

A TPD study on H₂O-gasified and O₂-chemisorbed coal chars

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INTRODUCTION

Steam gasification reaction of coal char is a very important reaction in both theoretical aspects and industrial applications. It is generally accepted that surface oxygen complexes on carbon substrate function as intermediate in gasification reaction and that such surface complexes are formed only at active sites (1, 2). Many investigators have studied oxygen chemisorption on a variety of carbons to estimate the amount of surface oxygen complexes (3-5). This amount is thought to correspond to the number of active sites or an active surface area. The reactivity of carbon was closely related to the active surface area on the carbon. However, the detailed feature of such surface complexes have not been well understood yet. Temperature-programmed desorption (TPD) technique is very useful in yielding information on surface oxygen complexes (6-8). By using TPD technique, this paper intends to clarify the nature of surface complexes on coal char after H₂O gasification or after O₂ chemisorption. In addition, the gasification reactivity was discussed in relation to TPD patterns of H₂O-gasified char or O₂-chemisorbed char. The effect of coal type and the mineral matter in coal on TPD pattern was also investigated.

EXPERIMENTAL

Materials

Five coals (16x32 mesh) varying in rank were used in this study. The ultimate and proximate analyses are presented in Table 1. The metal content of coals is given in Table 2. Some of the raw coals were demineralized by using a mixture of HCl and HF solutions. Ash content of the demineralized coal was: MW, 0.2; TH, 2.3; GV, 0.6 wt%(dry). The raw (Raw) and demineralized (Dem) coals were devolatilized in N₂ at 1100 K for 30 min in a small fluidized bed reactor as described in a previous paper (7).

Apparatus and procedure

Steam gasification, oxygen chemisorption and TPD were carried out in the same apparatus. A quartz basket containing about 50 mg of char was hung by a quartz spring in a quartz tube which was placed in a vertical furnace. The sample was heated to 1100 K under N₂ flow (40 ml(STP)/min) and then steam was introduced at the flow rate of 50 ml(STP)/min with diluent N₂ (10 ml(STP)/min). The weight change during gasification was followed by using a cathetometer. After the char conversion reached to 50 wt%(daf), the sample was cooled to 570 K in H₂O, followed by cooling to 420 K in N₂. This partially gasified char is referred to as G char in this paper. G char was outgassed to 0.1 Pa at 420 K and then subjected to TPD at a linear heating rate of 10 K/min up to 1100 K. A large portion of evolved gas was evacuated with a rotary pump and a slight portion of gas was introduced to a gas analysis system. The gases (CO₂, CO and H₂O) were analyzed with a quadrupole mass spectrometer. After TPD experiment of G char, the temperature was lowered to 420 K and oxygen at 0.1 MPa was admitted into the system for 1 h. This O₂-chemisorbed char is referred to as O char. O char was also subjected to TPD under the same conditions as above. The results are expressed per unit weight (daf). Although they are presented in arbitrary units, the peak intensity can be reasonably compared

with each other, because it was corrected by considering the pattern coefficient and the ionization efficiency of each gas.

RESULTS

The TPD patterns of Raw-G chars are shown in Fig. 1(a). MW Raw-G char yielded a sharp H₂O-peak at 590 K, a broad CO₂ desorption pattern in the range from 650 K to 1000 K and a sharp CO-peak at 1040 K. TH Raw-G char gave H₂O- and CO-peak at similar temperature ranges. YL Raw-G and WD Raw-G chars exhibited only a sharp CO-peak. It is noteworthy that all sharp CO-peaks from the above chars were observed in a similar temperature range. On the other hand, GV Raw-G char exhibited no clear peak and only a small amount of CO and H₂O was evolved over a wide range of temperature.

The TPD patterns of Raw-O chars (Fig 1(b)) are broad in comparison with those of Raw-G chars. All of Raw-O chars evolved CO₂ in the range from about 450 K to 1050 K. In addition to this CO₂ desorption, MW Raw-O gave a relatively sharp CO₂-peak at 770 K. With respect of ²CO, the desorption from Raw-O chars began at much lower temperature than that from Raw-G chars. The sharp CO-peak observed in Raw-G chars was not observed in Raw-O chars, but a small CO-peak appeared in YL and MW Raw-O chars.

In order to investigate the effect of mineral matter on the gas evolution, TPD were carried out with the chars prepared from the demineralized coals (Fig. 2). In the case of MW Dem-G char, the sharp peaks as observed in the Raw-G char completely disappeared as a result of the demineralization. A small amount of CO was evolved at a relatively high temperature. TH Dem-G char exhibited no sharp H₂O-peak, but the sharp CO-peak was still present in spite of the demineralization. The TPD pattern of GV Dem-G char was almost the same as that of GV Raw-G char. Generally the patterns of Dem-O chars resemble to those of Raw-O chars, that is, broad CO₂ and CO-desorptions were commonly observed in both chars. An exception was that the ²CO₂ peak at 770 K in MW Raw-O char was not observed in the pattern of MW Dem-O char.

Table 3 shows the gasification rate in steam at a char conversion of 50 % (daf) for Raw- and Dem-chars. The demineralization caused a considerable reduction in reactivity of MW char. This fact clearly shows that the mineral matter in MW coal was catalytically active in the gasification. On the other hand, the reactivity of TH char increased slightly and that of GV char was unchanged as a result of the demineralization.

DISCUSSION

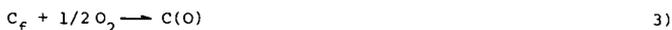
Since many relatively sharp peaks disappeared from TPD pattern as a result of demineralization, these peaks must be closely associated with the presence of mineral matter in char. For MW Raw-G char we have shown that the interaction between finely-dispersed Ca and carbon is responsible for CO₂ peak and that the decomposition of Ca(OH)₂ is responsible for H₂O evolution(7). The dispersed Ca is derived from exchangeable Ca cation on carboxyl groups in MW coal. Although WD and TH coals have a large amount of Ca as indicated in Table 2, their Raw-G and Raw-O chars did not exhibit such a CO₂ peak. This suggests that there is little finely-dispersed Ca in WD and TH chars, because of a smaller amount of carboxyl groups in the coals than in brown coal like MW coal. Many Raw-G chars exhibited a sharp CO-peak at around 1040 K. It is not clear which inorganic species are responsible for the sharp CO-peaks, but the peaks may possibly be ascribed to the same kind of species (Fe and/or Na). Though TH Dem-G char exhibited the CO-peak, this may be due to incomplete demineralization. On the other hand, the broad CO desorption as

observed in GV Dem-G char is not due to the interaction with mineral matter. This desorption is associated with carbon substrate itself. Thus TPD pattern is appreciably influenced by mineral matter but the effect of coal type is not so significant.

The total amount of CO₂ and CO gas evolutions in TPD pattern of G char or O char was correlated with the gasification reactivity (Fig. 3). Although the amount of gas evolution from O char was slightly larger than that from G char, good correlations were found for both cases. The relationship between the gasification reactivity and TPD pattern may be postulated as follows. During steam gasification, water vapor chemisorbs at active site on carbon surface and surface oxygen complexes are formed. Catalytically active inorganic species such as finely-dispersed Ca may also have an ability to accept oxygen from H₂O, and this activated oxygen is transferred to neighboring carbon substrate to form surface complex. These oxygen complexes, whatever they are produced non-catalytically or catalytically, decompose and desorb gaseous products.



where C_f is an empty active site and C(O) is surface oxygen complex. In some cases, oxygen may be retained in the inorganic species and may react with carbon at the gasification temperature. When a partially gasified char is cooled in H₂O after gasification, the extent of Reaction 2 becomes smaller as the temperature decreases and all available active sites may be covered with surface oxygen complexes. When this sample, G char, is subjected to TPD, gases such as CO₂ and CO are evolved either by the decomposition of such complexes (Reaction 2) or by the solid-solid reaction between oxygen-containing inorganic species and carbon (the sharp CO peak in TPD pattern may be due to this reaction). Active sites become unoccupied after TPD of G char. When the sample after TPD was exposed to O₂ at 420 K, the empty active sites may be occupied again:



During the subsequent TPD of O char, Reaction 2 occurs again. Therefore, TPD patterns of both G char and O char essentially give the same information about active site on carbon surface, although the absolute amount of desorbed gas is somewhat different with each other. This is why good correlations were observed between the reactivity and the amount of desorbed gas either from G char or O char (Figure 3).

In order to check whether the chemisorption sites for O₂ and for H₂O are the same or not, one O₂-chemisorption experiment was carried out with MW char. After MW Raw-G char was prepared in H₂O, it was exposed to O₂ before TPD experiment. The TPD pattern of this sample was almost the same as that of G char. This fact suggests that all active sites on G char have already been covered with the oxygen from H₂O. Surface complexes characteristic for O char can not be produced on the G char anymore. In other words, the adsorption site for H₂O and O₂ may be the same. Nevertheless, the TPD patterns of G char are quite different from those of O char. This can be explained as follows. In G char, since H₂O chemisorbs at high temperature, only thermally stable surface complexes such as heterocyclic ether group can be formed. This mechanism was also proposed by Huttering and he pointed out that these ether groups function as intermediate in gasification reaction (8). On the other hand, when unoccupied active surface after TPD of G char is exposed to O₂ at temperature as low as 400 K, various kinds of surface complexes such as lactone, carbonyl, ether and others may be formed on the O char. Some of these

complexes may be decomposed at relatively low temperatures upon heating. Therefore, O char gave a broad CO₂-peak and the evolution of CO began at low temperature.

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Table 1. Ultimate and proximate analyses for original coal

Coal	Code	Ultimate analysis (wt%, daf)					Proximate analysis (wt%)			
		C	H	N	S	O	Mois.	V.M.	Ash	F.C.
Morwell	MW	67.9	5.0	0.5	0.3	26.3	25.9	38.2	1.1	34.8
Yallourn	YL	66.1	5.3	0.6	0.3	27.7	14.3	47.3	0.8	37.6
Wandoan	WD	75.8	6.8	1.0	0.3	16.1	9.1	49.0	15.4	26.5
Taiheiyō	TH	77.0	6.3	1.5	0.3	14.9	5.8	46.5	10.8	36.9
Grose Valley	GV	81.7	5.1	1.4	0.4	11.4	3.4	29.7	16.6	50.3

Table 2. Metal content in original coal (wt%, dry)

Coal	Si	Al	Fe	Ca	Na	K
MW	0.04	0.01	0.10	0.30	0.05	0.00
YL	0.04	0.02	0.26	0.08	0.08	0.00
WD	4.21	3.24	0.20	0.60	0.12	0.16
TH	2.58	1.42	0.34	0.65	0.10	0.16
GV	4.97	3.27	0.46	0.01	0.02	0.11

Table 3. Reaction rate of char (h⁻¹)

Coal	Raw	Dem
MW	2.2	0.2
YL	1.3	n.d.
WD	1.6	n.d.
TH	1.0	1.7
GV	0.2	0.2

n.d., not determined

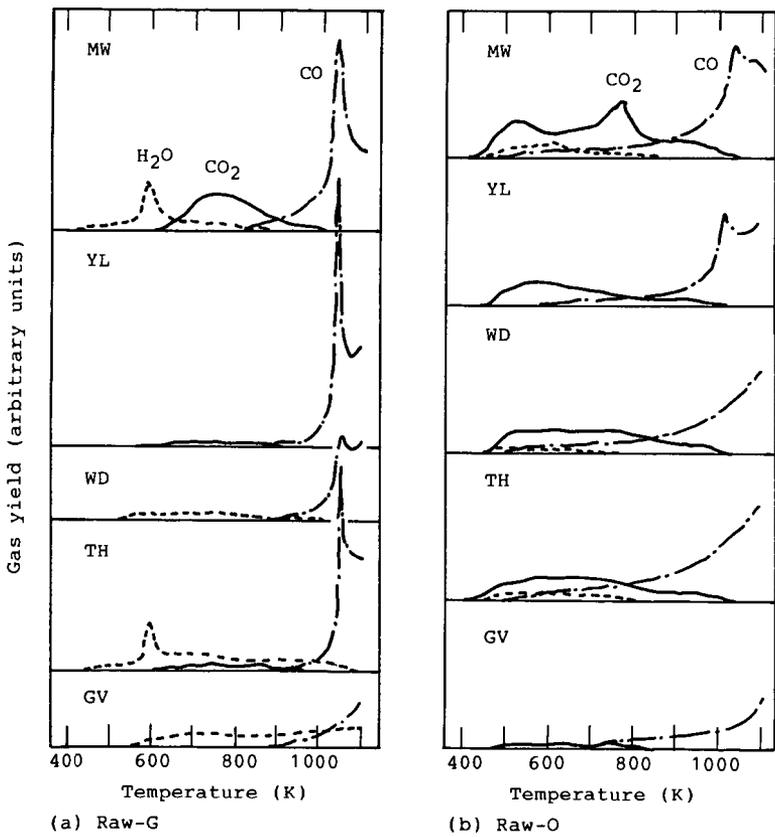


Figure 1. TPD patterns of raw coal chars.
 —, CO₂; - · - ·, CO; - - - -, H₂O

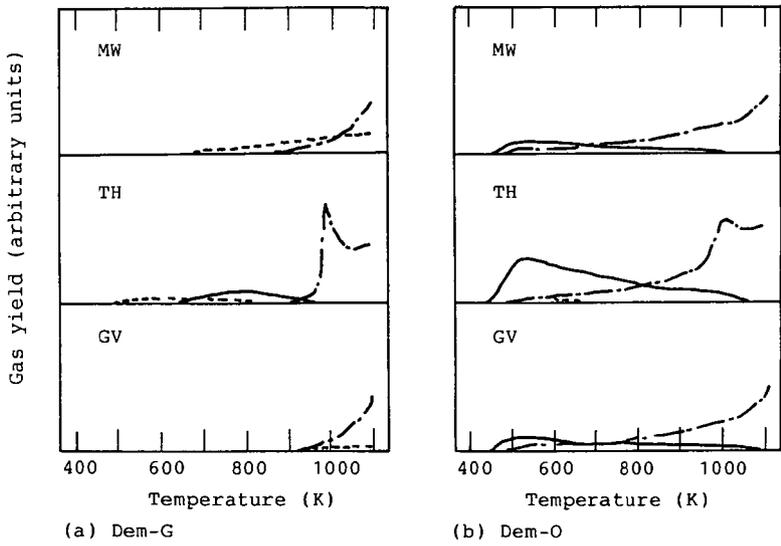


Figure 2. TPD patterns of demineralized coal chars.
 —, CO₂; - · - ·, CO; · · · · ·, H₂O.

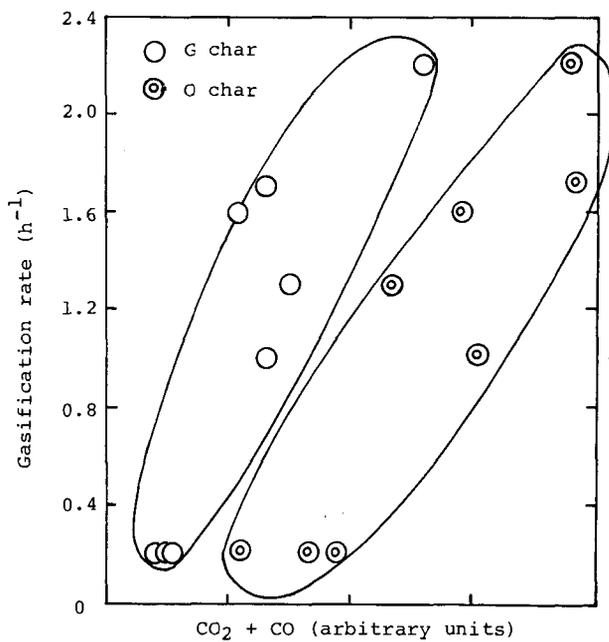


Figure 3. Correlation between the gasification rate and the amount of CO₂ and CO desorbed during TPD.