.

CO_2 press., 0.15 MPa; CO_2 flow, 100 μmol/s; 360 mg C. Line thickness indicates data scatter.

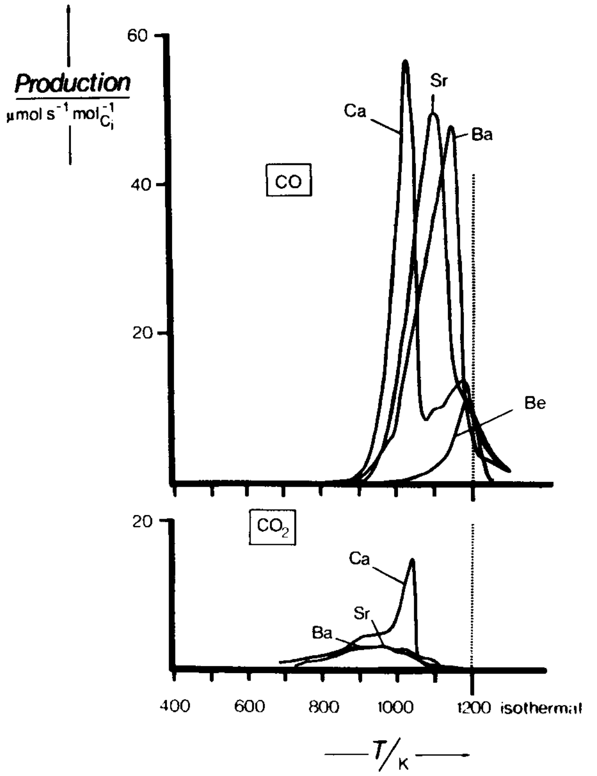

Figure 4. Outgassing patterns of earth alkaline nitrate/ Norit RX extra samples in He after temperature-programmed CO_2 gasification of Figure 2.

Heating rate, 10 K/min; He flow, 100 µmol/s; carbon to metal ratio, 51.8.

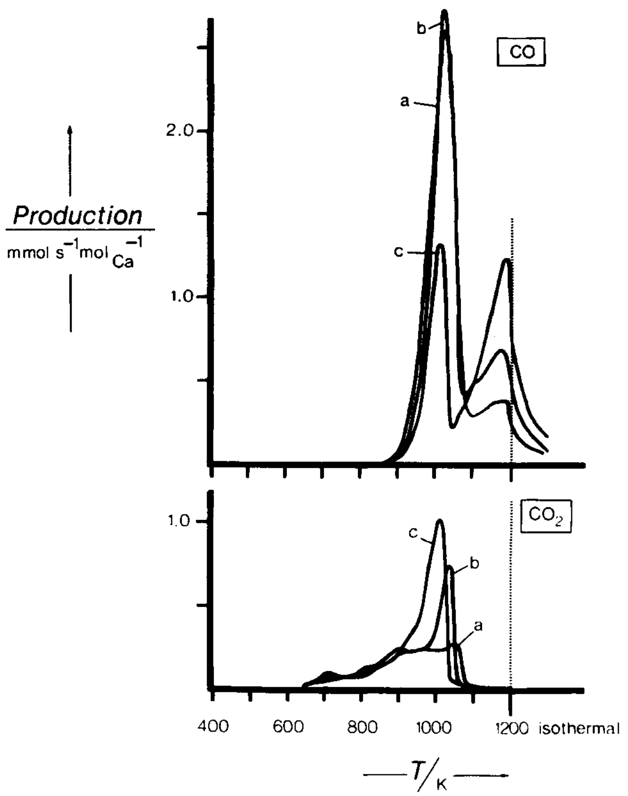

Figure 5. Outgassing patterns of calcium nitrate/Norit RX extra samples in He after temperature-programmed CO_2 gasification of Figure 3.

Heating rate, 10 K/min; He flow, 100 µmol/s; C/Ca ratio: (a) 25.3, (b) 51.8, (c) 107.

earth alkaline elements as calculated from the XRD peak broadening are given.

Discussion

The results presented above show that Ca is the most active earth alkaline element for the CO_2 gasification of activated carbon over the temperature range studied. Its initial activity is even about the same as for the well-known gasification catalyst potassium. Except for one study (Lang and Neavel, 1982), this result is in contrast with the periodic activity order reported in the literature for the steam (McKee, 1979; Otto et al., 1979) and carbon dioxide (McKee, 1980; Spiro et al., 1983) gasification. For the CO_2 gasification the differences are easily explained by the low surface areas of the graphite (McKee, 1980) and coal char (Spiro et al., 1983) used, which inevitably resulted in a low dispersion of the catalyst; as a consequence, not the intrinsic catalytic activity is measured but a combination of dispersion and intrinsic activity. Consequently, the rates reported in this study are higher. The reported absence of catalyst concentration dependency reported by Spiro et al. (1983) must also be due to the low dispersion, since increasing the Ca concentration increases the activity considerably (Figure 3). In agreement with other results on CO_2 gasification (Sears et al., 1980; Agarwal and Sears, 1980) and H_2O gasification (Otto et al., 1979; Walker et al., 1979; Lang and Neavel 1982; Hippo and Walker, 1975).

Recently, Baker et al. (1984) have shown by *in situ* electron microscopy studies that the temperature strongly determines the

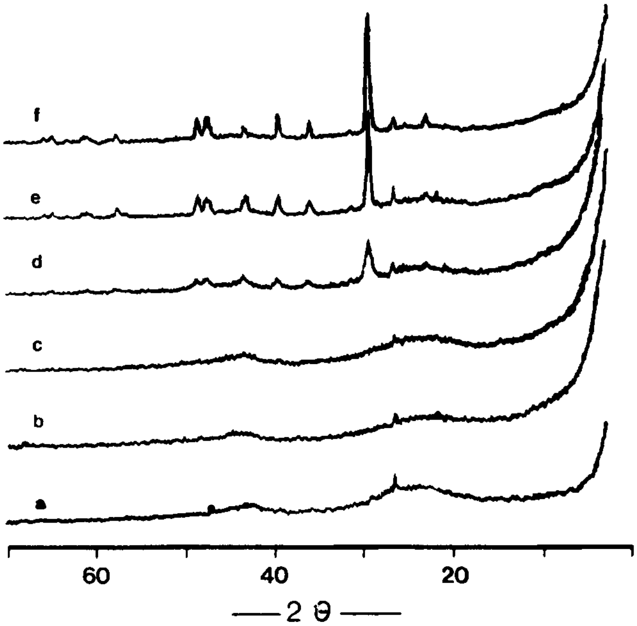

Figure 6. X-ray diffraction patterns of calcium nitrate/ Norit RX extra samples.

Carbon to metal ratio, 51.8.
a, Fresh sample.
b, After heat treatment in He at 1,200 K (10 min). After isothermal CO_2 gasification at 1,050 K and different burn-off levels: *c*, 0% *d*, 30%; *e*, 50%; *f*, 75%.

Table 2. Average Crystallite Sizes *d*, Estimated from X-ray Diffraction Line-Broadening for the Samples of Figures 1 and 6

Compound	% Burn-off	d/nm
BeO	10	—
MgO	10	150
$CaCO_3$	30	170
	50	320
	75	460
$SrCO_3$	65	420
$BaCO_3$	70	1,200

mode of the Ba-catalyzed gasification of graphite. In steam and carbon dioxide the catalyst acts as a highly dispersed film and gasification takes place by edge recession between 970 and 1,100 K. Above 1,100 K particles become apparent which gasify according to a channeling mode. So, differences in activity order can also be caused by the different temperature ranges that are applied.

In the literature the identity of the active species is still a matter of discussion. McKee (1980) infers the carbonate to be the active species which decomposes by reaction with the carbon:

$$MCO_3 + C \rightarrow MO + 2\,CO \qquad (1)$$

and the carbonate is reformed according to:

$$MO + CO_2 \rightarrow MCO_3 \qquad (2)$$

However, a reaction between carbonate and the carbon as an elementary step in the gasification process would not leave the activation energy unaffected. Our results and those of Otto et al. (1979) indicate that the activation energy is hardly changed by addition of the catalyst. This suggests that the catalyst only increases the number of active sites, provided there is no compensation effect. This increase in number of active sites is recently confirmed by transient kinetic studies made by Freund (1986). This method yields the intrinsic rate constant of the rate determining step. This rate constant was the same for both the Ca-catalyzed and the uncatalyzed reaction.

It is generally accepted that the rate-determining step in the CO_2 gasification of carbon is the release of CO from the carbon structure. Increase of the site density can be achieved by the formation of more surface CO groups by an oxygen transfer mechanism. Sears et al. (1980) explained the catalytic activity of Ca by the formation of a surface peroxide:

$$CaO + CO_2 \rightarrow CaO \cdot O + CO \qquad (3)$$

$$CaO \cdot O + C \rightarrow CaO + C[O] \qquad (4)$$

$$C[O] \rightarrow CO \qquad (5)$$

Radovic et al. (1983) propose an identical mechanism for the O_2 gasification of char in which Eq. 4 represents a spillover of oxygen to carbon-active sites. The oxygen transfer mechanism is supported by evidence from the outgassing patterns of Ca (Figure 5). The overall stoichiometry of the outgassing experiments and the X-ray diffraction patterns suggest that carbonate species are present after gasification followed by cooling in CO_2. Heating in He results in a decomposition of the carbonate:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (6)$$

This CO_2 will react further at active sites according to a gasification process. At low Ca concentration the density of the active sites is lower, so the CO formation will be lower than at high Ca concentrations, as is shown in Figure 5. In the literature more suggestions have been made that the oxide is the active species (Baker et al., 1984; Coates et al., 1983; zur Loye et al., 1984), but still no direct evidence is available. Especially in a CO_2 environment the CaO might be transformed into the carbonate via Eq. 2 (McKee, 1979). The observation that increasing the CO_2 pressure lowers the gasification rate appreciably (McCoy et al., 1983), is an indication that the oxide is the active species in the CO_2 gasification and that carbonate formation is a sink for these species. So, the number of active sites might increase upon temperature increase, resulting in a higher apparent activation energy, as is observed for calcium.

The outgassing of Sr and Ba samples takes place at higher temperatures (Figure 4), in agreement with the stability order of the carbonate phase of the earth alkaline elements (McKee, 1979). Due to this higher temperature level the CO_2 formed by decomposition of the carbonates is directly converted to CO according to a catalyzed or uncatalyzed reaction. The higher stability of the carbonate phase also explains the lower activity of these elements: at the same temperature the number of active sites is lower than in the case of Ca. For barium also another gasification mode or different active sites might be operative, as is reported by Baker et al. (1984).

Outgassing and XRD show that Mg and Be remain in the oxidic phase even in CO_2, in agreement with the results of McKee (1979). The lower activity of these elements can probably be explained by the unfavorable equilibrium in Eq. 3, in which the peroxide is formed, as has also been suggested in the literature (Sears et al., 1980; Radovic et al., 1983).

From the observation that deactivation during gasification (Figure 1) is accompanied by an evolving XRD pattern (Figure 6 and zur Loye et al., 1984), due to crystallite formation, it can be concluded that sintering, i.e., loss of dispersion, is responsible for deactivation.

In this study the earth alkaline elements were applied as nitrates. As these are soluble it has to be expected that the dispersion after impregnation is the same for the whole series. XRD confirms this. Similar samples could have been obtained by ion exchange but not by the often-applied carbonates. Because of the comparable initial dispersion the sequence reported in this study represents the intrinsic activity order of the elements. It should be kept in mind that the fraction active sites probably is a function of the temperature and CO_2 pressure and therefore under other conditions the sequence might be different.

Conclusions

Earth alkaline elements catalyze the CO_2 gasification of activated carbon in the effectiveness order: Be $\approx$ Mg $<$ Ba $\approx$ Sr $<$ Ca. It has been shown that in contrast with some reported results in the literature the activity of the elements increases with increasing catalyst concentration. It is remarkable that the initial activity of Ca around 1,000 K is equal to that of K, a well-known gasification catalyst. However, with increasing carbon burn-off the catalyst shows a severe deactivation due to sintering. Under the gasification conditions applied the catalyst is not able to redisperse itself.

The apparent activation energy for gasification is hardly affected by the addition of the catalyst. The catalyst only increases the number of active sites.

The active catalyst species is tentatively proposed to be the oxide. Gasification involves an oxygen transfer via a formal peroxide formation. The activity order is determined by the counteracting effects of peroxide and carbonate formation that differs for the different elements.

When the problem of sintering of the catalyst, resulting in carbonate crystal formation, can be suppressed the earth alkaline elements are promising catalysts for gasification. They show a comparable activity and are less corrosive than the alkali elements.

Acknowledgment

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Notation

E_a = apparent activation energy, kJ/mol
k_o = Apparent preexponential factor, mol/s · mol carbon initially present
r_n = observed normalized reaction rate, mol/s · mol carbon initially present

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