

POSTER

DYNAMICS OF SURFACE OXYGEN COMPLEXES DURING CARBON GASIFICATION WITH OXYGEN

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INTRODUCTION

The mechanism of carbon gasification with oxygen has been discussed in relation with surface oxygen complexes as reaction intermediates [1,2]. The full understanding of the chemical form of complexes and their dynamic behavior during gasification is essential for elucidating the gasification mechanism. In order to examine the behavior of the surface complexes during carbon gasification, isotope-labeling technique is quite useful. Several studies successfully used $^{18}\text{O}_2$ and $^{16}\text{O}_2$ for this purpose [3-5].

In the present study, the isotope labeling technique was combined with the transient kinetic (TK) method to obtain *in situ* information on the dynamics of surface oxygen complexes during the carbon gasification with oxygen. In addition, the surface complexes remaining in the gasified carbon was analyzed by the temperature programmed desorption (TPD) technique.

EXPERIMENTAL

Materials. The carbon sample used in this work was prepared by carbonizing phenol-formaldehyde resin (PF). The PF char was subjected to O_2 -gasification at 773 K up to a conversion of 52 % in a quartz reactor. Labeled $^{18}\text{O}_2$ gas was purchased from Isotec Inc., and its isotopic purity was 98.1 atom%.

Gasification, TK and TPD. The partially gasified PF char was first heat-treated in He at 1223 K for 30 min. Then the sample was cooled to the gasification temperature, 773 K, followed by the gasification with $^{18}\text{O}_2$ (5 % in He). After the $^{18}\text{O}_2$ -gasification for 3 min, the TK experiment was carried out: The flow of $^{18}\text{O}_2$ was switched to that of $^{16}\text{O}_2$ as quickly as possible with the temperature unchanged, and the $^{16}\text{O}_2$ -gasification was continued for 3, 10, 30 or 60 min. Then TPD experiment was carried out from 773 K to 1223 K at a heating rate of 10 K/min under a He flow. The gas analysis during gasification and TPD was made with a quadrupole mass spectrometer.

RESULTS AND DISCUSSION

Gasification and TK profile. The char was gasified with $^{18}\text{O}_2$ for 3 min and then the flow of $^{18}\text{O}_2$ was switched to $^{16}\text{O}_2$. Figure 1 illustrates the details of the gas profile upon the switching. The formation

rates of C^{18}O_2 and C^{18}O promptly dropped to a certain level and then gradually decreased; i. e., the decay of C^{18}O_2 and C^{18}O took place in two steps. At the same time, the rapid formation of $\text{C}^{16}\text{O}^{18}\text{O}$, C^{16}O_2 and C^{16}O was observed due to the gasification with $^{16}\text{O}_2$. Despite this switching, the rates of the total CO_2 formation as well as CO formation did not show any discontinuous change at this point. In the fast-decay step, the evolution of the C^{18}O_2 and C^{18}O suddenly dropped as $^{18}\text{O}_2$ started to decrease. Therefore, $^{18}\text{O}_2$ would be a major reactant for the reaction responsible for this step. The possible reaction is C^{18}O_2 and C^{18}O formation by the reaction of surface oxygen complex, $\text{C}^{18}(\text{O})$, with $^{18}\text{O}_2$. The slow decay of C^{18}O_2 and C^{18}O continued even after the complete flush out of $^{18}\text{O}_2$. Therefore, gaseous $^{18}\text{O}_2$ is not responsible for the evolution of C^{18}O_2 and C^{18}O in the slow decay period. After the $^{16}\text{O}_2$ -gasification of 30 min, the formation rate of C^{18}O_2 approached almost zero, whereas the evolution of C^{18}O lasted even after 30 min.

TPD analysis. After the $^{18}\text{O}_2$ -gasification and the subsequent $^{16}\text{O}_2$ -gasification, the surface oxygen complexes remained in the char were analyzed by TPD. The CO_2 and CO desorption patterns were very broad and had peaks at 900 K and 970 K, respectively. With an increase in $^{16}\text{O}_2$ -gasification time, the amount of C^{18}O_2 upon TPD rapidly decreased and its desorption could scarcely be observed after the $^{16}\text{O}_2$ -gasification for 30 min. The amount of $\text{C}^{16}\text{O}^{18}\text{O}$

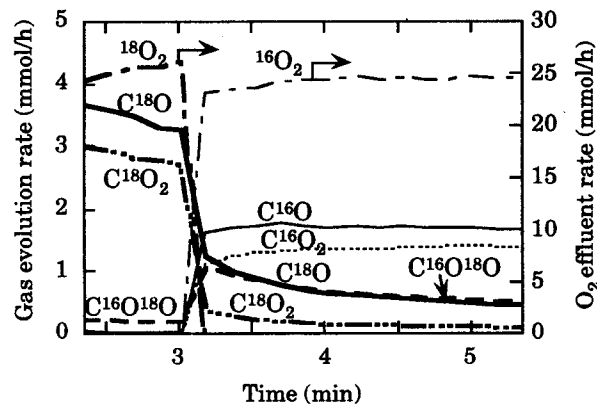


Figure 1 CO_2 and CO evolution profile in the $^{18}\text{O}_2$ -gasification and the subsequent $^{16}\text{O}_2$ -gasification at 773 K.

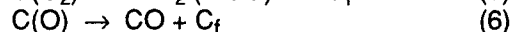
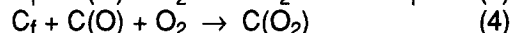
evolved was almost unchanged during the gasification period from 3 to 10 min and then it slowly decreased. The amount of C¹⁸O desorption decreased with ¹⁶O₂-gasification time. However, in contrast with the case of C¹⁸O₂, C¹⁸O desorption was still observed even after 60 min, indicating a higher stability of CO-yielding complexes.

Mass balance in gasification and TPD. The amount of oxygen trapped on the char during the gasification was calculated from the balance between the oxygen supply and the oxygen detected at the reactor outlet, and it was almost the same as that evolved upon TPD.

Figure 2 illustrates the ¹⁸O atomic balance of the gases evolved in each stage of the ¹⁶O₂-gasification and the ¹⁸O-containing surface complexes remained on carbon. In the previous TPD/DRIFT study, the CO₂ desorption at around 900 K was ascribed to the decomposition of acid anhydride and lactone, and the CO desorption mainly to carbonyl and ether complexes [6]. During the ¹⁶O₂-gasification, some of the ¹⁸O-containing complexes were evolved as CO₂ (C¹⁸O₂ and C¹⁶O¹⁸O) and C¹⁸O. The composition for such ¹⁸O-containing gases is illustrated in the upper part of each stack column in Figure 2 and ¹⁸O remaining on the char (¹⁸O evolved in the TPD after the ¹⁶O₂-gasification) is indicated in the lower part. It should be noted that the sum of ¹⁸O in C¹⁸O₂ evolved during the ¹⁶O₂-gasification and ¹⁸O in C¹⁸O₂ desorbed upon the TPD was almost constant whatever the gasification time was. This finding suggests that the C¹⁸O₂-yielding complexes desorb without a direct interaction of O₂ gas during the ¹⁶O₂-gasification. This desorption must be the origin of the slow decay of C¹⁸O₂ in the TK profile (Figure 1). On the other hand, the sum of C¹⁸O evolved during the gasification and C¹⁸O in the TPD decreased with gasification time. This result can not be interpreted only from the desorption of ¹⁸O-

containing carbonyl and ether complexes during the gasification. This unbalance is due to the formation of C¹⁶O¹⁸O. The formation of this gas confirms the presence of the direct reaction of ¹⁸O-containing carbonyl and ether with ¹⁶O₂ during gasification.

Mechanism of carbon gasification. On the basis of the above discussion, we propose the following mechanism;



where C_f, C(O), C(O₂) represent free carbon site, carbonyl and/or ether, and lactone and/or acid anhydride, respectively. The reaction 3 and the desorption reaction 5 correspond to the fast and the slow decays of C¹⁸O₂, respectively, in the TK profile.

Under the present conditions, the gasification reaction proceeds mainly *via* the reactions 1 and 3. In other words, O₂ chemisorbs on free site of carbon to form carbonyl and ether type complexes, and then some of them react with O₂ to produce CO₂ and CO. A part of surface complexes appears to be very stable, judging from the fact that the ¹⁸O-containing carbonyl and ether type complexes still remained after the ¹⁶O₂-gasification for 60 min.

Conclusions

The *in situ* information on the dynamics of surface oxygen complexes during the carbon gasification was obtained by the TK experiment using O₂ isotopes. The fate of ¹⁸O-containing complexes during the subsequent ¹⁶O₂-gasification was clarified in detail. Based on the above results, it was concluded that the main reaction path under the present condition was the formation of carbonyl and/or ether complexes followed by the direct interaction of these species with gaseous oxygen to form CO₂ and CO gases.

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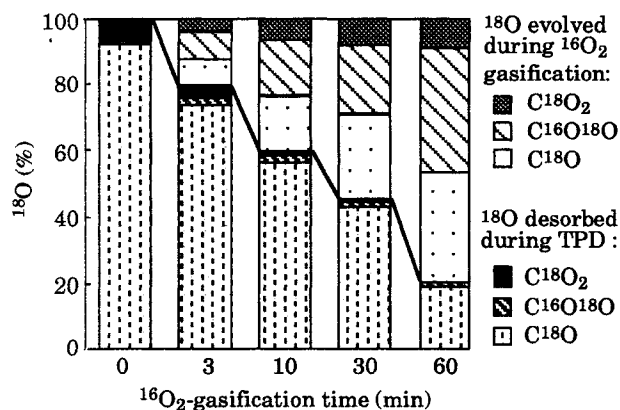


Figure 2 Fate of ¹⁸O in the ¹⁸O₂- and subsequent ¹⁶O₂-gasification. Upper part: ¹⁸O evolved during ¹⁶O₂-gasification; lower part: ¹⁸O remained on carbon which desorbed in the TPD.