MECHANISM OF CARBON DIOXIDE GASIFICATION STUDIED BY TPD

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ABSTRACT

Kinetic studies of carbon dioxide gasification are combined with TPD measurements. It is shown that this technique allows to calculate not only the concentration of surface complexes but also the true activation energies of gasification. It is followed that this procedure may be more successful than the determination of active sites by oxygen adsorption.

INTRODUCTION

The mechanism of carbon dioxide gasification was studied by applying (i) 'classical' kinetic measurements, whereby the temperature and partial pressures were varied, and (ii) TPD measurements in order to determine the concentration of surface complexes. The studies were performed by using a model coke from polyvinylchloride (HTT 900°C), which has neither cations nor heteroatoms. The TPD studies with samples which were quenched from reaction temperature allow to calculate the desorption kinetics of the C(O) and C(H) surface complexes and to determine the total concentration of these complexes. By combination of these results with the data of the kinetic studies of gasification (rate constants) it is possible to determine the concentration of occupied, free and total sites and also the true activation energies of the single steps of gasification.

EXPERIMENTAL

Gasification and TPD measurements were performed in one and the same reactor, which is described in an earlier paper (1). This also holds for the model coke made of polyvinylchloride (grain size: 0.1 mm to 0.2 mm). For the TPD measurements an argon atmosphere and a heating rate of 20 K min^{-1} were used, the final temperature was 1100°C which was held for 0.5 hours.

RESULTS AND DISCUSSION

Classical treatment of kinetics

Fig.1 shows carbon monoxide formation rates as function of carbon dioxide partial pressure after 10 h gasification. The rates vary only slightly with time and the mass loss even at 900°C at $p_{CO_2} = 1$ bar is below 15 %. The carbon monoxide formation rates are related on the initial amount of carbon, they only represent the formation of carbon monoxide which is produced by carbon gasification.

For evaluating kinetic data the oxygen exchange mechanism was used as basis:

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

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

From this mechanism the following rate equation is obtained:

$$r_s = c \cdot k_1 \cdot p_{CO_2} / [1+(k_1/k_2) \cdot p_{CO_2} + (k_{-1}/k_2) \cdot p_{CO}] \qquad (3)$$

The following rearrangement of this equation

$$r_s^{-1} = (c \cdot k_2)^{-1} + (c \cdot k_1 \cdot p_{CO_2})^{-1} \qquad (4)$$

shows that a plot of r_s^{-1} versus $p_{CO_2}^{-1}$ should give a straight line. In view of the experimental results it was assumed that the partial pressure of carbon monoxide is negligibly small. The experimental data of Fig.1 fulfill equation (4). Therefore, the values of c·k are directly given in Fig.2 using an ARRHENIUS plot. The following equations have been derived from Fig.2:

$$c \cdot k_1 = 5.6 \cdot 10^{12} \cdot \exp(-60000/RT), \text{mmol mol}^{-1}\text{h}^{-1}\text{bar}^{-1} \qquad (5)$$

$$c \cdot k_2 = 2.7 \cdot 10^{11} \cdot \exp(-54000/RT), \text{mmol mol}^{-1}\text{h}^{-1} \qquad (6)$$

These equations allow to calculate the ratio k_1/k_2:

$$k_1/k_2 = 20.9 \cdot \exp(-6000/RT), \text{ bar}^{-1} \qquad (7)$$

The total concentration of active sites c is unknown. It may vary with temperature. This means that the activation energies in eqs. (5) and (6) are probably not true activation energies.

TPD STUDIES

Fig.3 shows the quantity of carbon monoxide which was measured in the TPD experiments using the samples of Fig.1 (10 h gasification). In order to check the importance of these values the gasification rates were related on the quantity of desorbed carbon monoxide. The results are given in Fig.4. These related rates are constant over the entire range of carbon dioxide partial pressure at least for 800 and 850°C. The deviation at 900°C may be explained by the fact that the coke was only heattreated at this temperature.
If it is assumed that the quantity of desorbed carbon monoxide corresponds to the quantity of C(O) surface complexes it is now possible to calculate the quantity of the concentration of free sites. The derivation of eq. (3) is based on the assumption that the formation rate of the C(O) complex according to eq. (8):

$$r_{(1)} = k_1 \cdot c_{(\ )} \cdot p_{CO_2} \qquad (8)$$

is equivalent to the desorption rate of the carbon monoxide from the C(O) complex:

$$r_{(2)} = k_2 \cdot c_{(O)} \qquad (9)$$

With $r_s = r_{(1)} = r_{(2)}$ follows:

$$c_{(\ )} = (k_1/k_2) \cdot (1/p_{CO_2}) \cdot c_{(O)} \qquad (10)$$

The ratios k_1/k_2 are known from the gasification studies. Therefore, $c_{(\ )}$ can be calculated. The results are shown in Fig.5. The quantity or concentration of free sites decreases with increasing partial pressure and increases with temperature. As the concentrations of occupied and free sites are known, the concentration of total sites can additionaly be calculated:

$$c = c_{(O)} + c_{(\ )} \tag{11}$$

The results are also given in Fig.5. The concentration of total sites is independent on the partial pressure for the gasification temperatures 800 and 850°C. The deviation at 900°C has probably the same reason as already mentioned in relation to Fig.4. On the other hand, it has to be stated that the majority of the carbon edge atoms is saturated with hydrogen (C(H) complexes). The importance or value of the presented TPD measurements suffers from the fact that a ten hour gasification at different temperatures causes not only different mass losses but also different structural changes. For elimination of this disadvantage gasification and TPD studies were performed at different temperatures and additionally by variation of the reaction time. For these studies pure carbon dioxide was used. The Figs. 6 and 7 show the carbon monoxide formation rates and the relative quantities of desorbed carbon monoxide as function of the residual amount of carbon m/m_o.
As follows from Fig.7 the amount of desorbed carbon monoxide continuously increases with progressive gasification, but only at temperatures up to 850°C. The decrease at 900 and 950°C is confirmed by many measurements. It can not be explained by the decreasing amount of residual carbon. In any case, these results confirm that the concentration of C(O) complexes increases with decreasing gasification temperature. This means that the surface is loaded with oxygen because the desorption rate is too small.

The results of Figs. 6 and 7 offer three possibilities: (1) To calculate the activation energy of the overall rate of gasification $\dot{n}_{CO}/n_C^o$. (2) To calculate the temperature dependence of the concentration of C(O) surface complexes $n_{CO,des}^o/n_C^o$ using an ARRHENIUS plot. (3) To calculate the activation energy of the gasification rate related on the quantity of C(O) surface complexes $\dot{n}_{CO}/n_{CO,des}^o$. In all cases this was done for equal degrees of carbon conversion $(1-m/m_o)$ or residual carbon m/m_o. As the gasification rates are extremely low under all conditions it is assumed that the develoment of the pore structure is not significantly influenced by the gasification temperature. In the case of the overall rate nearly identical results are received whether the carbon monoxide formation rate is related on the initial quantity of carbon or the residual quantity of carbon, because the degree of carbon conversion is very low. The same argument is valid for $n_{CO,des}^o/n_C^o$.
The activation energies which were obtained by this procedure are shown in Fig.8 as function of the residual amount of carbon. Constant values are found if m/m_o is equal to or larger than 0.95. It may be assumed that steady-state gasification conditions are achieved beyond this degree of conversion. In the steady state region of gasification the following activation energies may be taken from Fig.8:

- For the carbon monoxide desorption $n^{\circ}_{CO,des}/n^{\circ}_{C}$: -31 kcal mol-1 (positive slope in the ARRHENIUS plot)
- For the overall rate $\dot{n}_{CO}/n^{\circ}_{C}$: 54 kcal mol^{-1}
- For the rate related on the quantity of C(O) complexes $\dot{n}_{CO}/n^{\circ}_{CO,des}$: 85 kcal mol^{-1}.

The value of 85 kcal mol^{-1} corresponds to the true activation energy of the desorption step E_2 as follows from the following equations:

$$r_s = r_{(2)} = k_2 \cdot c_{(O)} \tag{12}$$

$$k_2 = r_s/c_{(O)} = \dot{n}_{CO}/n^{\circ}_{CO,des} \tag{13}$$

The rate constant of the desorption step k2 is identical to the turnover rate of the surface complex.
With the known activation energy of k_2 the activation energy of the rate constant of the dissociation step k_1 may be calculated using eq. (7):

$$k_1 = k_2 \cdot 20.9 \exp(-6000/RT) \tag{14}$$

$$E_1 = E_2 + 6 = 91 \text{ kcal mol}^{-1} \tag{15}$$

These values of the true activation energies are very near to the values presented by Walker and others (2-4) for gasification of graphitized materials.
The TPD studies also allow to determine the desorption kinetics of the C(O) complex. Typical desorption rates are shown in Fig.9 after 10 h gasification. Using non-isothermal kinetics the desorption rate (first order reaction assumed) is as follows:

$$d(n_{CO,des})/dT = (dT/dt)^{-1} \cdot k_o \cdot \exp(-E/RT) \cdot (n^{\circ}_{CO,des} - n_{CO,des}) \tag{16}$$

The application of this equation to all experimental results (reaction times from 1 to 10 h, temperatures from 750 to 950 °C) yielded an average value of the activation energy of 53 kcal mol^{-1} (Fig.10). This activation energy corresponds to the following equation:

$$r_{(2)} = k_2\,(T) \cdot c_{(O)}(T) = k_2\,(T) \cdot n^{\circ}_{CO,des}/n^{\circ}_{C}(T) \tag{17}$$

The previous results yielded a value of 54 kcal mol^{-1} for the product of eq. (17). This agreement is really satisfying.

Finally it should be mentioned that the average value of the activation energy of hydrogen desorption resulting from the same experiments amounts to 62.5 kcal mol^{-1} by assuming a second order reaction:

$$2\ C(H) \rightleftharpoons H_2 + 2\ C_f \tag{18}$$

This value is identical to the result published by Yang and Yang (5). The difference of activation energies for carbon monoxide and hydrogen desorption confirms the inhibiting effect of hydrogen.

SUMMARY

The present paper represents an attempt to measure and calculate the concentration of the intermediate surface complexes and the true activation energies of carbon dioxide gasification by combining kinetik studies of gasification with TPD measurements. This route looks promising. The true activation energies for the dissociation and desorption step are 91 or 85 kcal mol^{-1} in comparison to 60 or 54 kcal mol^{-1} for the apparent activation energies. The difference results from the change of the concentration of the surface complexes with gasification temperature in gasification of the model coke used in these studies. Therefore, it is not surprising that the obtained true values of activation energies nearly correspond to values reported by other authors for carbon dioxide gasification of graphitized materials. The meaning of this agreement still has to be explained, it probably results from more or less constant concentrations of sites in gasification of graphitized materials.

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ACKNOWLEDGEMENT

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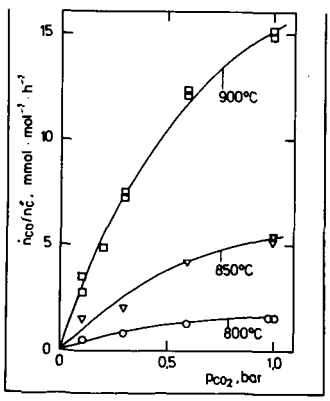

Fig.1: Carbon monoxide formation rates

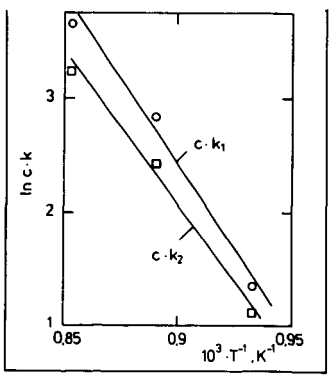

Fig.2: ARRHENIUS plot according to eq.(4)

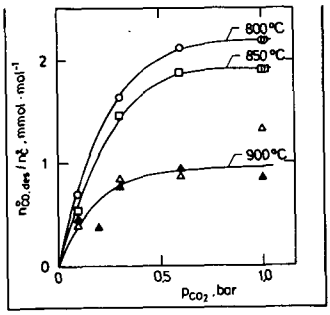

Fig.3: Concentration of C(O) complexes

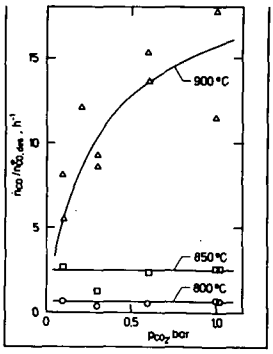

Fig. 4: Specific gasification rates acc. to eq. (11)

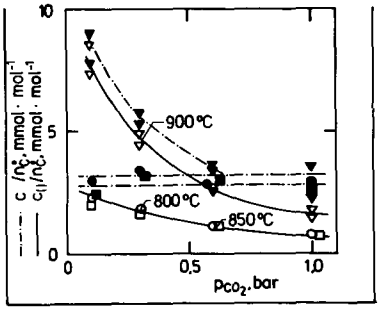

Fig.5: Concentration of free and total sites

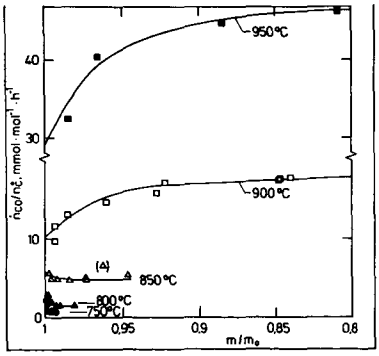

Fig. 6: Gasification rates versus residual carbon

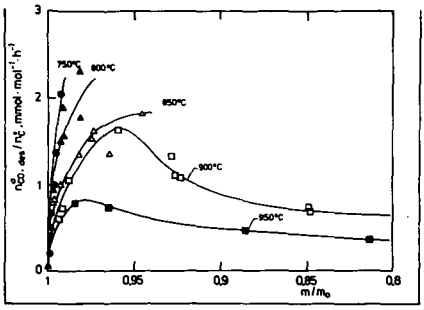

Fig.7: Concentration of C(O) complexes versus residual carbon

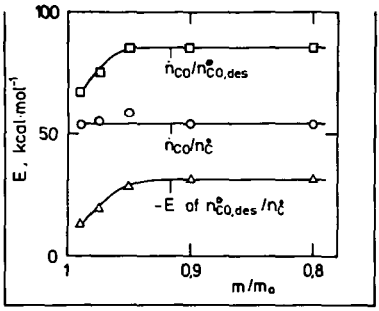

Fig.8: Activation energies versus residual carbon

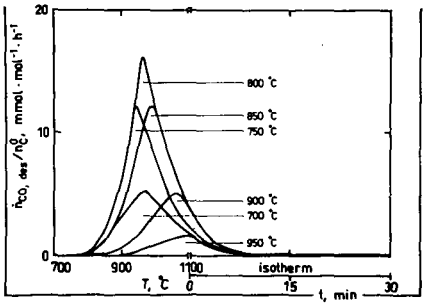

Fig. 9:
Temperature dependence of specific gasification rates according to eq. (11): ARRHENIUS plot

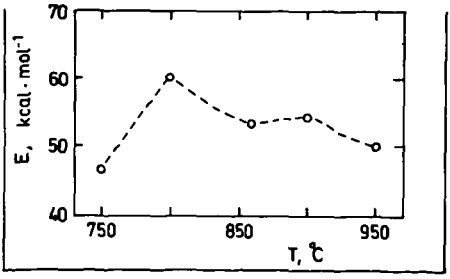

Fig. 10:
Activation energies of the desorption of the C(O) complexes