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RELATION BETWEEN THE GASIFICATION RATE AND THE AMOUNT OF OXYGEN ON CARBON SURFACE DURING THE GASIFICATION OF A CARBON SUPPORTING SEVERAL ALKALINE METAL SALTS

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The oxygen trapped by metal on the carbon surface was measured in terms of the so-called flash desorption method by use of a Curie-point pyrolyzer. The steam gasification rate of the carbon supporting several alkaline metal salts was found to be proportional to the amount of the oxygen measured by the method. Furthermore, the moles of the oxygen trapped by metal on the carbon surface were found to be equal to the moles of metal supported.

Recently, the mechanism of the catalytic gasification of carbon has been examined in relation to the role of oxygen on the carbon surface. Yokoyama et al.[1] found that the catalytic activity of metal was proportional to the amount of oxygen trapped on the carbon surface during the gasification of carbon in carbon dioxide. Wigmans et al.[2] suggested that oxygen is trapped by potassium on the carbon surface in th form of K-O-C bond and that the bond is broken up during the gasification. Kapteijn et al.[3] examined the role of oxygen in the CO_2 gasification of a carbon supporting alkaline metal salts by measuring the amount of CO and CO_2 released during the outgsassing of the sample. However, the method for measuring the oxygen trapped on the carbon surface has not been established. In this study, the amount of oxygen trapped on the carbon surface could be determined by use of the technique of flash desorption.

Several metal salts (K_2CO_3, KOH, KNO_3, K_2SO_4, KCl, Na_2CO_3, NaCl) were supported on a carbon black with a binder(microcrystalline cellulose). The atomic ratio of metal to carbon was adjustd to be 1/400, 1/200, or 1/100 in the char made from the pyrolysis of the sample. The weight decrease of the char was measured by use of a thermobalance type reactor during the gasification at 818°C in atmospheric pressure of steam. The relation between the conversion of fixed carbon X and the reaction time t was calculated from the weight decrease. The inital gasification rate $-r_{cm0}(= dX/dt\,|_{t=0})$ was determined for each sample. The oxygen trapped on the char was measured as follows: About 2 mg of samples were wrapped with a pyrolysis foil and heated up to 800°C, and kept there for 15 min to make the char. Then the char was cooled to room temperature and exposed to air for 5 min to adsorb oxygen. After that, the char was dropped into a Curie-point pyrolyzer (Japan Analytical Industry Co., JHP-2S) and heated up to 920°C rapidly (heating rate was ca. 3000°C·s^{-1}) and kept there for 30 s in He flow. The amount of oxygen contained in the evolved CO and CO_2, n_O, was regarded as the oxygen trapped on the char.

Figure 1 shows the typical X vs. t relationships obtained from the gasification experiments. All metal salts except KCl and NaCl greatly accelerate the gasification rate over the whole range of the gasification, while the activities of KCl and NaCl are low at the inital stage of gasification but become gradually high as the gasification proceeds.

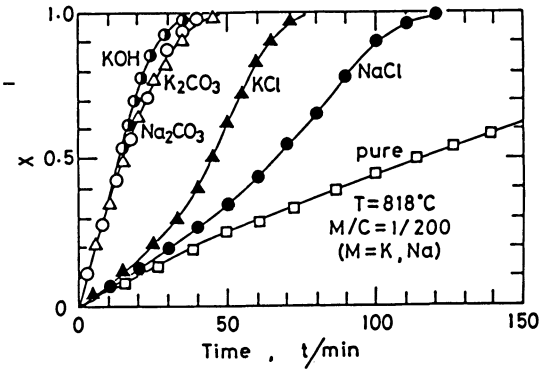

Fig.1. Effect of various alkaline metal salts on the gasification rate of carbon.

Figure 2 shows the relation between $-r_{cm0}$ and n_O. Very good linear correlation was found between the gasification rate and the oxygen trapped. The value of n_O for the pure sample was found to be so small that the oxygen was expected to be trapped by the metal supported.

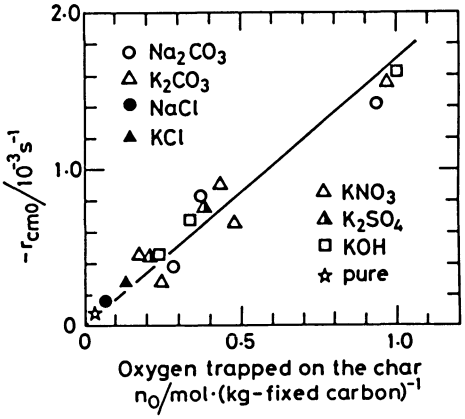

Fig.2. Relation between the initial gasification rate and the oxygen trapped on the char.

Figure 3 shows the relation between the amount of oxygen trapped on the char and the amount of metal supported, n_M. The oxygen trapped increased linearly with the amount of metal supported and the slope of the line was approximately unity. The result shows that one atom of metal retains one atom of oxygen on the carbon surface. To identify funtional groups on the carbon surface, the FTIR spectra of the char exposed to air were measured. For the sample supporting K_2CO_3, the existence of K-O-C bond was ascertained from the adsorption peaks at 1400 and 1650 cm^{-1}.[4]

From the above results, the alkaline metals salts were supposed to change as follows: During the pretreatment for making chars, the metal salts except KCl and NaCl are decomposed to form metal active species, while KCl and NaCl remain unchanged. During the steam gasification, KCl and NaCl also form similar active metal species via KOH and NaOH, respectively. The metal active species are expected to catalyze the gasification reaction through a redox cycle.

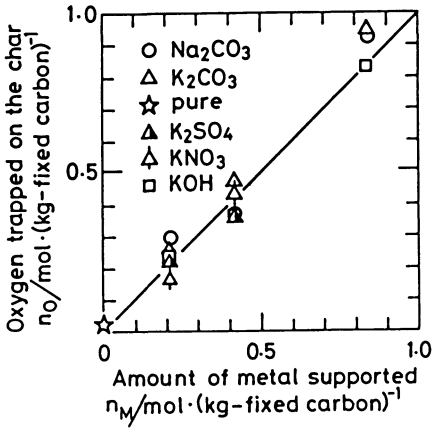

Fig.3. Relation between the oxygen trapped and the amount of metal supported.

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