

Potassium-Catalysed Carbon Gasification in CO₂ studied by Transient Techniques.

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ABSTRACT

The K₂CO₃/carbon system has been studied under gasification conditions applying transient techniques, *i.e.* temperature programmed desorption and step-response experiments, in combination with labelled CO₂ (¹³CO₂ and C¹⁸O₂). Detailed information on the mode of catalytic action of potassium, the composition of the catalytically active alkali species and the rate of the different processes, is obtained.

Step-response experiments reveal that the potassium/carbon system is very dynamic. Upon a gas phase step change from a reactive to an inert gas phase at 1000 K the effluent gas composition is strongly affected by secondary reactions of desorbed species with the alkali catalyst on the carbon surface. The composition of the catalytically active alkali species changes with increasing gasification temperature. At 1000 K it can be represented by a cluster composed of several potassium phenolate species and contains chemisorbed CO₂ and reactive oxygen, whereas at 1200 K merely highly reactive potassium phenolate species are present. From step-response and temperature programmed desorption experiments it can be concluded that during gasification in CO₂, gas phase CO is inserted into the carbon matrix.

A model proposed for the mechanism of the potassium-catalysed gasification of carbon in CO₂ can adequately describe the observed transient and steady state behaviour taking into account that during steady state gasification in CO₂ carbon-oxygen intermediates of different stability are present which, depending on temperature, simultaneously desorb on exposure to an inert.

INTRODUCTION

Potassium-catalysed gasification is usually kinetically described by a two step model, in which the oxidation/reduction cycle (eq. 1) represents all (faster) steps preceding gasification (eq. 2) [1].



Kinetic studies [1-3] have shown that addition of alkali catalysts increases the steady state concentration of carbon-oxygen intermediates and does hardly affect the equilibrium ($K_1 = k_1/k_{-1}$) and intrinsic rate constant (k_2).

By applying labelled molecules [4-6] it was concluded that oxygen exchange between H₂O, H₂ and CO₂, CO is catalysed by the alkali catalyst and occurs without involvement of carbon-oxygen intermediates. The catalytically active site is envisaged as an alkali cluster M_xO_y (*), anchored to the carbon surface via phenolate groups. This cluster can contain chemisorbed CO₂ (CO₂-*), up to CO₂/M_a = 0.3 [3,4,7-9], which is present at gasification temperatures. This CO₂ is easily exchanged with gas phase CO₂ through eq. 4 [10].

A model for the potassium-catalysed gasification of carbon in CO₂ can be represented by eqs. (1,2,4-7), in which *, O-* and CO₂-* represent the different states of the catalytically active alkali cluster, and C_f and C(O) the carbon sites active for gasification.





Temperature programmed desorption (TPD) and step-response experiments (SRE) in principle provide information on the reaction, intermediates and rates of elementary processes, especially when labelled molecules are applied [4,11-13]. Application of $^{13}\text{CO}_2$ enables us to distinguish between CO originating from gas phase reactant (^{13}CO) and CO from the carbon (CO), C^{18}O_2 to trace the behaviour of the oxygen in the system under study.

In this paper the results are presented of applying ^{13}C and ^{18}O labelled CO_2 in TPD and SRE experiments, that were designed to obtain detailed mechanistic information on the reactions taking place during catalysed CO_2 gasification and the role of the catalyst.

EXPERIMENTAL

Throughout this paper all labelled species are addressed with a prefix, viz. ^{18}O and ^{13}C , whereas in all cases C and O without prefix refer to ^{12}C and ^{16}O . Experimental details can be found elsewhere [14].

All gases used are of HP or UHP grade and are purified (O_2 and/or H_2O removal) before being fed to the gas mixing sections. $^{13}\text{CO}_2$ and C^{18}O_2 (MSD isotopes; 99.3 % ^{13}C and 90-91 % ^{18}O pure, respectively) were used as received. The ^{18}O in the C^{18}O_2 feed is present as CO^{18}O ($\approx 20\%$ of the total CO_2).

The catalysed gasification in CO_2 was studied with 50-200 mg samples of $\text{K}_2\text{CO}_3/\text{Norit RX}$ extra ($\text{K}/\text{C}_i = 0.019$). The alkali-metal content of fresh and used samples was determined by ICP-AES.

In step-response experiments (SRE) CO_2/Ar mixtures that flow through the sample at gasification temperatures are exchanged with an Ar flow and *vice versa* and the response of the sample on this change is followed continuously by a PC controlled MS. The raw MS data are corrected for background levels, fragmentation contributions (CO_2 to CO) and MS sensitivity for the different molecules, and converted into molar flowrates of the gaseous species leaving the reactor.

For the TPD experiments the samples were pretreated by TPD of the fresh sample (reduction) and exposed to a reactive gas mixture at different temperatures. The TPD patterns were obtained in a helium flow of $20 \mu\text{mol}\cdot\text{s}^{-1}$ at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ up to 1200 K, followed by an isothermal period of 30 minutes at 1200 K. The desorption rates of CO and CO_2 are expressed as (mol desorbed).(mol K actually present) $^{-1}\cdot\text{s}^{-1}$. Simultaneously GC analysis was performed to quantify the (labelled) CO and CO_2 production rates monitored by the MS.

RESULTS AND DISCUSSION

Upon introduction of Ar after $^{13}\text{CO}_2$ exposure at 1000 K (figure 1A) a fast declining $^{13}\text{CO}_2$, CO_2 and ^{13}CO production, reaching the baseline within 50 seconds, and a tailing CO production, lasting up to 5 minutes, is observed. The composition of the product gas in the initial period is strongly influenced by fast CO_2 and oxygen exchange reactions, by which part of the primary desorption products ($^{13}\text{CO}_2$ and CO) are converted into CO_2 or ^{13}CO . Figure 1B shows after correction for oxygen exchange reactions the primary desorption rates of CO (amu 28+44), ^{13}CO (amu 29-44) and $^{13}\text{CO}_2$ (amu 45+44). Amounts are given in table 1.

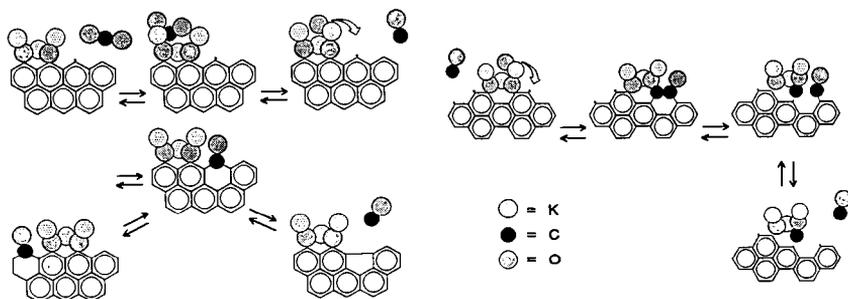
Upon reintroduction of $^{13}\text{CO}_2$ (figure 1C) chemisorption and sample oxidation is observed. Sample oxidation can be deduced from the data in figure 1C by considering that under steady state conditions CO and ^{13}CO are produced in a 1:1 ratio (corrected for oxygen exchange with $^{13}\text{CO}_2$). Chemisorption amounts can be calculated by comparing the total carbon in the product gas molecules with that of a blanc run with an inert SiC sample (figure 1D). After approximately 50 seconds steady state gasification and oxygen exchange conditions are reached. Variation of the time span in argon at 1000 K before exposure to $^{13}\text{CO}_2/\text{Ar}$ did not have any significant influence on these results.

In figure 2 the response curves for a gas phase step change from 10% $^{13}\text{CO}_2/\text{Ar}$ to Ar and *vice versa* at respectively 1100 and 1200 K are shown, with an analogous data treatment.

At 1200 K all $^{13}\text{CO}_2$ is converted, resulting in equal CO and ^{13}CO production rates, whereas at 1100 K also $^{13}\text{CO}_2$ and CO_2 are present under steady state conditions. Upon a gas phase step

change to Ar no $^{13}\text{CO}_2$ or CO_2 is produced at both temperatures. However, it is striking that together with CO and in the absence of $^{13}\text{CO}_2$ a considerable amount of ^{13}CO desorption is observed. Reintroduction of $^{13}\text{CO}_2$ at 1100 K shows both a CO overshoot due to gasification and a ^{13}CO overshoot due to oxidation. At 1200 K steady state gasification conditions are directly restored without any overshoot and no $^{13}\text{CO}_2$ or CO_2 is detected in the product gas. All $^{13}\text{CO}_2$ is converted. However, a mass balance calculation shows that upon reintroduction of $^{13}\text{CO}_2$ at 1200 K a certain amount of ^{13}C is not accounted for in the product gas, suggesting an incorporation in the sample.

Similarly to the uncatalysed gasification [15] the CO release can only be well described by two parallel desorption processes. Therefore it is proposed that, apart from the catalytic clusters, two types of carbon-oxygen complexes are present, in semiquinone structures and in carboxylic structures. The former can be converted in to the more reactive latter species on armchair edges of the carbon [15]. A schematic picture is given below. Left are indicated reaction on the zig-zag edge and right on the armchair edge.



The main desorption products in a TPD after exposure to 10% $^{13}\text{CO}_2$, Ar at 673 to 1000 K are $^{13}\text{CO}_2$, released between 500 to 900 K, followed by CO above 900 K (figure 3). Additionally, between 700 and 1000 K, smaller amounts of CO_2 and ^{13}CO are observed. After exposure at 1000 K also a small amount of ^{13}CO above 1000 K is observed (figure 3C). This amount increases if the sample has been exposed to a higher partial pressure of $^{13}\text{CO}_2$.

Apparently the reduced sample is only partially reoxidised by CO_2 at 673 K, and increasingly more at higher temperatures. Therefore, the CO_2 desorption amounts decrease with exposure temperature, whereas the CO release increases. The latter is ascribed to the reduction of the potassium oxide in the cluster by the carbon or the decomposition of the phenolate groups. The small CO evolution around 950–1000 K is ascribed to decomposition of chemisorbed CO_2 into CO and O^* . This is the unlabelled CO_2 since the $^{13}\text{CO}_2$ had already been replaced by fast exchange.

During TPD oxygen exchange takes place when $^{13}\text{CO}_2$ and CO are both present (around 900 K). TPD confirms the SRE experiments that some ^{13}CO is inserted in the sample, probably in the carbon, analogously to the uncatalysed case.

A TPD pattern obtained after C^{18}O_2 exposure at 673 K (figure 4A) shows C^{18}O_2 and CO^{18}O desorption below 1000 K and a CO and C^{18}O release spread over a wide temperature range. After C^{18}O_2 exposure at 1000 K (figure 4B) the CO and C^{18}O desorbed is much larger and mainly takes place above 1000 K, in agreement with fig. 3. After gasification in C^{18}O_2 and subsequently in CO_2 , the TPD pattern (figure 4C) shows low temperature CO_2 desorption and CO has become the main desorption product above 1000 K, whereas still a small amount of C^{18}O desorption is observed. Compared to fig. 3C it is obvious that chemisorbed C^{18}O_2 must have been exchanged rapidly with CO_2 , but that part of the ^{18}O in the sample is hard to exchange (fig. 4B and C).

SRE experiments with CO_2 and C^{18}O_2 indicate that the oxygen in the potassium cluster can be exchanged (1000 K) within 5 minutes ($^{18}\text{O}/\text{K} = 1$) by direct exchange of CO_2 with chemisorbed C^{18}O_2 and exchange of oxygen in the cluster with chemisorbed CO_2 , yielding C^{18}OO .

Also in figures 4 the shoulder in the CO release, around 950-1000 K can be ascribed to decomposition of strongly chemisorbed CO₂.

In summary the step-response and temperature programmed desorption experiments, using labelled CO₂, have revealed the following principal phenomena. The active potassium oxide cluster still contains chemisorbed CO₂ at 1000 K, not above 1100 K. This chemisorbed CO₂ is easily exchanged with gas phase CO₂, and can exchange oxygen present in the cluster. It can decompose upon formation of CO and reactive oxygen in the cluster. The amount of oxygen in the cluster decreases with increasing temperature. This oxygen reacts with the carbon where it forms surface complexes, that can decompose to CO, which represents the gasification step. Two surface complexes are distinguished that decompose at different rates. The CO desorption is reversible and accounts for the incorporation of CO in the sample. All these phenomena will contribute to the gasification rate.

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Table 1. Desorption products (μmol) after a gas phase step change from 10% ¹³CO₂/Ar to Ar at different temperatures. $F_t = 20 \mu\text{mol}\cdot\text{s}^{-1}$, $K_a = 115 \mu\text{mol}$

	CO	¹³ CO	CO ₂	¹³ CO ₂
T = 1000 K	9.8	4.8	2.8	8.0
T = 1100 K	6.5	2.3	-	-
T = 1200 K	19	8.5	-	-

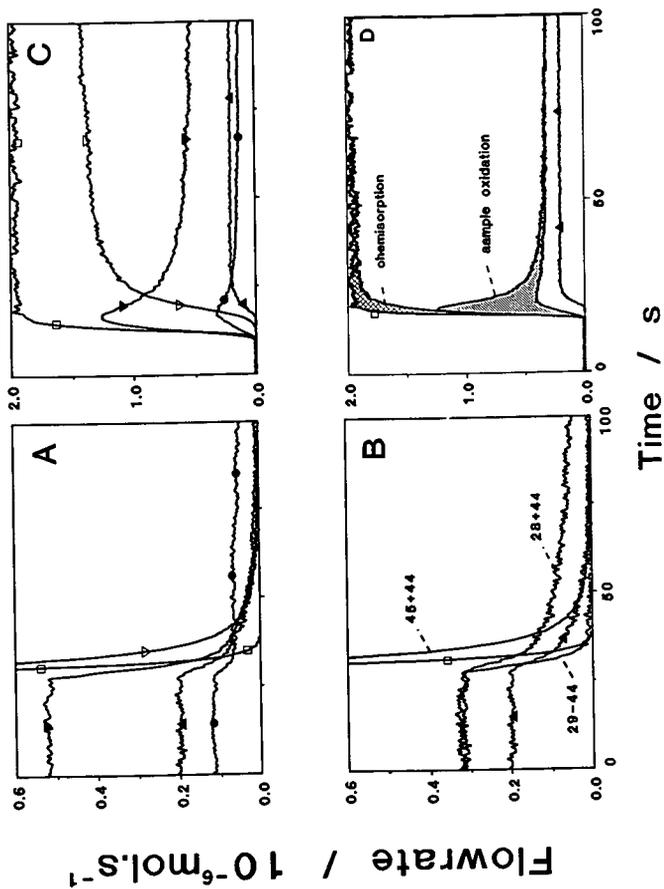


Figure 1 : Response curves for a gas phase step change from 10% ¹³CO₂,Ar to Ar (A,B) and vice versa (C,D) at 1000 K. (A and C represent the measured signals, B and D the converted data (see data handling)).

Key: CO; ¹³CO; C¹⁸O; CO₂; ¹³CO₂;
 CO¹⁸O; C¹⁸O₂; blanc run.

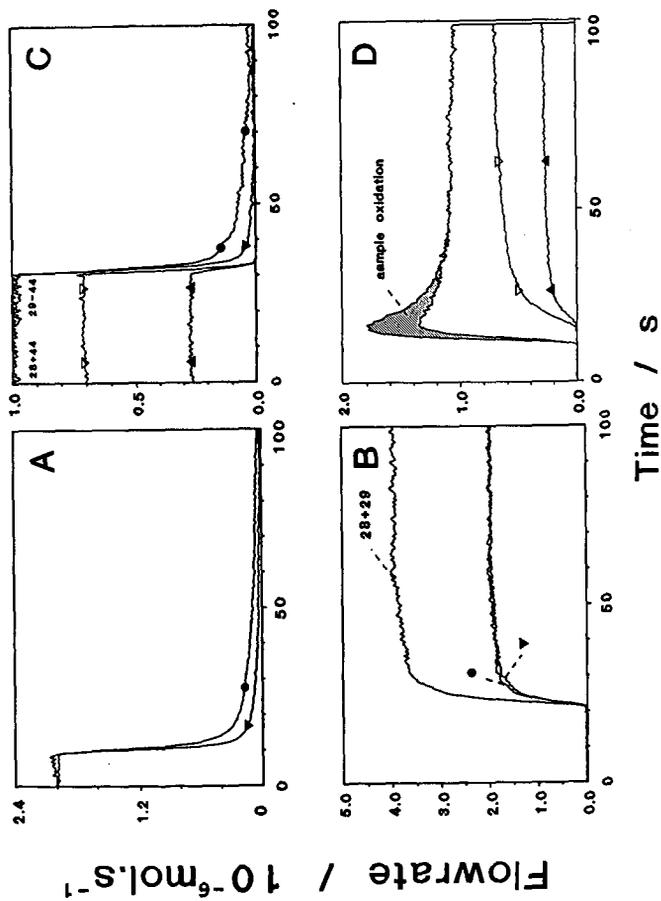


Figure 2 : Response curves for a gas phase step change from 10% $^{13}\text{CO}_2$, Ar to Ar (A,C) and vice versa (B,D) at different temperatures (key as in figure 1).
 A,B. $T = 1200 \text{ K}$; C,D $T = 1100 \text{ K}$.

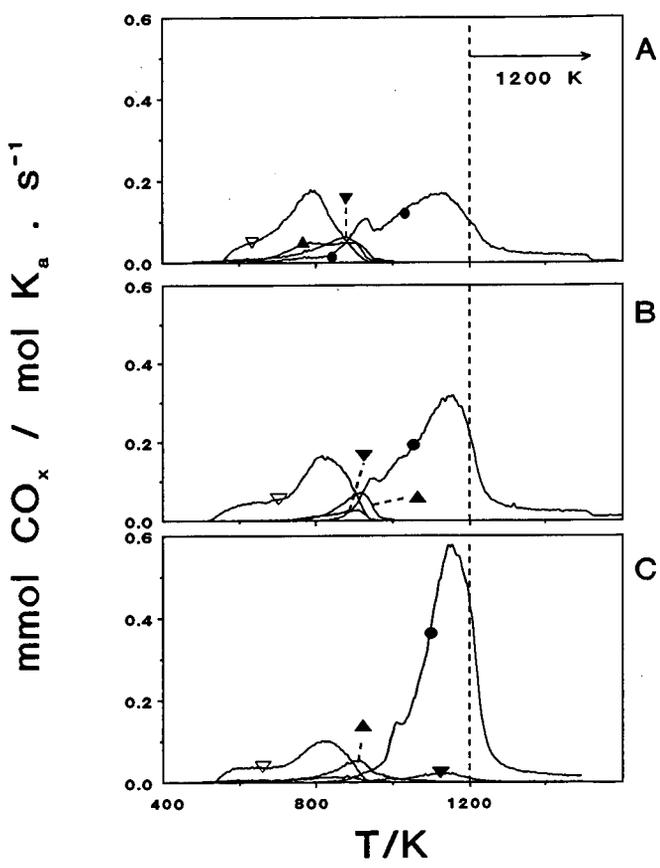


Figure 3 : TPD patterns obtained after exposure in 10% $^{13}\text{CO}_2$, Ar at: A. 673 K; B. 873 K; C. 1000 K (key as in figure 1)

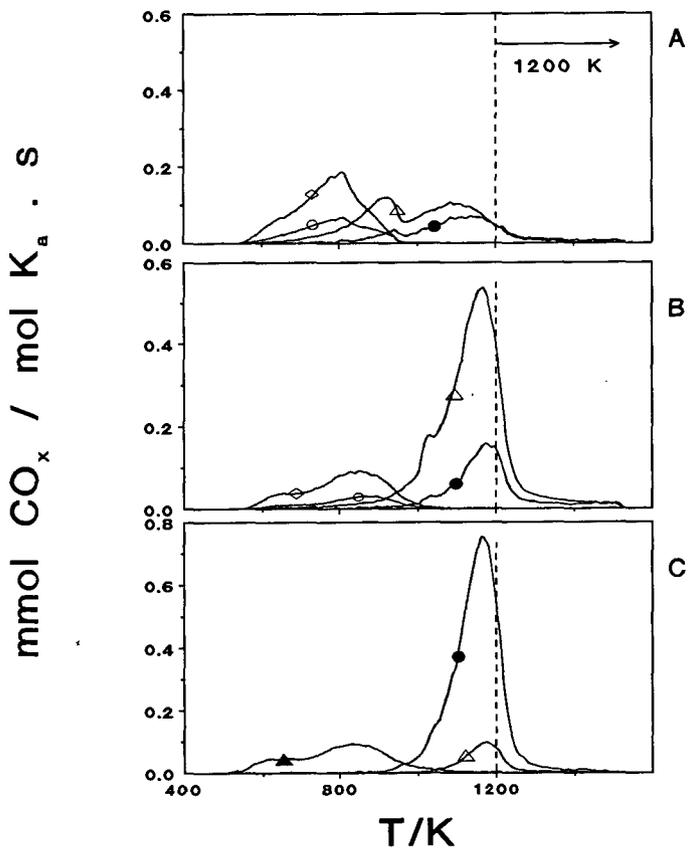


Figure 4 : TPD patterns obtained after different sample treatments:
 A. C^{18}O_2 @ 673 K
 B. C^{18}O_2 @ 1000 K
 C. C^{18}O_2 @ 1000 K \longrightarrow CO_2 @ 1000 K (key as in figure 1)