

A Transient Kinetic study of the Gasification of Carbon in CO₂.

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ABSTRACT

A transient kinetic study, using labelled CO₂, has been conducted on the gasification of carbon in CO₂. Step-response (SRE) and temperature programmed desorption (TPD) experiments indicate that during steady state gasification at least two types of oxygen complexes are present at the carbon surface, both yielding CO. Upon exposure to an inert gas at gasification temperatures the decomposition of one of these complexes is fast and decays within seconds, whereas the other lasts for several minutes. However, both contribute to the overall gasification activity. Moreover, from the presence of ¹³CO in both SRE and TPD experiments it is concluded that CO chemisorption or insertion takes place. A mechanism for the gasification reaction in CO₂ is proposed in which stable carbon-oxygen complexes can be transformed into the more reactive complexes, and in which CO insertion is included.

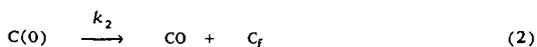
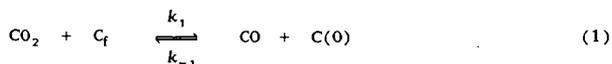
INTRODUCTION

The kinetics of carbon and coal gasification have been extensively studied. In most studies the rate of gasification is measured and interpreted under specified conditions. From both a practical and theoretical point of view it would be highly desirable if a method existed by which, independent of carbon type, heat treatment history or burn-off, the rate parameters which govern the gasification process could be determined.

Temperature programmed desorption (TPD) and step-response experiments (SRE), two commonly applied techniques in the field of heterogeneous catalysis, are increasingly used to determine the rate parameters and the total number and stability of active carbon-oxygen complexes present during steady state gasification of carbonaceous materials. Kapteijn and Moulijn [1] already outlined the possibilities of these transient techniques, compared to steady state measurements, in studies concerning (catalysed) carbon gasification. This experimental approach is gaining a lot of attention [2-7].

A step change in the gas phase composition at reaction temperatures, *i.e.* from a reactive to an inert gas flow and *vice versa* or from one reactive to another (labelled) reactive gas flow and analysis of the response curves of the sample under investigation, provides information on the reaction, *viz.* the amount and stability of carbon-oxygen complexes and rates of elementary processes.

An important feature of applying ¹³CO₂ is that it enables us to distinguish between ¹³CO produced by gas phase oxidation of the active carbon sites and CO production originating from the carbon structure. The assumption in this two-step model (eqs.1,2) that equation (2) is the rate determining step can easily be confirmed by a gas phase step change from ¹³CO₂ to an inert at gasification temperature; a fast declining ¹³CO production is accompanied by a long tailing CO production.



A gas phase step change from ¹³CO₂ to Ar will show if desorbing CO is capable of picking up a surface oxygen by reversed reaction (1) (¹²CO₂ formation) and if during gasification insertion of gas phase CO has taken place, which is the case if a tailing ¹³CO production is observed.

The most important feature of step-response experiments between $C^{18}O_2$ and CO_2 is that it provides a means to trace and quantify all reactive oxygen present on the carbon sample, while maintaining steady state gasification conditions.

The aim of this study was to obtain a more detailed description for the mechanism of the carbon gasification reaction, thus providing a sound basis for the selection of a kinetic model and its derived rate expression. In this paper results are presented of transient kinetic gasification experiments (1200–1250 K) with (labelled) CO_2 , together with TPD experiments after partial gasification. These results and their implications with respect to the mechanism of the gasification reaction are discussed.

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 .

Reactants/samples

The model carbon used in this study is Norit RX1 Extra, an acid washed, steam activated peat char with a high specific surface area [6].

All gases used were of HP or UHP grade and are purified (O_2 and/or H_2O removal) before being fed to the gas mixing sections. $^{13}CO_2$ and $C^{18}O_2$ were used as received (99% pure ^{13}C and 90–91% pure ^{18}O , MSD Isotopes) and mixed with Ar in lecture bottles. The O present in the $C^{18}O_2$ feed is present as $CO^{18}O$ ($\approx 20\%$ of the total CO_2).

Apparatus

The kinetic equipment, described in detail elsewhere [6], basically consists of three gas mixing sections. By means of a pneumatically actuated four-way valve in SRE two selected gas flow lines can be exchanged instantaneously and isobaric over the carbon sample.

The product gas is analysed by GC and by MS. Signal analysis, mass selection and sampling rate are controlled by a personal computer, equipped with Analog Devices RTI cards, through which data were collected and stored for further quantitative analysis. Up to 12 m/e values can be scanned consecutively with a minimum delay of 47 ms per m/e value. The raw MS data are corrected for background levels, fragmentation contributions (CO_2 to CO) and MS sensitivity for the different molecules. Quantitative interpretation of the step-response curves was performed by comparison with a gas phase step change performed over an inert SiC sample under exactly the same experimental conditions. These blank runs exhibit the same response curves for CO_2 and showed that under reaction conditions the equipment had a time constant (the time to fall to 1/e of the initial step change) of less than 1 s. Thus the rate processes with larger time constants, i.e. with rate constants smaller than 1 s^{-1} , can be determined.

Experimental procedures

Step-response and steady state gasification experiments were performed at 1200 and 1250 K with, unless stated otherwise, a carbon sample of initially 100 mg and a flow rate of $20\ \mu\text{mol}\cdot\text{s}^{-1}$. In order to obtain a reproducible carbon sample each sample was dried *in situ* ($T = 423\text{ K}$, He) and was gasified at 1200 K up to approximately 20% burn-off.

All step-response experiments were performed several times in order to check their reproducibility. The response curves after a gas phase step change from CO_2 , Ar to Ar and *vice versa* were investigated as a function of temperature (1200–1250 K), partial pressure of CO_2 (4 – 100% CO_2) and carbon burn-off (20–50%).

In some cases at the end of the step-response or gasification experiment a temperature programmed desorption (TPD) in helium, in order to characterise the sample by its desorption products, was performed. TPD was done with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ up to 1273 K, followed by an isothermal period of 10 min at 1273 K. The amounts of CO released, expressed as $\text{mol CO}\cdot\text{mol C}_a^{-1}\cdot\text{s}^{-1}$, are plotted as a function of temperature. During TPD experiments none or a negligible amount of low temperature CO_2 desorption was observed, which, for clarity, is not shown in the figures.

RESULTS AND DISCUSSION

After a gas phase step change from 10% $^{13}\text{CO}_2$, Ar to Ar at 1200 and 1250 K, besides CO also ^{13}CO production is observed (figure 1). In both cases $^{13}\text{CO}_2$ disappears nearly instantaneously and the total CO production ($\text{CO} + ^{13}\text{CO}$) immediately drops to about half the steady state value and exhibits a fast continuing decay in the first ten seconds, followed by a tailing that lasts for several minutes, which is mainly due to CO. This behaviour is observed after all gas phase step changes from a reactive to an inert gas phase at gasification temperatures. These results indicate that ^{13}CO is inserted or chemisorbed at the carbon surface [9-11], and is released in two distinct ways. The CO production could only be described by two different parallel desorption processes. A single exponential decay or Elovich type desorption [8] were unable to do so.

In figure 2 the response curves for different gas phase step changes involving C^{18}O_2 at 1200 K are shown. A gas phase step change from C^{18}O_2 to Ar shows a tailing C^{18}O production (figure 2B, insert), similar to the results of figure 1. A step change to CO_2 results in a sharp CO^{18}O production peak and a decaying C^{18}O production that disappears earlier (figure 2A) than upon exposure to an inert. The total $\text{CO} + \text{C}^{18}\text{O}$ production remains constant, indicating no disturbance of the steady state gasification. A blank experiment with a SiC bed (figure 2C) shows that the sharp CO^{18}O production peak in the initial seconds after the step change, when both C^{18}O_2 and CO_2 are present, must be ascribed to gas phase exchange through eq.(3).



The longer tailing CO^{18}O evolution in figure 2A compared to that in figure 2B indicates that CO, produced by CO_2 gasification, picks up ^{18}O from the carbon surface, confirming the reversibility of reaction (1). The faster disappearance of C^{18}O by a step change to CO_2 instead of Ar is only partially explained by this removal, since it is also observed in the case of SRE with $^{13}\text{CO}_2$. Apparently, the presence of CO_2 speeds up the release of CO. The released amounts of CO are given in table 1 and 2.

TPD patterns obtained after steady state gasification at 1200 K in various CO_2 , Ar mixtures and cooling to 673 K (figure 3), all show CO desorption above 1000 K, which can be ascribed to the decomposition of carbon-oxygen complexes from the carbon surface. In all cases the total amount of CO desorption observed during TPD upto 1273 K exceeds the amount of CO produced after a gas phase step to an inert at 1200 K (table 3).

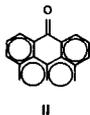
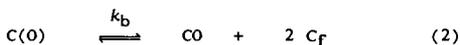
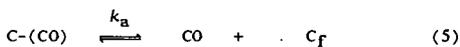
From the CO desorption patterns after gasification in pure CO_2 at 1200 K and assuming irreversible first-order desorption, an activation energy of 213 $\text{kJ}\cdot\text{mol}^{-1}$ ($k_0 N_{\text{CO}} = 6.6 \cdot 10^3 \text{ mol}\cdot\text{mol C}_a^{-1}\cdot\text{s}^{-1}$) is calculated (figure 3A), for the fractional coverage range between 0.3 to 0.9. If after TPD the carbon sample is exposed to CO at 373 K in a subsequent TPD (figure 3B) again a considerable CO desorption is observed, but with a lower activation energy ($E_a = 160 \text{ kJ}\cdot\text{mol}^{-1}$, $k_0 N_{\text{CO}} = 11.4 \text{ mol}\cdot\text{mol C}_a^{-1}\cdot\text{s}^{-1}$), indicating a weaker interaction.

It is striking that during TPD after gasification in $^{13}\text{CO}_2$ (figure 3C) above 1000 K ^{13}CO desorption is observed, indicating that during gasification in $^{13}\text{CO}_2$ insertion of ^{13}CO has taken place, confirming the SRE results. The C^{18}O desorption, which is observed in TPD after gasification in C^{18}O_2 followed by that in CO_2 (figure 3D), indicates that not all oxygen present on the carbon surface is actively taking part in the gasification reaction. The amount of C^{18}O desorption is higher after the reversed gasification order.

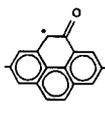
In summary the most important observations are (i) two CO desorption rates are operative, (ii) CO can be inserted or adsorbed on the carbon, yielding both types of desorption, (iii) oxygen is removed from the surface by reaction with CO, (iv) CO_2 enhances the CO desorption process. This led us to the following tentative proposal for the gasification mechanism. Reaction (1) yields semiquinone structures [12,13] at the zig-zag (II) or armchair (V) edges of the graphitic carbon planes by interaction of the CO_2 with the active sites (unsaturated carbons, not terminated with hydrogen). Decomposition of this structure yields the slow desorbing CO. At the armchair edges an adjacent site can also be oxidised, yielding a diketone (IX). This is more unstable than the

semiquinone and readily breaks open resulting in two adsorbed CO molecules, carbonylic structures (X). These represent the faster CO desorption species. The release of the CO molecules is in both cases assumed to be reversible, accounting for the observed CO insertion or chemisorption. Only in the presence of CO₂ the diketone structures will be formed continuously, and part of the semiquinone structures on the armchair edges are transformed into the faster desorbing CO species. This process might explain the discrepancy that was noticed between steady state gasification rates and those calculated on the basis of rate constants and surface occupancy obtained from step response experiments [7].

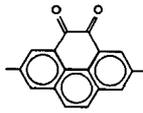
The SRE results presented here agree with the TPD analysis of Magne and Duval [14], who observed four types of CO release: two easily and two less easily decomposing surface complexes, yielding CO. Apparently, our results can only discriminate between the two groups.



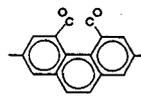
II



V



IX



X

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Table 1 : The total amount of CO production, relative to the amount of carbon actually present, observed after a gas phase step change from CO₂ to Ar at 1200 K as a function of carbon burn-off, together with the gasification rate, r_w , and the average rate constant for CO desorption

Burn-off (%)	N_{CO}/C_a mol.mol ⁻¹	r_w mol.mol ⁻¹ .s ⁻¹ (* 10 ⁴)	k_{mean} s ⁻¹
20	0.0028	1.53	0.055
35	0.0026	1.55	0.060
45	0.0030	1.58	0.053

Table 2 : Total amounts of desorption products (μ mol) observed after a gas phase step change from various CO₂,Ar mixtures to Ar at gasification conditions (sample sizes 30-80 mg carbon actually present).

gasification conditions		CO	¹³ CO	C ¹⁸ O
CO ₂	1200 K	20.8	-	-
¹³ CO ₂	1200 K	17.4	4.3	-
10% ¹³ CO ₂ , Ar	1250 K	4.7	1.4	-
	1200 K	2.4	0.4	-
4% C ¹⁸ O ₂ , Ar	1200 K	-	-	6.2
C ¹⁸ O ₂	1200 K	-	-	11.1

Table 3 : Total amounts of desorption products, relative to the amount of carbon actually present (mol/mol), observed in TPD up to 1273 K after different treatment at 1200 K:

treatment	CO/C _a	¹³ CO/C _a	C ¹⁸ O/C _a
SSG (CO ₂)	0.0042	-	-
SSG (¹³ CO ₂)	0.0038	0.0005	-
SSG (4% C ¹⁸ O ₂ , Ar - 7% CO ₂ , Ar)	0.0010	-	0.0001
SSG (7% CO ₂ , Ar - 4% C ¹⁸ O ₂ , Ar)	0.0007	-	0.0004
CO at 373 K after TPD	0.0015	-	-

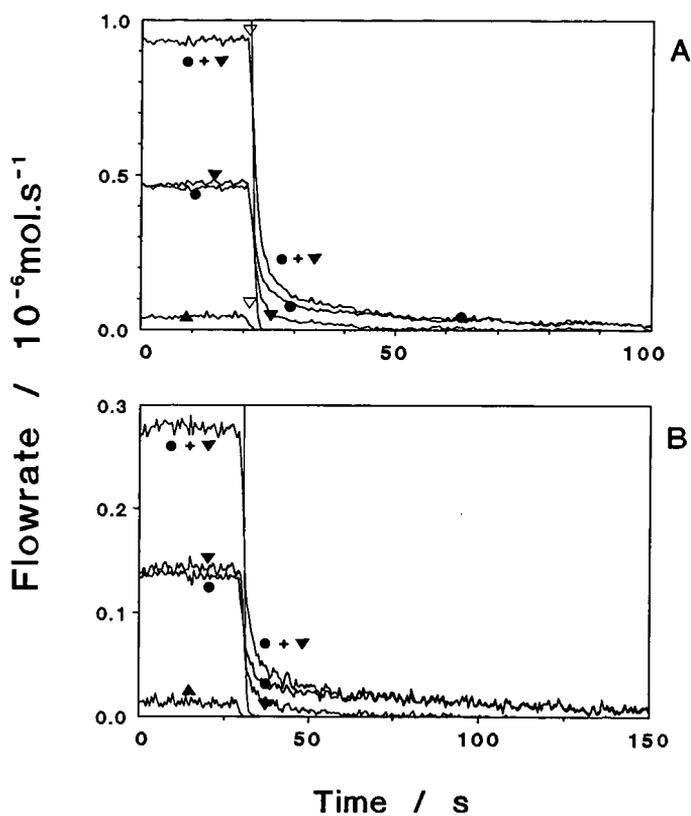


Figure 1 : Response curves after a gas phase step change from 10 % ¹³CO₂,Ar to Ar at different temperatures.
 A. T = 1250 K; B. T = 1200 K.
 Key: CO; ¹³CO; C¹⁸O; CO₂;
¹³CO₂; CO¹⁸O; C¹⁸O₂.

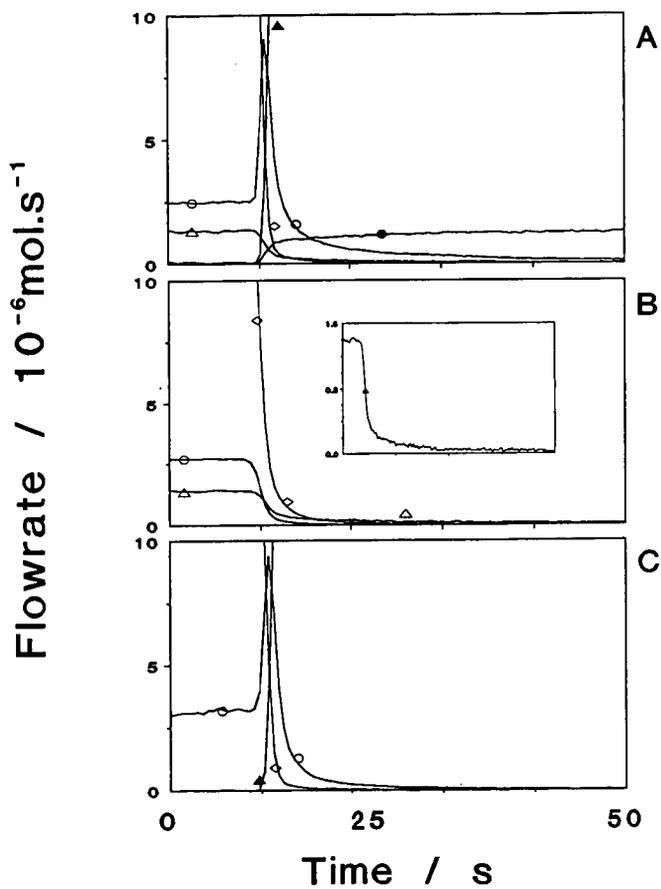


Figure 2 : Response curves after gas phase step changes at 1200 K:
 A. $C^{18}O_2 \rightarrow CO_2$ (Norit)
 B. $C^{18}O_2 \rightarrow Ar$ (Norit)
 C. $C^{18}O_2 \rightarrow CO_2$ (SiC)
 (key as in figure 1).

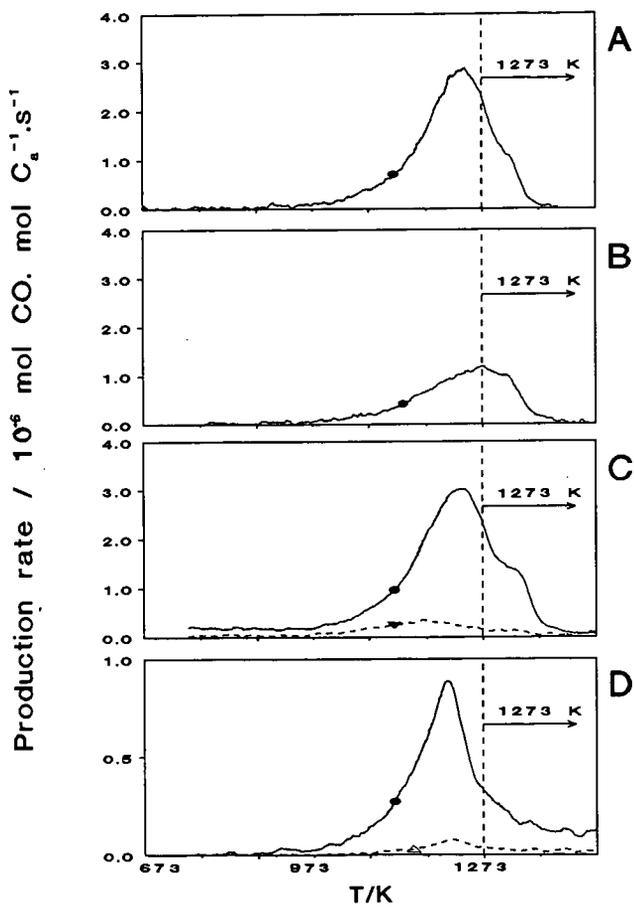


Figure 3 : TPD pattern after different treatments (key as in figure 1):
 A. SSG 1200 K in CO_2 ;
 B. TPD - CO at 373 K
 C. SSG 1200 K in CO_2 followed by $^{13}\text{CO}_2$
 D. SSG 1200 K in 4% $^{18}\text{O}_2$, Ar followed by 7% CO_2 , Ar.