

A TDS STUDY ON THE REACTION INTERMEDIATES IN THE CATALYZED GASIFICATION OF ACTIVATED CHARCOAL

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Abstract—Catalytic coal gasification was studied by using thermal desorption spectroscopy (TDS) under high vacuum conditions. Activated charcoal was used as a model compound of coal, and Na_2CO_3 and K_2CO_3 as catalysts. Catalysts enhanced oxygen adsorption and decomposed at temperatures below their own decomposing temperatures. After pretreatment of the catalyst at high temperature the CO_2 desorption pattern represented characteristics of reaction intermediates. There were two peaks, α -peak and β -peak, in CO_2 TDS curves. From the experimental results, α -peak was interpreted to the result from intercalated metal-carbon (M-C) complex, and β -peak from metal-oxygen (M-O-C) complex. A higher pretreatment temperature led to decrease both the number of M-O-C complex and its thermal stability. The increase of catalyst loading in Na_2CO_3 -containing sample resulted in relative increase of the number of M-O-C complex than that of intercalated M-C complex, and also increase of thermal stabilities of both reaction intermediates. Major difference between K_2CO_3 and Na_2CO_3 appeared in α -peak, intercalated M-C complex. That is, the contribution of intercalated metal-carbon complex to total reaction intermediates was larger in K_2CO_3 than Na_2CO_3 . This could be attributed mainly to the better intercalating ability of potassium due to its lower ionization potential.

INTRODUCTION

There has been broad interest in the development of more economic coal gasification process. The enhancement of the reactivity of coal toward gasification by addition of some minerals has been reported and many investigations confirmed that alkali and alkaline earth metal carbonates are the most effective catalysts [1-3]. Extensive and systematic studies have been performed in order to elucidate the mechanism of catalytic coal gasification and the nature of active species which are formed from catalysts during gasification. Although much efforts have been paid to explore the nature of the active species, the explicit answers are hampered by the complexity of gasification reaction. Unlike metals which are popular as catalysts, the catalysts used in coal gasification are decomposed during reaction and converted into other compounds. This obstructs the way to develop the catalysts in coal gasification.

In this paper, catalytic coal gasification was studied using oxygen as an oxidant gas by thermal desorption spectroscopy (TDS) under high vacuum conditions.

Now we give an overview of the studies on the nature of reaction intermediates formed on activated charcoal containing alkali metal carbonates.

EXPERIMENTAL

Experiments were conducted in a high vacuum reaction chamber that was pumped by an oil diffusion pump (Varian, M4) whose operating pressure was $2-3 \times 10^{-6}$ Torr. The total pressure was monitored by a Bayard-Alpert type ionization gauge (Anelva, NI-10D), and the partial pressure by a quadrupole mass spectrometer (Anelva, AGA-100). The samples used in the study were prepared by incipient wetting method which permits catalyst loading large enough [4]. Activated charcoal was selected as a model compound of coal, and Na_2CO_3 and K_2CO_3 as catalysts. All the samples were loaded on a 400 mesh stainless steel net welded to tantalum foil (0.025 mm thickness) which was resistively heated by a.c. power. The heating mode was not linear with time but somewhat parabolic. The heating rate of the sample was about 4 K/sec. The temperature of the sample was measured by a chromel-alumel thermocouple spot-welded on the back of the tantalum foil support. Generally, thermal desorption spectra

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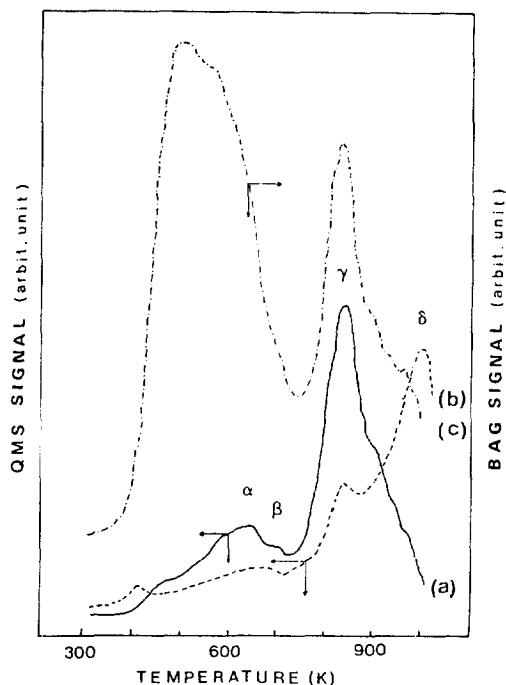


Fig. 1. (a) CO_2 , (b) CO thermal desorption spectra and (c) total pressure variation curve from activated charcoal containing 10 wt% K_2CO_3 during outgassing upto 1030 K.

(TDS) were obtained by O_2 exposures after outgassing. During the acquisition of TDS curves, sample temperature, total pressure, and specific mass intensity were recorded at the same time.

RESULTS AND DISCUSSIONS

1. Outgassing Spectra

Fig. 1 shows the curves of CO_2 TDS (a), CO TDS (b), and total pressure variation with sample temperature (c) during outgassing of activated charcoal containing 10 wt% K_2CO_3 . The decomposition of the sample is observed at considerably low temperature. The peak maximum in the CO_2 TDS is shown at about 850 K, around which total pressure variation curve shows its peak maximum. Peak maximum temperature in CO TDS is higher than that in CO_2 TDS by about 150 K. The shoulder at 800-900 K in curve (b) is attributed to a fragment of desorbing CO_2 in mass spectrometer. The broad peak in curve (c) at about 500 K seems to be the result of desorptions of water or volatile compounds adsorbed on the sample which is confirmed by mass number 18 monitored during the same experiment. It is generally accepted that when alkali

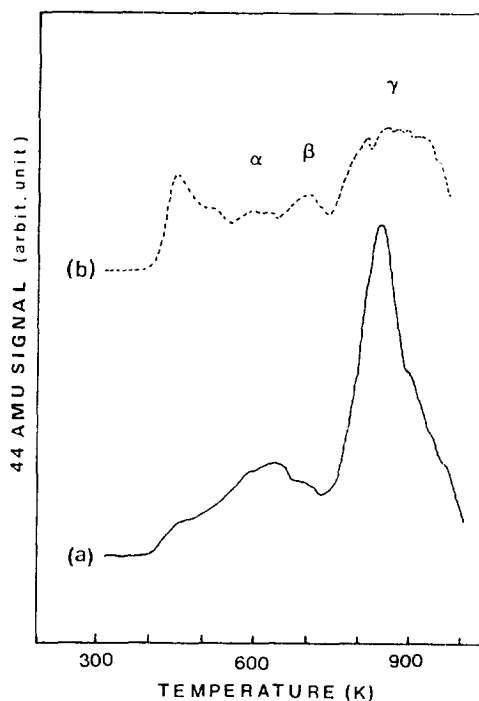
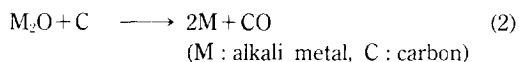
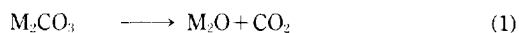


Fig. 2. CO_2 thermal desorption spectra from activated charcoals containing 10 wt% (a) and 40 wt% (b) K_2CO_3 during outgassing upto 1030 K.

metal carbonates are mixed with carbonaceous compound they are decomposed during outgassing at high temperature through the following reactions [5,6].



Reaction (2) is proceeded only after reaction (1). Therefore the γ -peak in the CO_2 TDS is supposed to be due to reaction (1) and the δ -peak in the CO TDS due to reaction (2), respectively. Generally, pure alkali metal carbonates are decomposed above 1000 K, but when they are mixed with carbonaceous compounds decomposition begins at lower temperature which is originated from the contact with carbon [6]. No noticeable desorption is observed when the sample is reheated after outgassing without gas exposure. The result indicates that most of the catalyst decomposes during outgassing. Fig. 2 shows CO_2 TDS from activated charcoals containing 10 wt% (a) and 40 wt% (b) K_2CO_3 . The temperature and extent of decomposition of alkali metal carbonates, when they are mixed with carbonaceous compounds, depend on the contact area

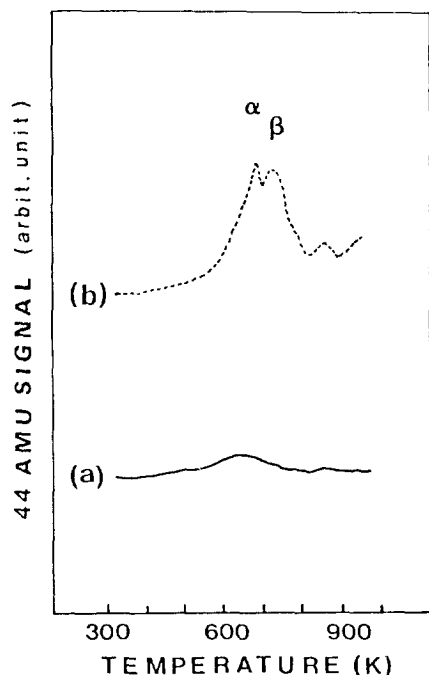


Fig. 3. CO₂ thermal desorption spectra on activated charcoals without catalyst (a) and containing 10 wt% K₂CO₃ (b) by 24000 L O₂ exposure at RT after outgassing for 10 min at 950 K.

of alkali metal carbonates and carbonaceous compounds [7, 8]. The broader γ -peak in curve (b) than that in curve (a) could be attributed to poorer contact between catalyst and carbon in the case of 40 wt% addition. The discussion is supported by TEM photographs. The desorption below 500 K has little importance because it is suggested to be the result of the desorptions of water or volatile compounds adsorbed weakly on the sample after outgassing.

2. O₂ Adsorption

Exposure of activated charcoal containing 10 wt% K₂CO₃ at room temperature to O₂ results in two distinct CO₂ desorption peaks (α -, β -peak) between 600 K and 800 K [Fig. 3(b)]. Unlike the sample containing catalyst, the sample without catalyst (a) shows only a very small peak around 650 K and no noticeable peak on the total pressure variation curve. The peak temperature from the sample without catalyst [Fig. 3 (a)] coincides with the α -peak temperature from the sample containing catalyst [Fig. 3(b)]. This suggests that catalyst on the sample enhances O₂ adsorption and CO₂ formation from adsorbed oxygen, and that thermal stability of reaction intermediates giving α -peak is similar to that of the groups on activated char-

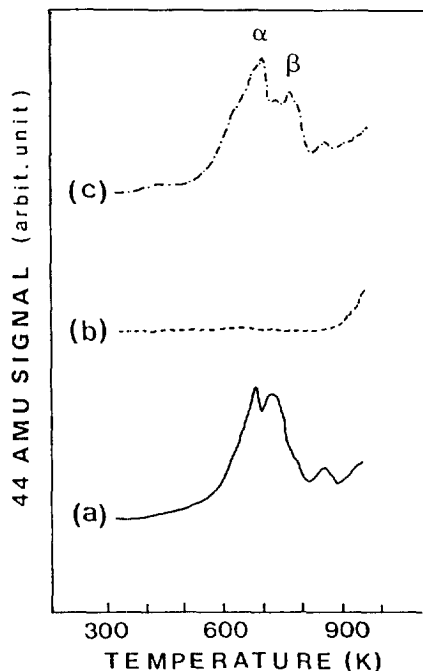


Fig. 4. Sequential CO₂ thermal desorption spectra on activated charcoal containing 10 wt% K₂CO₃: (a) 24000 L O₂ exposure at RT after outgassing for 10 min at 950 K, (b) no exposure after (a), and (c) 24000 L O₂ exposure at RT after (b) and outgassing for 5 min at 950 K.

coal.

Curve (a) of Fig. 4 is a CO₂ TDS curve from activated charcoal containing 10 wt% K₂CO₃ with 24000L O₂ exposure at room temperature. Curve (b) is a CO₂ TDS from the same sample without O₂ exposure after getting curve (a), which shows no distinct peak. Curve (c) is obtained after 24000L O₂ exposure at room temperature after getting curve (b). In curves (a) and (c) two distinct peaks (α -, β -peak) are observed unlike in curve (b). This indicates that α - and β -peak in curves (a) and (c) come from O₂ exposure. In brief, the α - and β -peak in Figs. 3 and 4 are the consequences of catalyst addition and O₂ exposure. In curves (a) and (c) peak temperature of β -peak is somewhat different. This will be explained by catalyst recrystallization afterward.

Fig. 5 shows a series of CO₂ TDS from activated charcoal containing 3 wt% Na₂CO₃ with three different outgassing temperatures. Two distinct peaks are also observed in each curve. The higher outgassing temperature, the bigger peak height ratio of α - to β -peak. Although it is less pronounced, the decrease of peak

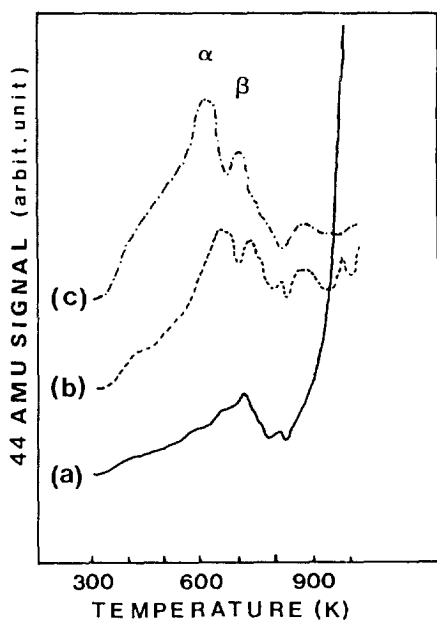


Fig. 5. CO_2 thermal desorption spectra on activated charcoal containing 3 wt% Na_2CO_3 by 24000 L O_2 exposure at RT after outgassing for 10 min. The outgassing temperatures are (a) 900 K, (b) 950 K, and (c) 1030 K.

temperatures of α - and β -peak is also observed. Fig. 6 shows a series of CO_2 TDS from the same sample as in Fig. 5 with three different outgassing times at 1030 K. The longer outgassing time increases peak height ratio of α - to β -peak and decreases peak temperature of α -peak. The small peaks above 800 K seem to be the result of the decomposition of catalyst which is formed by the recrystallization of carbonates during TDS or thermal decomposition of charcoal because CO_2 desorption peak appears at the same temperature as on outgassing spectrum which results from catalyst decomposition. In curve (a), the rising peak after 800 K is outstanding. This is attributed to decomposition of the catalyst which is incompletely decomposed during outgassing or decomposition of functional groups existed on the sample because of short outgassing time.

Fig. 5 suggests that the number and thermal stability of the reaction intermediates which give β -peak decrease relatively at higher outgassing temperature. From this, TDS curves could be used for the study of the reaction intermediates during gasification. Catalysts are converted into reaction intermediates through decomposition and interaction with the activated charcoal during outgassing [10]. These reaction interme-

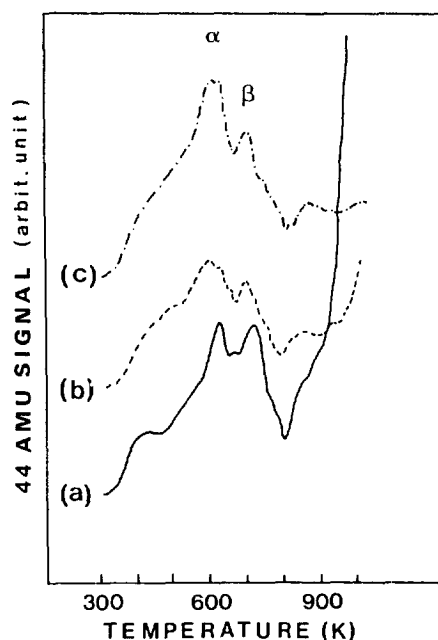
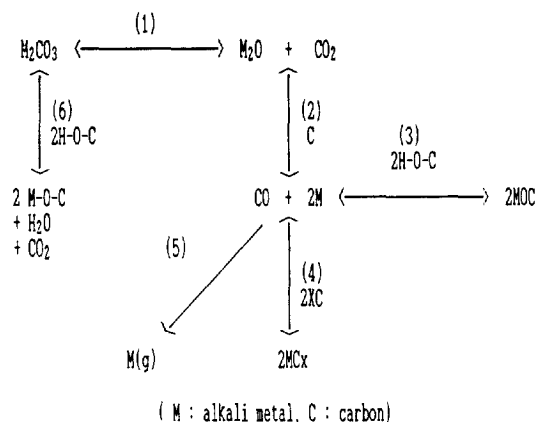


Fig. 6. CO_2 thermal desorption spectra on activated charcoal containing 3 wt% Na_2CO_3 by 24000 L O_2 exposure at RT after outgassing at 1030 K. The outgassing times are (a) 0 min, (b) 5 min, and (c) 10 min.

diates are responsible for the real activity for coal gasification [11].

Fig. 6 suggests that reaction intermediates are decomposed during outgassing. The fact that peak temperature of α -peak is lower than that of β -peak indicates that the thermal stability or binding energy is lower for reaction intermediate giving α -peak than for that giving β -peak. In Fig. 3, the fact that peak temperature of α -peak coincides with the CO_2 desorption peak from the sample without catalyst indicates that reaction intermediate giving α -peak is similar in thermal stability and structure to functional groups of activated charcoal which give small peak on CO_2 TDS.

In comparison with previous reports [9,10], although this gives indirect information about the nature of reaction intermediates, two candidates that could result in α - and β -peak can be assumed. One is metal-oxygen-carbon (M-O-C) complex and the other metal-carbon (M-C) complex suggesting the precursors of α - and β -peak, respectively. The latter is another name of alkali-metal intercalated carbon complex [12]. The possible reaction scheme that is occurred during outgassing is drawn on Scheme 1 [13]. Path 1 is related to γ -peak in Fig. 1(a) and Fig. 2. CO TDS peak in Fig. 1



Scheme I. Reaction network of alkali metal carbonate [11].

(b) seems to be the result of path 2. There are three competitive reaction paths [(3), (4), and (5)] for reduced alkali metal formed during outgassing. What path is dominant over others depends on outgassing conditions. Path 3 is suggested to be the cause of β -peak in Figs. 4-6, and path 4 that of α -peak. H-O-C group is a functional group existed on activated charcoal. Reduced metal can be sublimed and this causes catalyst loss [14].

The above mentioned two reaction intermediates (M-O-C and M-C complexes) get oxygen to be adsorbed on the sample and facilitate the reaction between carbon and oxygen. Therefore the amount of oxygen trapped by catalyst that is synonym of the amount of reaction intermediates, is directly related to reaction activity. During outgassing, M-O-C complex can be decomposed into M-C complex or resulted in metal sublimation. Decomposition will be more intense at higher temperature and for longer time. This explains the trend of decrease of peak height ratio of α - to β -peak in Figs. 5 and 6. M-O-C complex is bound together through chemical bond that is stronger than van der Waals interaction that brings about intercalation. The intercalated compound (M-C complex) has a little difference in structure and thermal stability with functional groups of activated charcoal. Therefore α -peak temperature coincides with CO_2 desorption peak from activated charcoal.

Fig. 7 shows the effect of amount of the catalyst added to activated charcoal on CO_2 TDS. Curves (a) and (c) are obtained from activated charcoal containing 3 wt% Na_2CO_3 , and curves (b) and (d) from 10 wt% sample. For both outgassing temperatures, the β -peak temperature and peak height ratio of α - to β -peak are

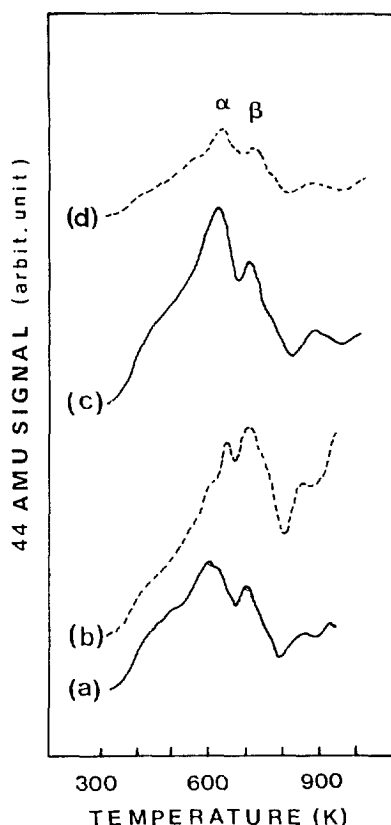


Fig. 7. CO_2 thermal desorption spectra on activated charcoals containing 3 wt% Na_2CO_3 [(a) and (c)] and 10 wt% Na_2CO_3 [(b) and (d)] by 24000 L O_2 exposure at RT after outgassing for 10 min. Outgassing temperatures are 950 K [(a) and (b)] and 1030 K [(c) and (d)].

higher for the 10 wt%-containing sample. This result can be explained as follows: For the case of sodium, the known intercalated compound with carbon is only C_{64}Na . In the 3 wt%-containing sample, the atomic ratio of carbon to Na is about 40, and in the 10 wt% one is about 140. Therefore, Na in the 10 wt%-containing sample can be more intercalated than the 3 wt% one and also form more M-O-C complex. Thermal stability of M-C complex is less affected by its amount on the sample because this complex makes carbon stable through only the weak interaction and the interaction is exerted over the long range, while thermal stability of M-O-C complex depends strongly on that because the interaction is exerted over the short range.

Fig. 8 is the result of CO_2 TDS from the non-treated sample (a) and the sample that is thermally pretreated

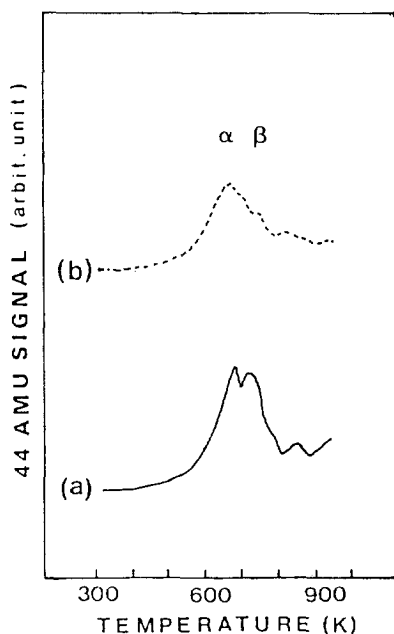


Fig. 8. CO_2 thermal desorption spectra on activated charcoal containing 10 wt% K_2CO_3 by 24000 L O_2 exposure at RT after outgassing for 10 min at 950 K. (a) fresh sample and (b) sample pretreated at 700 °C for 30 min in 1 atm N_2 before using in TDS.

in nitrogen atmosphere (b) and for the non-treated sample (a). The β -peak in curve (b) is less distinct than in curve (a). This could be attributed to the loss of functional groups on the sample by thermal treatment. The M-O-C complex is formed via metal bound to functional group which contains oxygen. Therefore, the loss of functional group results in lower number of M-O-C complex being formed.

3. Comparison between K_2CO_3 - and Na_2CO_3 -containing Activated Charcoals

Fig. 9 shows the difference in CO_2 TDS shape between Na_2CO_3 - and K_2CO_3 -containing activated charcoal. The peak height ratio of α - to β -peak is bigger for the K_2CO_3 -containing sample. In addition to this, the higher outgassing temperature, the more distinct this effect. Because K has lower ionization energy than Na, K can be more easily intercalated into carbon than Na. Therefore, the peak height ratio of α - to β -peak is higher for the case of addition of K_2CO_3 . M-O-C complex is easily decomposed to M-C complex and it sublimes more easily than M-C complex. Therefore, at higher outgassing temperature the difference of the number of M-O-C complex and that of M-C complex

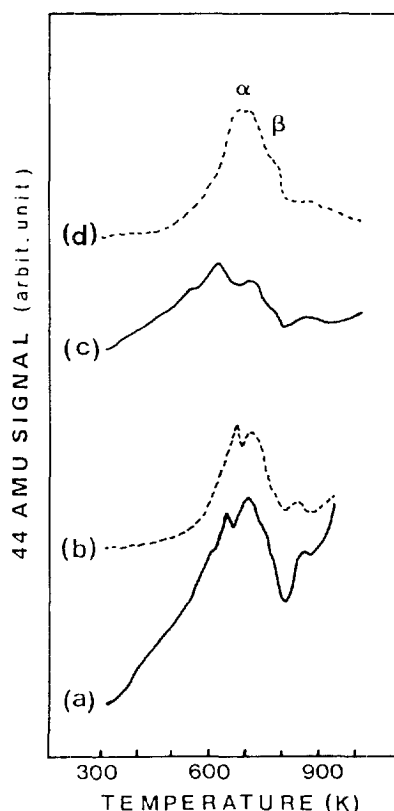


Fig. 9. CO_2 thermal desorption spectra on activated charcoals containing 10 wt% Na_2CO_3 [(a) and (c)] and 10 wt% K_2CO_3 [(b) and (d)] by 24000 L O_2 exposure at RT after outgassing for 10 min. Outgassing temperatures are 950 K [(a) and (b)] and 1030 K [(c) and (d)].

is more outstanding.

CONCLUSIONS

CO_2 thermal desorption spectra of the alkali metal carbonate-containing samples after outgassing followed by O_2 exposure reflects the characteristics of the reaction intermediates which are formed on the sample after outgassing. Catalysts enhance O_2 adsorption and CO_2 formation from oxygen adsorbed on the sample. Reaction intermediates inferred from TDS results are metal-oxygen-carbon (M-O-C) and metal-carbon (M-C) (intercalated compound) complex. Higher outgassing temperature and longer outgassing time lead to decreases of the number of M-O-C complex and its thermal stability. Major difference in TDS pattern between K_2CO_3 - and Na_2CO_3 -containing samples ap-

pears in α -peak depending on the intercalation abilities of K and Na.

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