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Alkali-Catalyzed Carbon Gasification in CO/CO$_2$ Mixtures: An Extended Model for the Oxygen Exchange and Gasification Reaction

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Based on the results of reactivity measurements and step–response experiments with labeled molecules an extended model for the oxygen exchange and gasification of carbon in CO/CO$_2$ atmospheres over alkali carbonate/carbon systems is given. The alkali catalysts studied (Na, K, Cs) contain considerable amounts of chemisorbed CO$_2$, nearly temperature and pressure independent, but easily exchangeable with gas-phase CO$_2$. For all three catalysts the gasification rate correlates well and in the same way with the amount of chemisorbed CO$_2$. Gasification is envisaged as the decomposition of C(O) complexes which are formed by interaction of the catalyst and the carbon. Oxygen exchange is catalyzed by the alkali catalyst species. Carbon–oxygen complexes, C(O), are not involved in this process. The proposed model can account for the observed pressure dependences; i.e., oxygen exchange is only proportional to the CO pressure and the gasification rate is proportional to the ratio of the CO and CO$_2$ partial pressures. In both reactions chemisorbed CO$_2$ is the important intermediate.

INTRODUCTION

Due to the increased effort in coal research at the beginning of this decade, recently much information on alkali-catalyzed carbon gasification has been published (*1–6*).

In their classical papers Walker *et al.* (*7*) and Ergun (*9*) assumed that the uncatalyzed gasification reaction with CO$_2$ proceeds via a two-step oxidation reduction cycle. Later this was confirmed by Strange and Walker (*9*) for the uncatalyzed gasification of high-purity graphite:

$$C_f + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C(O) + CO \qquad [1]$$

$$C(O) \xrightarrow{k_2} CO + C_f \qquad [2]$$

In the first reaction carbon "free sites" are oxidized by CO$_2$ to carbon–oxygen complexes C(O), a reaction step referred to in this paper as carbon oxidation. These C(O) complexes decompose in the rate-determining second step to CO; carbon gasification occurs.

The authors mentioned above explained the inhibiting effect of CO by a lowering of the steady-state concentration of C(O) complexes by the reverse of Reaction [1].

Kinetic measurements by Freund (*3*) on K- and Ca-catalyzed gasification of carbon with CO$_2$, and by Cerfontain *et al.* (*10*) and Kapteijn *et al.* (*11*) on the alkali–metal-catalyzed gasification indicate that catalysis is achieved by increasing the number of C(O) complexes reacting to CO. The fact that the activation energies for uncatalyzed and catalyzed carbon gasification are essentially the same (*11*) also reflects this. In the catalyzed reaction the inhibiting effect of CO is also proposed to be caused by lowering of the C(O) concentration according to Reaction [1] (*3, 11*). Based on the two-step mechanism (*3, 7, 11*) rate expressions have been derived for the uncatalyzed and catalyzed gasification. Under steady-state conditions and the assumption that the carbon oxidation (Reaction [1]) is in quasi equilibrium, generally these can be simplified (*3,*

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5, 8) to

$$r_n = \frac{k_2 N_c}{1 + (p_{CO}/K_1 p_{CO_2})} \qquad [3]$$

with

r_n = normalized gasification rate (mol C reacting per second and per mol C initially present).

k_2 = rate constant of Reaction [2] (s^{-1}).

K_1 = equilibrium constant of Reaction [1], usually between 0.05 and 0.2 (*4, 11*).

N_c = total number of carbon active sites: $[C_f] + [C(O)]$ (mol/mol C_i). Equation [1] is also a pathway for the oxygen exchange between CO_2 and CO. Using labeled molecules oxygen exchange can be measured directly:

$$^{13}CO_2 + CO \rightleftarrows {}^{13}CO + CO_2. \qquad [4]$$

The two-step kinetic reaction scheme (Eqs. [1] and [2]) implies that the same intermediate C(O) is operative in the oxygen exchange as well as in the gasification. Hence a similar dependence of the reaction conditions is expected.

In gasification the C(O) concentration is governed by the p_{CO}/p_{CO_2} ratio in the gas phase (cf. Eq. [3]). Cerfontain *et al.* (*10*) found, however, that the alkali-catalyzed oxygen exchange rate is only (linearly) dependent on the CO pressure, suggesting that the C(O) concentration is independent of the CO/CO_2 ratio. In order to shed more light on this apparent contradiction and to characterize the catalyst/carbon system, chemisorption experiments, employing ^{13}C-labeled CO_2 and CO, have been performed. Additionally, the pressure dependences of the gasification and oxygen exchange rate have been investigated in more detail. The results of these studies are presented in this paper.

EXPERIMENTAL

Experimental Apparatus

The experimental apparatus (Fig. 1) basically consisted of a flow control and gas-mixing section, two four-way valves (Valco) for switching three gas streams, a temperature programmable oven with reactor, a mass spectrometer (M.S., Balzer QMG 112) equipped with a turbomolecular pump unit (Balzer TSU 110), and a gas chromatograph (G.C., 2.5 m × 3.16 mm column packed with Porapak QS, TCD, 373 K, He flow rate 22 μmol/s) with an integrator (Spectra Physics 4270) for CO and CO_2 analysis. By using five (flexible) feed lines and miniature "quick-connects" (Swagelok), gas mixtures of up to three different gases could be applied.

The gases used (Matheson UHP for CO, H_2, He, and Ar and Matheson Purity for CO_2) were passed over a molecular sieve (Merck 3A) and, except for CO_2, over a copper catalyst (BASF BTS) to remove traces of water and oxygen. $^{13}CO_2$, 99.3% ^{13}C pure (Merck, Sharp, and Dohm), and ^{13}CO, 99% ^{13}C pure (Isotec), were used as received.

The samples were prepared by pore vol-

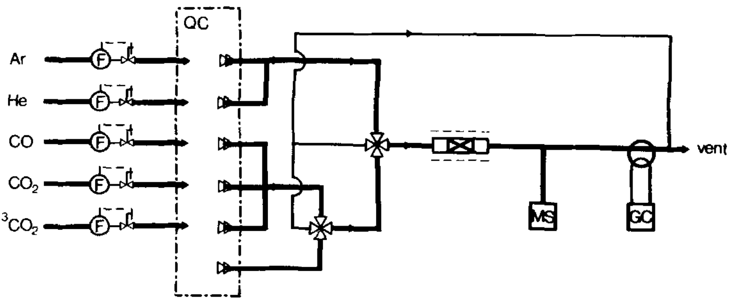

FIG. 1. Flow diagram of the experimental apparatus.

ume impregnation of Norit RX extra-activated carbon, $0.2 < d_p < 0.6$ mm, with an aqueous solution of alkali carbonate (Merck analytical grade). Samples containing 50 to 800 mg carbon were used in a quartz reactor (i.d. ranging from 3 to 10 mm, 15 cm length, a quartz frit, and at the outlet a quartz capillary, i.d. 1 mm). This reactor was connected to the system with (Swagelok) couplings, glued to the reactor. The reactor outlet contained a 20-μm stainless-steel frit to prevent blockage of the M.S. system. The flow leaving the reactor was split by a low volume tee for separate G.C. and M.S. analysis. Gas introduction in the M.S. was achieved by differential pumping through a 0.6-m-long, 0.1-mm-i.d. capillary past a leak valve with a rotary oil pump.

Before use, the samples were dried for 600 s at 473 K in a flow of 20 μmol/s Ar and subsequently gasified in CO_2 (20 μmol/s, 1000 K, 100 kPa) to approximately 20% burn off (B.O.). This pretreatment was used to avoid initial effects. The normalized gasification rate r_n, which is fairly constant between 20 and 50% B.O., was calculated from the G.C. analysis.

Gasification

Gasification rate measurements at a constant p_{CO_2}/p_{CO} ratio but at different partial pressures were performed by dilution of the CO_2 and CO feed flow with He at 1050 K and 125 kPa total pressure. CO and CO_2 pressures were varied between 15 and 90 kPa. Flow rates used were 30 μmol/s CO_2 and 30 μmol/s CO or 40 μmol/s CO_2 and 17.5 μmol/s CO. Each data point in the figures presented is the average of at least 5 G.C. analyses, with a standard deviation less than 2%.

Oxygen Exchange

Oxygen exchange measurements were performed below gasification temperatures with a $^{13}CO_2/^{12}CO$/He feed flow, after the gasification pretreatment. The oxygen exchange rate r_{ox} (mol oxygen transferred between CO and CO_2 per mol carbon initially present per second) was calculated both from the $^{12}CO_2$ and ^{13}CO production and from the ^{12}CO and $^{13}CO_2$ consumption rate. Conversions were always lower than 15% except for the highest rate measured at 30% conversion. In these experiments the CO or CO_2 pressure was varied (7–67 kPa), while keeping constant the other reactant pressure by dilution with helium.

CO_2 Chemisorption

CO_2 chemisorption measurements were performed in two ways: (a) by switching from $^{12}CO_2$ to Ar and after 30 s switching to $^{13}CO_2$ and vice versa, and (b) by directly switching from a $^{13}CO_2$ flow to a $^{12}CO_2$ flow which contained a small amount of the inert tracer He or vice versa. In both cases, referred to as type (a) and type (b), the total flow rate was 10 μmol/s. Chemisorption temperatures were varied between 473 and 973 K. Below 473 K physical CO_2 adsorption became evident. Moreover, at 673 K the CO_2 pressure was varied between 25 and 100 kPa by He dilution. The response of the catalyst system to these step changes was followed continuously by the mass spectrometer.

RESULTS

Figure 2 shows the oxygen exchange rate r_{ox} as a function of p_{CO_2} and p_{CO}. The oxygen exchange rate increases linearly with p_{CO} and is independent of p_{CO_2} over the pressure range studied. On the other hand, the gasification rate r_n, shown in Fig. 3 as a function of p_{CO_2}, reveals a fundamentally different pressure dependence. It only depends on the p_{CO_2}/p_{CO} ratio and not on the absolute partial pressure of CO_2 and CO, in agreement with other publications (*3*, *11*). The ratio between the reactivities of the samples, approximately 3, at the two different p_{CO_2}/p_{CO} ratios, $p_{CO_2}/p_{CO} = 1$ and $p_{CO_2}/p_{CO} = 2.3$, is somewhat higher than that predicted according to Eq. [3]. This difference can be explained bearing in mind that during the measurement with $p_{CO_2}/p_{CO} = 1$

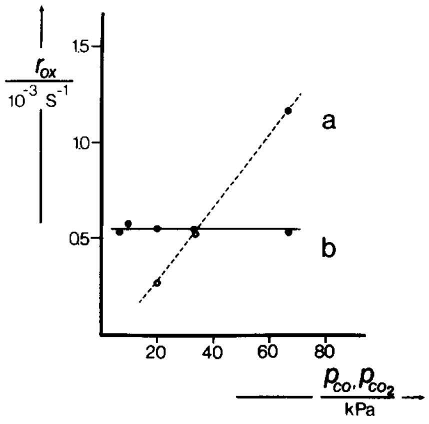

FIG. 2. Oxygen exchange rate r_{ox} at 950 K over K_2CO_3/Norit RX extra as a function of p_{CO_2} and p_{CO} (K/C = 0.019, total flow 30 μmol/s). (a) p_{CO_2} = 33 kPa. (b) p_{CO} = 33 kPa.

the p_{CO_2}/p_{CO} ratio is closer to thermodynamic equilibrium than during the measurement with $p_{CO_2}/p_{CO} = 2.3$ and, as a consequence, the driving force is smaller.

In the oxygen exchange measurements introduction of the $^{13}CO_2/^{12}CO$/He flow mixture consistently resulted in a desorption of $^{12}CO_2$. In order to quantify this CO_2 exchange, type (a) and type (b) chemisorption measurements were performed. As can be seen in Fig. 4, CO_2 exchange during measurements of type (a) is evident from the observed CO_2 desorption peak after introduction of the other CO_2 isotope, while during type (b) the CO_2 exchange is evident from the fact that $^{12}CO_2$ evolution still continues after the disappearance of He in the gas phase. In both cases the CO_2 exchange rate was very fast and, under the conditions used, only determined by the CO_2 flow rate. The amount of exchangeable CO_2 did not depend on sample size, CO_2 partial pressure, and temperature, even up to 973 K where gasification already takes place. The exchangeable CO_2 will subsequently be referred to as chemisorbed CO_2.

Both type (a) and type (b) measurements with samples of different loadings gave the same results except at very low loadings (K/C = 0.0091) where lower CO_2/M values were obtained in type (a) experiments. This is shown in Fig. 5, which gives the amount of chemisorbed CO_2 per alkali amount initially present as a function of the M/C ratio. For each alkali metal the CO_2/M ratio is not constant but increases with increasing M/C ratio. Furthermore, it is observed that the CO_2 chemisorption capacity increases in the series Na, K, Cs.

The carbon support itself did not chemisorb CO_2 to any measurable extent.

Similar experiments were carried out with $^{12}CO \rightarrow Ar \rightarrow {}^{13}CO$ step changes (flow rate, 10 μmol/s) over a sample that showed a large CO_2 chemisorption capacity (30 wt% K_2CO_3/Norit RX extra). This revealed that at temperatures below 573 K, where no CO disproportionation occurred, the alkali carbon system did not chemisorb any CO.

In Fig. 6 the gasification rate r_n at 1000 K is shown for catalytic systems studied as a function of the amount of chemisorbed CO_2 per amount of carbon initially present, CO_2/C. Clearly, the gasification rate at 1000 K increases with CO_2/C. The data points for all three catalysts (Na, K, and Cs) fall roughly on one single curve.

DISCUSSION

Comparison of Figs. 2 and 3 reveals that the oxygen exchange reaction at 950 K is already much faster than the gasification reaction at 1050 K. With an activation energy

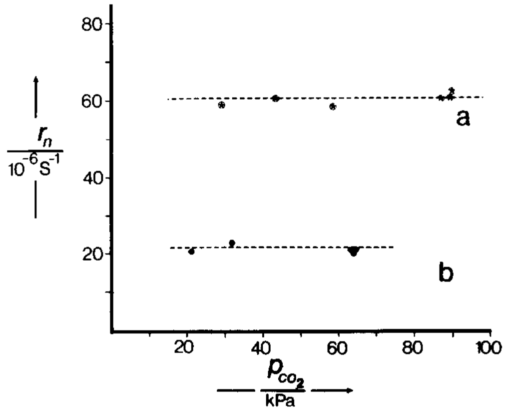

FIG. 3. Carbon gasification rate r_n at 1050 K of K_2CO_3/Norit RX extra as a function of p_{CO_2} and p_{CO} (K/C = 0.019). (a) p_{CO_2}/p_{CO}= 2.3, (b) p_{CO_2}/p_{CO} = 1.0.

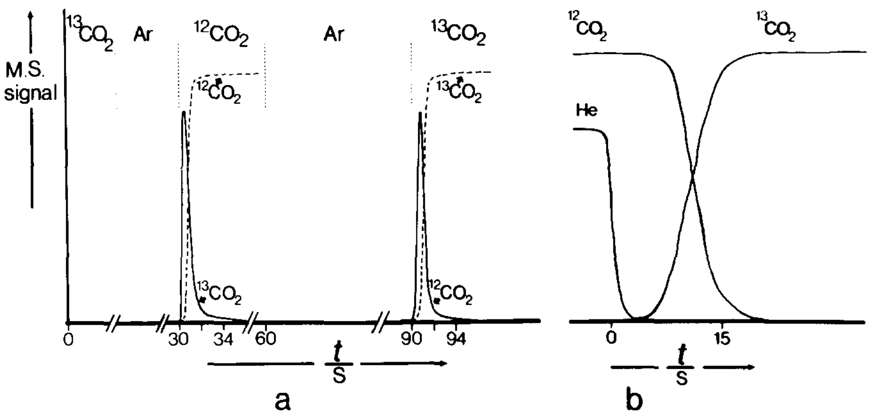

FIG. 4. Typical response curves of the alkali carbonate/Norit RX extra system on step changes of the gas phase. Type (a), $^{13}CO_2 \rightarrow Ar \rightarrow {}^{12}CO_2 \rightarrow Ar \rightarrow {}^{13}CO_2$, etc. Type (b), $^{12}CO_2$ (He trace) $\rightarrow {}^{13}CO_2 \rightarrow {}^{12}CO_2$ (He trace).

for oxygen exchange between CO_2 and CO over alkali carbonate/carbon systems of the order of 120–150 kJ/mol (*10*), the oxygen exchange will be faster by a factor of 150 than the gasification reaction at 1050 K in a CO and CO_2-containing atmosphere at $p_{CO_2}/p_{CO} = 1$. Thus, in principle the condition of fast oxygen exchange, in order to describe the gasification reaction by a two-step process (Eqs. [1]–[3]) is fulfilled. As pointed out in the Introduction, the observed pressure dependences of the oxygen exchange and gasification reaction (Figs. 2 and 3), however, cannot satisfactorily be explained by this simple scheme. An extended reaction model will be discussed.

The oxygen exchange can be described by

$$^{13}CO_2 + * \xrightarrow{k_5} {}^{13}CO + (O)* \quad \text{(forward)} \qquad [5a]$$

$$CO + (O)* \xrightarrow{k_{-5}} CO_2 + * \quad \text{(backward).} \qquad [5b]$$

Under the assumption of steady-state conditions and a constant total number of active sites N_t, the rate expression becomes

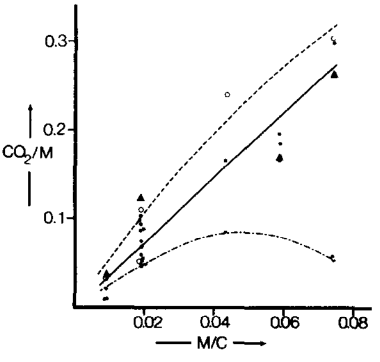

FIG. 5. The amount of CO_2 chemisorbed per alkali atom initially present as a function of the alkali/carbon atomic ratio for different alkali carbonate-impregnated Norit RX extra samples, determined from step-response experiments. (★) Na, (●) K, (○) Cs (type (a) measurements); (▲) K (type (b) measurements).

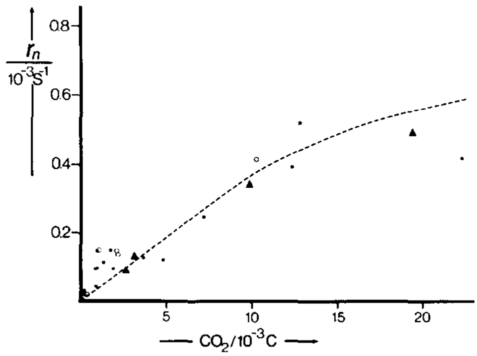

FIG. 6. Carbon gasification rate r_n at 1000 K of alkali carbonate/Norit RX extra as a function of chemisorbed CO_2 per amount of carbon initially present (CO_2 flow 20 μmol/s). Key as in Fig. 5.

$$r_{ox} = r_5 = r_{-5} = \frac{k_5 N_t p_{CO_2}}{1 + K_5(p_{CO_2}/p_{CO})} \quad [6]$$

with $K_5 = k_5/k_{-5}$.

Equation [6] describes the observed CO pressure dependence (Fig. 3) only if the equilibrium of Reaction [5] is far to the right, i.e., K_5 large, and hence

$$r_{ox} = k_{-5}N_t p_{CO}. \quad [7]$$

This Rideal-type reaction mechanism is supported by the absence of any CO chemisorption, in agreement with the fact that the catalyst has no *d*-electrons available for coordination of the CO molecule.

On the other hand, CO_2 interacts so strongly with the alkali system that its chemisorption is nearly temperature and pressure independent. This polar molecule probably forms mono- or bidentate carbonate ions as has been proposed for basic oxides, such as ZnO and MgO (*13, 14*). In view of this strong interaction it seems logical that the *(O) species in Eq. [5a] does not represent the stoichiometry of the active site, but that a carbonate moiety $*(CO_3)$ is a more appropriate description. Recent results support this. Hence the oxygen exchange is written as

$$*(CO_2) + CO_2 \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} *(CO_3) + CO. \quad [8]$$

The fact that K_8 must be large implies that almost all sites for oxygen exchange are in the $*(CO_3)$ form, independent of the gas-phase composition. Therefore, if these sites were identical to the oxygen-containing complexes proposed in the two-step gasification model (Eqs. [1] and [2]), the gasification rate, proportional to the number of these sites, would be independent of the CO_2 and CO partial pressure. Obviously, this is in contradiction with Fig. 3. Hence it is concluded that the oxygen exchange occurs on alkali catalyst sites without direct involvement of the carbon itself. Additional evidence supporting this result comes from similar observations made for the comparable reaction system D_2/H_2O by Mims and Pabst (*1*). In their study the oxygen exchange rates are even much higher and probably reflect the lower bond strength of the oxygen in the H_2O molecule than that in the CO_2 molecule.

In the alkali/carbon system chemisorbed CO_2 is, although strongly bonded, easily exchanged ("refreshed") with gas phase CO_2:

$$*(CO_3) + {}^{13}CO_2 \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} *({}^{13}CO_3) + CO_2. \quad [9]$$

The amount of chemisorbed CO_2 shows a good correlation with gasification activity, as is evident from Fig. 6. This relation also becomes evident from other observations. Ratcliffe (*15*) has carried out temperature-programmed desorption experiments with alkali/carbon systems on which $^{13}CO_2$ had been chemisorbed. In the temperature range of 700–760 K the chemisorbed complex decomposed into ^{13}CO and an oxidized catalyst. After this decomposition the release of ^{12}CO was observed at higher temperatures. The intermediate stage of oxidation of the carbon in CO_2 by the catalyst with formation of C(O) has been demonstrated recently by measurements of *in situ* FTIR spectroscopy (*16*). To account for the fact that the C(O) formation must be dependent on the CO_2 pressure, cf. Eq. [3], it is assumed that this reaction is "CO_2-assisted;" the incoming CO_2 pushes the oxygen to the carbon surface. At first sight this might seem far-fetched but even inert gas molecules can enhance the migration of oxygen atoms over a carbon surface in CO_2 gasification (*18*). In the present model the catalyst acts as a "service-hatch" of oxygen to increase the concentration of C(O) species. Indications for this can be found in the observation of Dunks (*17*) that the gasification rate of graphite with CO_2 in molten Na_2CO_3 is a function of the amount of carbonate ions present in the melt. Such a carbonate ion might be considered as a transition state between an oxidized catalyst site plus CO_2 and the oxidized carbon.

These considerations lead to the carbon

oxidation reaction

$$*(CO_3) + C_f \xrightarrow[k_{10}]{CO_2} *(CO_2) + C(O), \quad [10]$$

where C_f denotes a carbon "free-site" in the vicinity of the catalyst species.

Equation [10] is followed by a fast removal of the $*(CO_2)$ via Eq. (8). Finally the gasification step is similar to that of the uncatalyzed reaction:

$$C(O) \xrightarrow{k_2} CO + C_f. \quad [2]$$

The inhibition of the gasification by CO can be explained either by blocking of the carbon free sites, $C_f + CO \rightarrow C_f(CO)$, or by removal of the C(O) complexes according to the backward reaction [1]. The absence of CO chemisorption observed here below 573 K does not favor the first possibility.

Based on the kinetic scheme constituted by Reactions [1], [2], and [8]–[10] and under the assumption of steady-state conditions, a constant number of catalyst sites N_t and carbon sites N_c, and Reaction [2] being the slowest step in the gasification process, the following rate expressions can be derived,

$$r_{ox} = k_{-8}[*(CO_3)]p_{CO} = \frac{k_{-8}N_t p_{CO}}{R} \quad [11]$$

$$r_n = k_2[C(O)] = \frac{k_2 k_{10} N_c p_{CO_2}}{k_{10} p_{CO_2} + k_{-1} R(p_{CO}/N_t)} \quad [12]$$

where

$$R = 1 + \frac{p_{CO}}{K_8 p_{CO_2}} + \frac{k_{10}[C_f]}{k_8}. \quad [13]$$

Since the oxygen exchange reaction [8] occurs at a much higher rate than the carbon oxidation [10] and $K_8 \gg 1$, R approaches 1. Hence Eqs. [11] and [12] take the form of Eqs. [7] and [3], respectively. This shows that the extended reaction scheme proposed here is in agreement with the experimentally established rate expressions.

In the foregoing considerations chemisorbed CO_2 plays a crucial role. In view of the correlation between the amount of chemisorbed CO_2 and gasification activity, *grosso modo* irrespective of loading and alkali metal (Fig. 6) this is not surprising, but it needs more specification.

Per alkali atom the amount of chemisorbed CO_2 increases with the alkali loading. This indicates that although the specific surface area is sufficiently large (1200 m^2/g), the alkali atoms will form clusters at increasing loading; otherwise the increasing amount of chemisorbed CO_2 cannot be explained. In the limit carbonate crystals will be formed which do not exchange CO_2 any longer. Therefore the curve for Na (Fig. 5) passes through a maximum. Na has a high tendency to form crystals, whereas Cs has the least tendency and remains in a dispersed state on the carbon, as follows from *in situ* FTIR spectra (*16*).

From the presented results it is concluded that the amount of chemisorbed CO_2 is a measure for the number of active sites in the oxygen exchange. The gasification rate is proportional to this amount since the free carbon sites that can be oxidized must be located in the vicinity of the catalyst.

The complete reaction scheme describing the oxygen exchange, CO_2 chemisorption, and gasification is depicted in Fig. 7. The kinetic considerations indicate that $*(CO_3)$ and C_f are the principal species under reac-

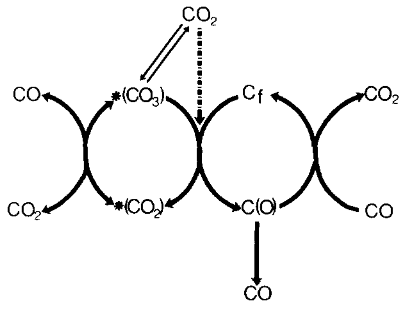

FIG. 7. Reaction scheme for oxygen exchange and carbon gasification in CO/CO_2 atmospheres over alkali/carbon systems.

tion conditions. The dashed line indicates the CO_2-assisted carbon oxidation. On the left-hand side the oxygen exchange takes place with sole involvement of alkali species. The right-hand side represents the CO inhibition. The carbon is gasified by decomposition of the C(O) into gaseous CO.

CONCLUSIONS

Based on reactivity measurements and step–response experiments with labeled molecules an extended model is proposed for oxygen exchange and carbon gasification in CO/CO_2 atmospheres over alkali/carbon systems. This model can account for the observed dependence of the reaction rates on the partial pressure of CO and CO_2.

An important role in this reaction model is played by chemisorbed CO_2. The amount is nearly independent of pressure and temperature and increases with increasing alkali loading. All this chemisorbed CO_2 is easily exchanged with gas-phase CO_2. For all three catalysts studied (Na, K, Cs) the gasification rate correlates well and in the same way with the amount of chemisorbed CO_2.

Oxygen exchange occurs by reaction of gaseous CO with the chemisorbed CO_2 accompanied by formation of CO_2, followed by a back reaction with another CO_2 molecule. The gasification phenomena proceed at a much lower rate. It is proposed that the oxidized catalyst site is able to oxidize the carbon in its vicinity, thereby assisted by CO_2. The oxidized carbon sites either slowly decompose with formation of CO (gasification) or are reduced by gas-phase CO (inhibition).

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