CHARACTERIZATION OF CARBON ACTIVE SITE BY CO_2 GASIFICATION

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Introduction

The CO_2 gasification with a carbon is widely applied in coal gasification and iron making etc. This reaction was extensively studied in 1980-90s, and McEnaney summarized CO_2 reaction with coal char [1]. Recently, reforming CO_2 to CO, which is used as syn gas, has been studied as one of the recycling technologies for emitted CO_2 [2]. In the gasification reaction of carbon with CO_2 is proposed as follow;

$$C_{active} + CO_2 \rightarrow C(O) + CO \quad (1)$$

$$C(O) \rightarrow CO + C_{active} \quad (2)$$

$$C + CO_2 \rightarrow 2CO \quad (3)$$

The eq(2) is reported to be a rate determining step. Therefore, the concentration of the C(O), an intermediate form for CO_2 gasification, is important to promote the CO_2 gasification reaction [3]. But, there is no quantitative research to investigate the relationship between the amount of C(O) and the reactivity in CO_2 gasification. In this study, activated carbons were oxidized to introduce the diffferent amount of C(O) on the carbon surfaces by varying the oxidation conditions. The reactivity of oxidized activated carbons with CO_2 estimated by Temperature programmed desorption (TPD) technique.

Experimental

The activated carbon (AC), derived from phenolic resin, was immersed in HCl and HF solutions and then washed thoroughly in distilled water to remove impurities. The demineralized AC thus prepared is donated as BEL. The BEL sample was oxidized to introduce the C(O) complexes in HNO_3 solution(N-BEL) or in air(A-BEL). The amount of C(O) was adjusted by varying oxidation time and temperature.

The rate of gas evolution and consumption was estimated by TPD technique. The TPD measurements in Ar were performed to estimate the amount of C(O) present on the carbon surfaces. The TPD techniques were also performed in 1.95vol. %H_2 (Ar balanced) to estimate the amount of C_{active}. The TPD runs were carried out under a flowing of 3.06vol.% CO_2 (Ar balanced) to evaluate the CO_2 gasification rate. All the TPD measurement in different atmospheres was made at 5 K/min up to 1273 K in a horizontal furnace equipped with a quartz tube. Before the measurement, sample was dried in the furnace. During TPD runs, the concentrations of CO, CO_2, H_2 and other two gases (H_2O, CH_4, not shown in this article) were monitored by a set of gas chromatographs to estimate the rate of gas evolution of gases and that of CO_2 consumption.

Results and Discussion

The amount of C(O) was estimated from the amount of CO gas during TPD in Ar up to 1273K. The oxidation of BEL in various oxidation condition successfully varied the amount of C(O) on the carbon sample of BEL.

The amount of C_{active} of oxidized BELs was estimated from the amount of the H_2 chemisorption on C_{active}. The decomposition of C(O) and the chemisorption of H_2 were monitored simultaneously during the TPD runs in a flowing 1.95vol.% H_2. Fig.1 shows the relationship between the amount of H_2 chemisorbed and that of C(O) complexes present in the oxidized carbons of N-BEL and A-BEL. The H_2 chemisorption increased proportionally with the amount of C(O). The approximated curve indicates that the ratio of H_2 chemisorbed / C(O) is about 0.3. Making an assumption where H/C_{active} =1, the ratio of C_{active}/C(O) is about 0.6. This implies that only ca. 60% of C(O) can generate the C_{active}.

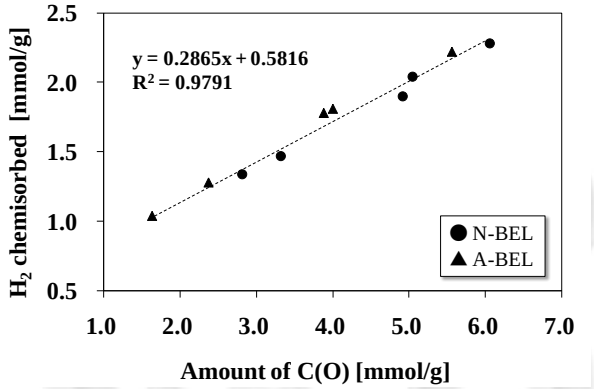

Fig.1 Relationship between the amount of C(O) and H_2 chemisorbed on the BELs oxidized in various conditions.

To further discuss eq(2), the CO_2 gasification rate of the BELs containing various amounts of C(O) was measured by monitoring CO gas evolution. In order to distinguish CO gas evolved as a result of CO_2 gasification from CO gas decomposed from C(O), the rate of CO gas evolved in Ar was subtracted from that in 3.06% CO_2 . The values thus calculated are differential rates of CO evolution presented as $\triangle$CO. Similarly the CO_2 consumption associated with gasification was calculated from a differential rate of CO_2 gas evolution/consumption. The $\triangle$CO and CO_2 consumption profiles for various oxidized BELs were shown in Fig.2A and B. The $\triangle$CO profile for BEL, which contained a small amount of C(O), appeared over 973K (peak3, in Fig.2A). In the same temperature range, CO_2 consumption profile for BEL also showed the peak (peak2, in Fig.2B), suggesting that the peak3 in $\triangle$CO profile is attributed to CO evolved as a result of the gasification of carbons with CO_2. The similar peak in size and position was also seen in this temperature range for all $\triangle$CO profiles for N-BELs. Therefore, CO gas evolved as peak3 in the $\triangle$CO profiles is nothing to do with the existence of C(O). Introducing C(O) on the carbon surfaces resulted in the appearance of other two peaks in $\triangle$CO profiles at lower temperatures. One is located round 900 K (peak1, in Fig.2A),

the other is at 1100 K (peak2, in Fig.2A). For peak1 in ⊿CO profiles, the corresponding CO_2 consumption peak was not detected in CO_2 consumption profiles. The CO_2 consumption peak (peak1 in Fig.2B) was detected at ca. 1100K, where the peak2 located in ⊿CO profile. If these peaks are attributed to the CO_2 gasification, CO/CO_2 obeys a stoichiometric ratio; 2. The amount of ⊿CO in peak2 is plotted against the amount of CO_2 consumption in peak1 (Fig.3). The slope of approximated curve is about 2. Therefore, the CO gas evolution from peak2 in ⊿CO profile is attributed to CO_2 gasification.

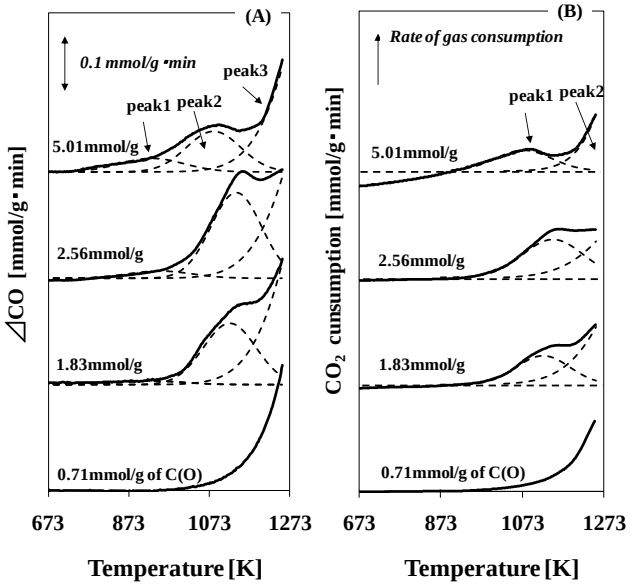

Fig.2 ⊿CO profile(A) and rate of CO_2 consumption profile(B) for BEL, N-BELs performed by TPD in CO_2.

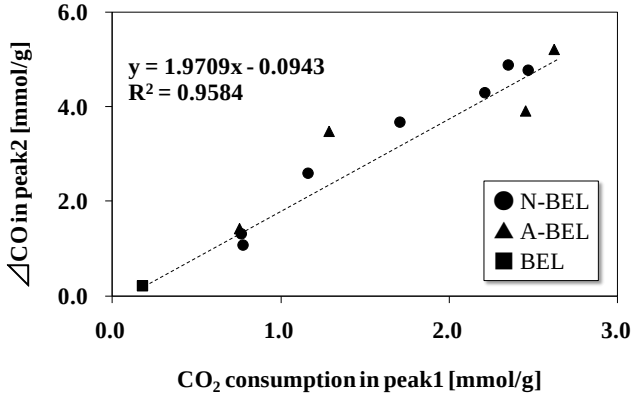

Fig.3 Relationship between CO_2 in peak1 and ⊿CO in peak2

In order to discuss CO_2 gasification in terms of reaction rate, we define the maximum rate in peak2 in ⊿CO profile as a rate of CO_2 gasification (r_{max}). Fig.4 shows the relationship between the amount of C(O) and r_{max}. The values of r_{max} increased and then decreased with the amount of C(O). The increase in the concentration of C(O) promotes the rate determining reaction expressed in eq(2). Introducing larger amount of C(O) results in the increase in concentration of CO in eq(1), which should retard CO_2 gasification. In order to ensure the role of excess C(O), CO_2 gasification was performed by intentionally adding 1.6vol.% CO, together with 3.06% CO_2 (Fig.5). The r_{max} decreased by mixing 1.6vol.% CO, suggesting the formation of excess amount of C(O) may inhibit CO_2 gasification of carbon.

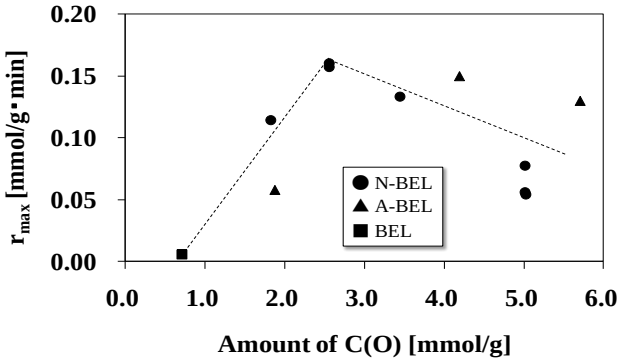

Fig.4 Relation between the rates of CO_2 gasification and the amounts of C(O) on the various oxidized BELs.

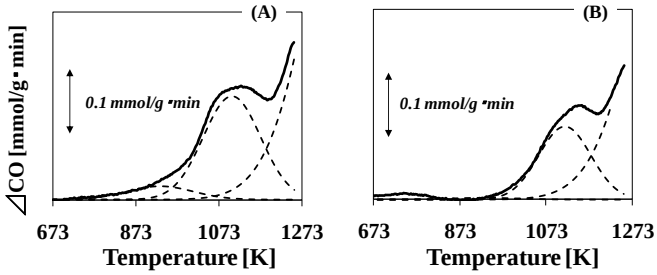

Fig.5 Rate of ⊿CO gas evolution profile from A-BEL in CO_2 (A) and in mixture of CO_2 /CO (B).

Conclusions

The decomposition of surface C(O) complexes in part generates C_{active} , the amount of which is characterized by H_2 adsorption. These C_{active} are also removed as a result of CO_2 gasification. Introducing C(O) promotes the CO_2 gasification, whereas the formation of large amount of C(O) reduces the reaction rate for CO_2 gasification.

References

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