SH Radical: The Key Intermediate in Sulfur Transformation during Thermal Processing of Coal

JINDING YAN,[†,‡] JIANLI YANG,[†] AND
ZHENYU LIU*,[†]

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Post Office Box 165, Taiyuan 030001, People's Republic of China, and Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

To uncouple the complex behavior of sulfur transformation during thermal processing of coal and to elucidate the main mechanism, typical organic and inorganic sulfur compounds impregnated on or mixed with a low-ash char are studied through temperature-programmed decomposition coupled with online mass spectrum analysis (TPD-MS) and followed by temperature-programmed oxidation coupled also with online mass spectrum analysis (TPO-MS) in a temperature range of up to 800 °C. It is evident that the cleavages of C_{al}−S and C_{ar}−S bonds, where the subscripts al and ar stand for aliphatic and aromatic carbon, respectively, in the organic compounds result in the formation of •SH radicals, which then undergo secondary reactions with the char to form various sulfur compounds such as H_2S, SO_2, COS, and elemental sulfur, as well as sulfur structures in the char. H_2 has the ability to stabilize the •SH radicals and weaken the interactions between the •SH radicals and the char. For the sulfur compounds, which do not generate the •SH radical, the only sulfur products detected are those formed directly from the decomposition of the starting sulfur compounds, H_2S from FeS_2 in H_2 or SO_2 from $Fe_2(SO_4)_3$ in He, for example, and no sulfur structure is formed in the char. Minerals have significant effects on the bond cleavage temperature and the reactions of the •SH radicals with the char. It is clear that the •SH radical is a key species interacting with the char to form secondary sulfur compounds, while H_2S and SO_2 play no role in the sulfur transformation to the carbon structure.

Introduction

Sulfur is present in many hydrocarbon fuels, such as coals, petroleum fuels, and natural gases as well as biomass and wastes, with concentrations from trace amounts to several percent (*1*, *2*). In coal, sulfur usually occurs in both inorganic and organic forms. The inorganic sulfur includes mainly disulfides (pyrite and marcasite) and sulfates (mainly calcium, iron, and barium). The organic form, which is bound directly to the organic matrix of coal, generally occurs in the forms of sulfides, disulfides, thiols, thiophenes, and cyclic sulfides (*3*−*5*). These sulfur forms undergo transformation during thermal processing, such as pyrolysis, gasification, liquefac-

tion, and combustion, which result in release of various types of sulfur compounds into the environment. Understanding the sulfur transformation in thermal processing is essential for the development of effective and economical sulfur removal techniques and consequently for environmental protection (*6*−*9*).

For this purpose, transformation of coal sulfur during thermal conversions has been extensively investigated (*10*−*21*). It is clear that, in addition to the reaction conditions, the type of sulfur, the properties of the carbon matrix surrounding the sulfur structure, the inorganic materials in the coals, and the secondary reactions all affect the sulfur transformation significantly (*22*, *23*). However, no general theory has been obtained to describe the sulfur transformation behavior well. Present understanding of the sulfur transformation remains superficial and vague, such as transformation of the sulfur form from organic to inorganic, or vice versa; or transformation of the sulfur form from the solid phase to the gas phase, or vice versa; or evolution of a specific sulfur form in a specific temperature range. These descriptions, although correct under specific circumstances, are not very useful because they do not show mechanisms involved in the sulfur transformation and are inadequate for advancement of sulfur transformation chemistry, and therefore are difficult to utilize for the development of sulfur emission control techniques. To forward the understanding of sulfur transformation in coal, behavior of typical sulfur structures, instead of every compound, during heating and their interactions with coal components and the environment need to be studied and summarized.

In a previous report (*24*), we investigated pyrolysis behavior of five organic sulfur compounds supported on a char and proposed that the transformation of organic sulfur on a char surface may proceed through the formation of the free sulfur radical, •S•. This is important because it may suggest that the transformation of many types of organic sulfur forms in coal can be rationalized through a common mechanism. However, a char of high ash content was used in the work, which might confound the interactions between the sulfur radical and the carbon structure with the effects of undefined minerals. Furthermore, transformation of the sulfur into the char, the effect of atmosphere on the reactivity of the sulfur radical, and the behavior of other sulfur sources that do not generate the sulfur radical upon heating were not evaluated. Most importantly, the formation of the free sulfur radical, •S•, seems unrealistic from the thermal dynamic point of view, because the quantum chemistry calculations, by density functional theory (DFT), indicate that 596.2 kJ/mol is required for scission of two C_{al}−S bonds simultaneously to form •S•, while only 210.8 kJ/mol is needed for scission of a C_{al}−S bond and 29 kJ/mol is needed for the hydrogen abstraction. To have a correct and clear mechanism of sulfur transformation in coal, a systematic study is performed in this work on pyrolysis behavior of some organic and inorganic sulfur compounds impregnated on or mixed with a low-ash char under different environments and in the presence of some typical metals found in coal. The samples are subjected to temperature-programmed decomposition coupled with online mass spectral analysis (TPD-MS) and then followed by temperature-programmed oxidation coupled also with online mass spectral analysis (TPO-MS). This study shows that the •SH radical is a key intermediate in sulfur transformation during thermal processing of coal.

Experimental Section

Materials. The char used was made from coconut shell (DC-42, a commercial product from Guangdong Xinxing Co. in

* Corresponding author: phone: +86-351-4053091; fax: +86-351-4050320; e-mail zyl@public.ty.sx.cn.
† State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences.
‡ Graduate School of Chinese Academy of Sciences.

TABLE 1. Proximate and Ultimate Analyses of the Char[a]

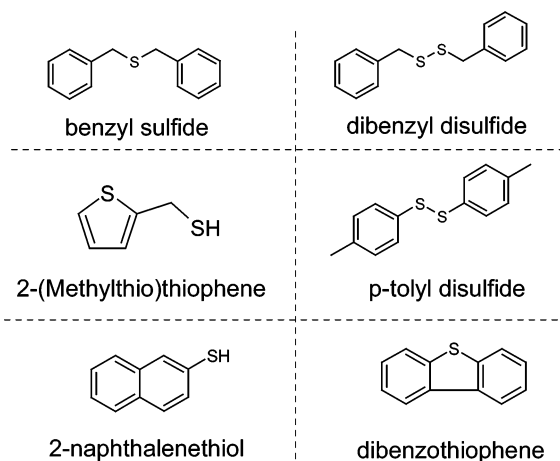|	proximate analysis		ultimate analysis (dry basis)				
sample	V	A	C	H	O	N	S
char	3.13	0.74	78.61	6.63	14.16	0.58	0.02

[a] V, volatile matter; A, ash.

China) and is of low sulfur and low ash content as indicated by the proximate and ultimate analyses shown in Table 1. Before use, the char was pulverized to pass through a 100-mesh screen (0.149 mm).

Six organic sulfur compounds, shown in Figure 1, including benzyl sulfide, dibenzyl disulfide, 2-(methylthio)-thiophene, 2-naphthalenethiol, p-tolyl disulfide, and dibenzothiophene, were chosen to represent different types of organic sulfur bonds commonly encountered in coal or in other fossil fuels, that is, C_{al}–S, C_{ar}–S, and C_{ar}–S–C_{ar}, where the subscripts al and ar stand for aliphatic and aromatic carbon, respectively. Dibenzyl disulfide (99.5% minimum) was purchased from Tokyo Kasei Kogyo Co. Ltd., and the other five compounds (99% minimum) were purchased from Acros Organics. Each of these compounds (0.03 g) was impregnated onto the char (0.2 g) by the incipient wetness method in tetrahydrofuran (THF) solutions (2 mL) at 25 °C for 1 h, followed by drying at 60 °C under a nitrogen atmosphere for 3 h. The content of each compound in the char was about 15 wt %, corresponding to sulfur content of 2–4 wt %.

The inorganic sulfur compounds studied were pyrite (FeS_2), ferrous sulfide (FeS), iron(III) sulfate, and zinc sulfate. FeS_2 of 91% purity was provided by a geologic institute in China. FeS of 99.9% purity was purchased from Sigma–Aldrich Co. with a particle size range of 100–120 mesh. The loading of the sulfates (0.02 g) on the char (0.2 g) was made by the incipient wetness method in aqueous solutions (3 mL and 0.02 N for the iron sulfate; 6 mL and 0.02 N for zinc sulfate) at 25 °C for 12 h. Mixtures of FeS_2 (0.02 g) and the char (0.2 g) or FeS (0.02 g) and the char (0.2 g) were prepared by mechanical grinding at 25 °C for 2 h. The loading content of the inorganic compounds was about 10 wt % in the char, corresponding to sulfur content of 2–5 wt %.

Cation-exchange treatments of the char were performed as follows. Aqueous solutions containing Na^+, K^+, Ca^{2+}, Fe^{2+}, Fe^{3+}, and Ni^{2+} ions (0.1 N) were prepared by dissolving an appropriate amount of the metal acetate in deionized water. The char (0.2 g) was added into the solutions (25 mL) under stirring in a nitrogen atmosphere at 25 °C for 48 h. The mixtures were then filtered and rinsed with deionized water. The metal ion loading in the char samples was determined by mass balance based on ion chromatography and ICP

benzyl sulfide

dibenzyl disulfide

2-(Methylthio)thiophene

p-tolyl disulfide

2-naphthalenethiol

dibenzothiophene

FIGURE 1. Structure of the organic sulfur compounds used.

analysis of the filtrate and the water used in washing, which is in the range of 3–5 wt %. The samples were dried under vacuum at 110 °C for 12 h. The metal-loaded char samples were then impregnated with benzyl sulfide by the incipient wetness method in THF solution.

TPD-MS and TPO-MS. All the samples were subjected to TPD-MS analysis, to explore the transformation of sulfur into the gas phase, and then followed by TPO-MS analysis, to explore transformation of sulfur into the char during the TPD. All the experiments were conducted in a fixed-bed quartz tube reactor (4 mm i.d.) coupled with a mass spectrometer (Balzers QMS422). In a typical TPD experiment, about 40 mg of sample was placed into the quartz reactor and heated from room temperature to 800 °C at a heating rate of 5 °C/min under a flow of helium. After being maintained at 800 °C for 20 min, the sample was cooled to room temperature. The TPO-MS experiment was then carried out on the residue char in a gas stream containing 20% oxygen in helium. During the TPD and TPO, the effluent gases were monitored for H_2O ($m/z = 18$), CO_2 ($m/z = 44$), CH_4 ($m/z = 16$), H_2S ($m/z = 34$), SO_2 ($m/z = 64$), COS ($m/z = 60$), CS_2 ($m/z = 76$), C_7H_6 ($m/z = 91$), C_6H_6 ($m/z = 78$), $C_{10}H_8$ ($m/z = 128$), and C_5H_6S ($m/z = 97$).

Density Functional Theory Calculation. To understand the experimental results thoroughly, quantum chemistry calculations for C–S bond rupture were made using Gaussian 98 programs. The molecular geometrical parameters were optimized first by density functional theory (DFT) by the UB3LYP/ 6-31G(d) method. Each optimized structure was confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency. Then the zero-point energies (ZPE) and thermochemical data were estimated by frequency calculations at the B3LYP/6-311++G-(d,p) level. The bond dissociation energies (BDE) of C–S bonds are defined as the enthalpy difference between the radicals generated and the parent molecule.

Results and Discussion

Behavior of the Char. As a reference, the char itself was subjected to TPD-MS and TPO-MS studies. Figure 2 shows that no sulfur-containing compounds are found in the effluent gases, such as H_2S, SO_2, COS and CS_2 in the TPD and SO_2 in the TPO. This suggests that the low sulfur content in the char has little influence on studies of the samples loaded with sulfur compounds. Furthermore, benzene, toluene, and naphthalene are also not detected, suggesting that the char does not generate these compounds during the TPD. The significant evolution of CO_2 during the TPD indicates that the char contains some oxygen functional groups (25, 26).

Behavior of Organic Sulfur Compounds Containing C_{al}–S Bond. TPD-MS and TPO-MS analyses of benzyl sulfide (Figure 1) impregnated on the char are shown in Figure 3. The structure of benzyl sulfide suggests that its decomposition may involve scission of C_{ar}–C_{al} or C_{al}–S bonds and yield toluene, benzene, or other products. However, only a single toluene peak, but no benzene peak, was observed in TPD-MS. This is very important because it suggests cleavage of C_{al}–S bonds in benzyl sulfide but not the C_{ar}–C_{al} bonds. The scission of a single C_{al}–S bond generates benzyl and benzyl-thiyl radicals, which may undergo various recombination and disproportionation reactions to form toluene, benzyl mercaptan, dibenzyl, or other products. However, the on-line MS, in an m/z range up to 300, detected no benzyl mercaptan, dibenzyl, and other products, the same as in a hydrogen atmosphere as presented later in this paper. This is very interesting because although the reactions possibly involved may be very complex, the final products are relatively simple. This suggests that the radicals generated over the char are more likely to be stabilized through abstraction of hydrogen from the char, as evidenced by the rapid release of toluene
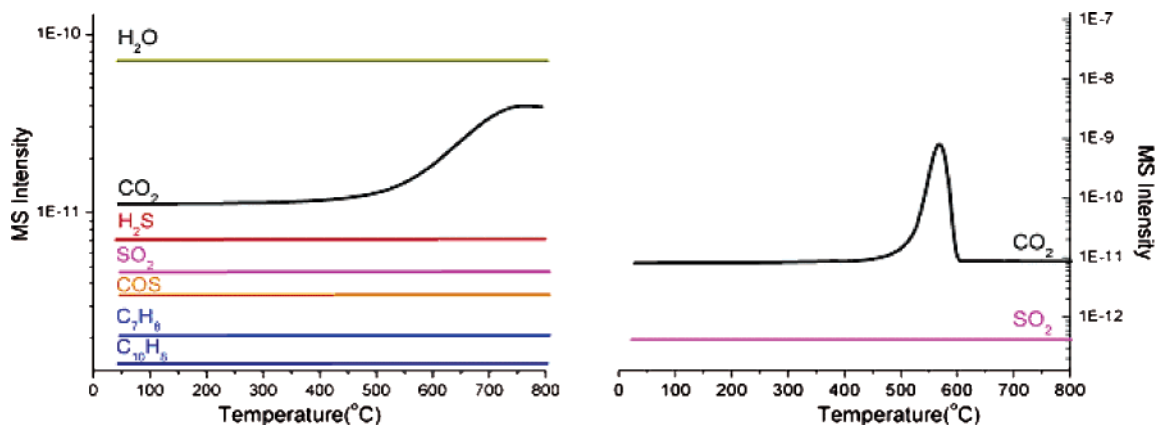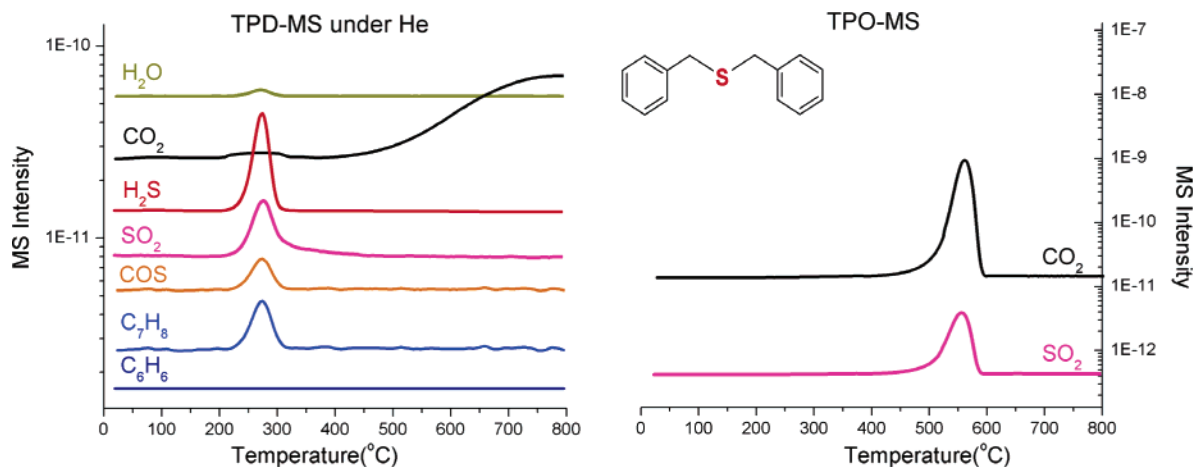
FIGURE 2. TPD-MS/TPO-MS analysis of the char.

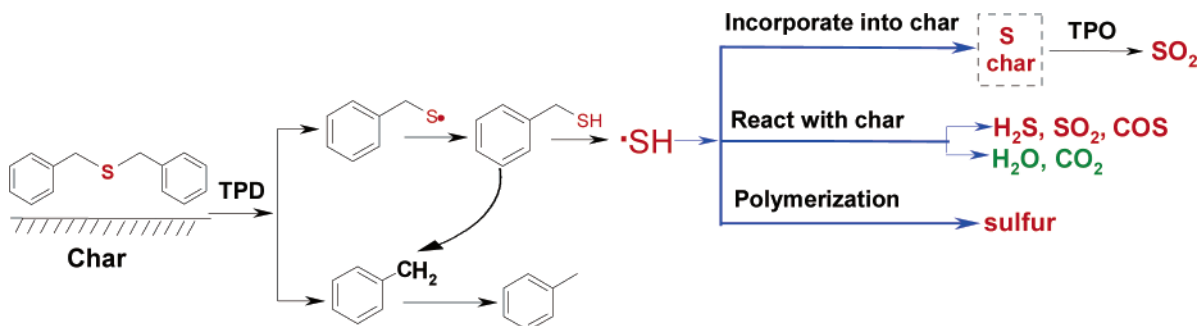**FIGURE 3. TPD-MS/TPO-MS analysis of benzyl sulfide loaded on the char.**

FIGURE 4. Sulfur transformation in decomposition of benzyl sulfide on the char.

and the absence of dibenzyl in the products. The absences of benzyl mercaptan in the gas phase indicates that the benzyl-thiyl radicals formed abstract hydrogen from the char structure and undergo further cracking to form •SH radicals and benzyl radicals at temperatures not much higher than that of the primary C_{al}−S bond scission. It is important to note that these behaviors are very different from that of benzyl sulfide decomposition in the absence of a char and the donatable hydrogen in the char is very important to the formation of the benzyl and •SH radicals. The formation of •SH radicals is supported by the deposition of elemental sulfur at the reactor outlet resulting from polymerization of the •SH radicals (27, 28).

The evolution of H_2S, SO_2, and COS in the effluent gas is also very important. Since the decomposition of benzyl sulfide on the char yields only benzyl and •SH radicals, the C and O atoms in COS and the O atom in SO_2 must also come from the char as the H does, suggesting various reactions between the •SH radical and the char or the functional groups on the

char surface. The similar peak shape and peak temperatures, including the same peak initiation temperature of 215 °C, for toluene and the gaseous sulfur compounds suggest that the reactivity of the •SH is high, which quickly reacts with the char upon its formation. The absence of sulfur compound evolution in the higher temperature range after the first peak may indicate that there is no sulfur structure formed in the char or that the sulfur structure formed in the char is thermally stable under the TPD conditions.

It is interesting to note that our earlier study (24) of a high-ash char loaded with benzyl sulfide showed the formation of CS_2 along with H_2S, SO_2, and COS in TPD. The absence of CS_2 evolution observed in this work seems to suggest that the ash in the char plays an important role in catalyzing CS_2 formation.

It is also interesting to note that H_2O and CO_2 peaks are visible with the same peak temperature as that of toluene and gaseous sulfur compounds. Since the char itself does
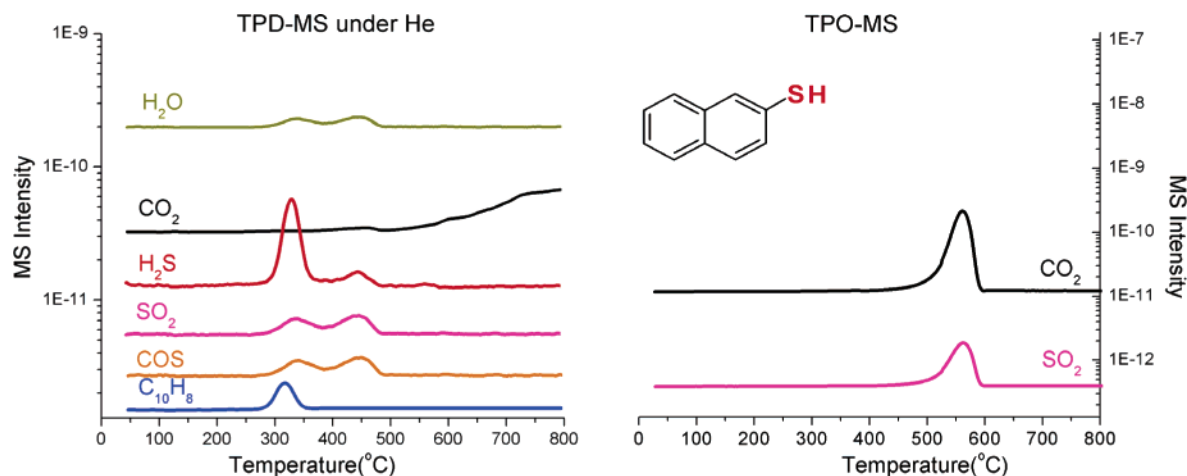
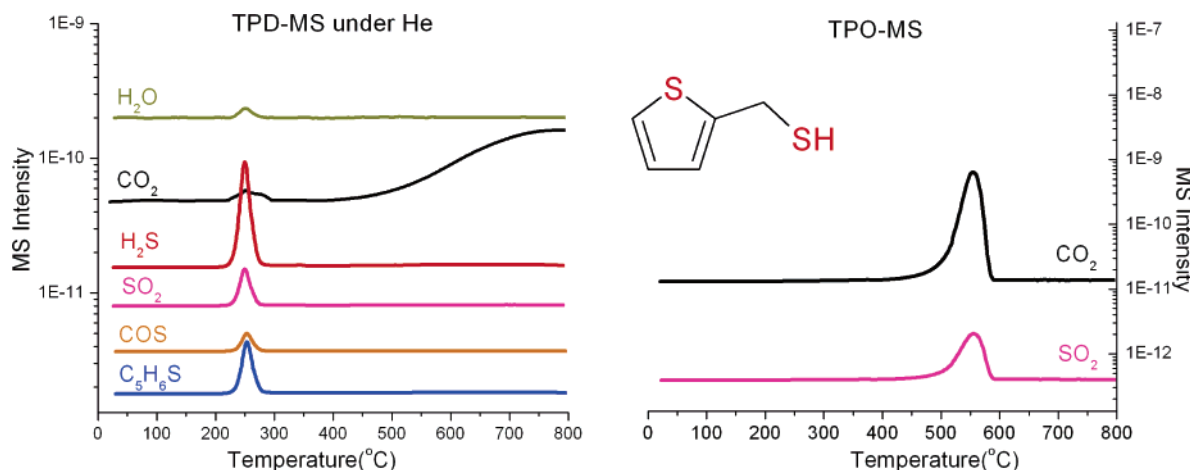**FIGURE 5.** TPD-MS/TPO-MS analysis of 2-naphthalenethiol loaded on the char.

FIGURE 6. TPD-MS/TPO-MS analysis of 2-(methylthio)thiophene loaded on the char.

not evolve these compounds in the temperature range, it indicates that the formation of H_2O and CO_2 are induced from or related to the reactions of the $\cdot$SH radical with the char. It is logical to believe that the formation of COS and SO_2 from interactions of the $\cdot$SH radicals with the char would yield hydrogen-containing compounds such as H_2O. Since the formation of H_2O and CO_2 is not the focus of this paper, the possible mechanisms responsible for their formation are not discussed further.

The results of TPO experiments are also shown in Figure 3. Because the char itself has no contribution to sulfur evolution during the TPD and TPO process, the significant SO_2 evolution accompanied by CO_2 evolution indicates the formation of sulfur structures in the char resulted from interactions between the $\cdot$SH radical and the char. On the basis of this information, transformation of sulfur in decomposition of benzyl sulfide impregnated on the char is presented simply in Figure 4, ignoring many possible intermediate reaction steps.

TPD-MS and TPO-MS experiments on dibenzyl disulfide (Figure 1) were also performed under the same conditions (data not shown) and yield similar results as those of benzyl sulfide: that is, (1) rupture of the C_{al}–S bond starting at 215 °C to form the benzyl radical and the Ph–Ch_2–S–S$\cdot$ radical, where Ph and Ch_2 denote the phenyl group and the CH_2 group, respectively; (2) hydrogen abstraction of the Ph–Ch_2–S–S$\cdot$ radical from the char to form Ph–Ch_2–S–SH, which undergoes further cracking to form the Ph–Ch_2–S$\cdot$ and $\cdot$SH radicals; (3) hydrogen abstraction of the Ph–Ch_2–S$\cdot$ radical from the char to form Ph–Ch_2–SH, which undergoes further cracking to form toluene and $\cdot$SH radicals; and (4) fast reaction

of the $\cdot$SH radical with the char to form various sulfur-containing compounds, evolving into the gas phase or incorporating into the char. All these reaction steps proceed very quickly, resulting in single MS peaks for toluene and for each gaseous sulfur compound.

It must be noted that the cleavage temperature of the C_{al}–S bond observed in this work for a low-ash char, 215 °C, is much higher than that observed earlier for a high-ash char, 150 °C (24). This significant difference may suggest that the ash or, in a more strict term, the minerals in the chars play important roles in C_{al}–S bond cleavage.

Behavior of Organic Sulfur Compounds Containing C_{ar}–S Bonds. TPD-MS and TPO-MS results for 2-naphthalenethiol (Figure 1) are shown in Figure 5. The single naphthalene peak, starting at 280 °C and peaking at 315 °C, suggests cleavage of the C_{ar}–S bond and generation of the $\cdot$SH radical in one step. The H_2S, SO_2, and COS peaks as well as the small H_2O and CO_2 peaks in the same temperature range as that of naphthalene indicate that the reactions of $\cdot$SH radical with the char, starting at 280 °C, are similar to that observed for the compounds with C_{al}–S bonds discussed earlier starting at 215 °C. It is surprising, however, to see additional H_2S, SO_2, and COS peaks as well as H_2O and CO_2 peaks in the MS spectra, starting from 395 °C, in Figure 5. This suggest that the new sulfur structures formed in the char resulting from interactions between the $\cdot$SH radical and the char at 280 °C are different from those at 215 °C, and some of the new sulfur structures formed in the char decompose at temperatures greater than 395 °C.

To explore this difference further, TPD-MS and TPO-MS of 2-(methylthio)thiophene (Figure 1) loaded on the char
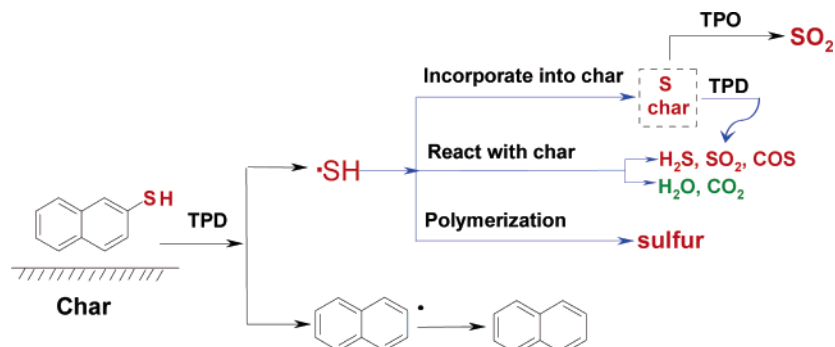
FIGURE 7. Sulfur transformation in decomposition of 2-naphthalenethiol on the char.
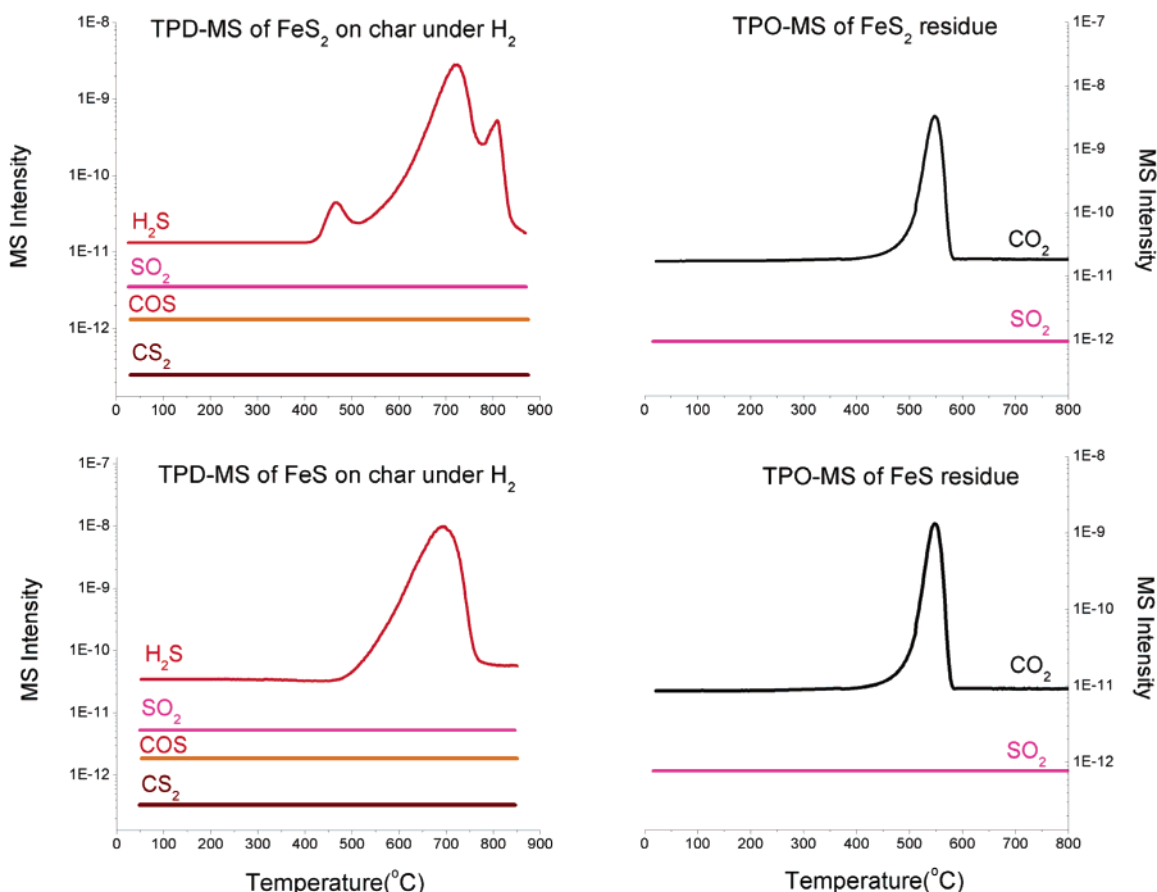

FIGURE 8. TPD-MS/TPO-MS analysis of FeS$_2$ and FeS mixed with the char.

were also studied. Figure 6 shows a single 2-methylthiophene peak appearing at around 255 °C along with the release of H$_2$S, SO$_2$, and COS in the same temperature range, indicating cleavage of the C$_{al}$—S bond and direct formation of the •SH radical as 2-naphthalenethiol does. The absence of sulfur compound evolution in the higher temperature range after the first peak indicates that the sulfur compounds formed in the char are thermally stable. This finding suggests that the sulfur structures formed in the char from the reactions of •SH radical and the char are temperature-related. These results may also suggest that the 2-methylthiophene radical, although containing a sulfur atom, has no significant ability to react with the char to form sulfur structures in the char.

The TPO-MS study on the TPD residue of 2-naphthalenethiol shows the same behavior as that of benzyl sulfide: simultaneous SO$_2$ and CO$_2$ peaks at 560 °C. This suggests interactions of the •SH radical with the char and the formation of stable sulfur structures in the char. On the basis of this information, sulfur transformation during decomposition of 2-naphthalenethiol can be written as in Figure 7.

TPD-MS and TPO-MS studies are preformed also on *p*-tolyl disulfide (Figure 1) loaded on the char. The results (data not shown) are similar to those for 2-naphthale-nethiol: a single toluene peak, starting at 280 °C and peaking at 315 °C, accompanied by evolution of H$_2$S, SO$_2$, and COS as well as small H$_2$O and CO$_2$ peaks in the same temperature range. It is important to point out that the TPD of *p*-tolyl disulfide also yields two peaks for all the gaseous sulfur compounds as 2-naphthalenethiol does, although it does not directly form the •SH radical upon the primary S—S bond scission. This further suggests that the sulfur structures responsible for the second sulfur compound peak in the TPD result from high-temperature interactions between the •SH radical and the char. The deposition of elemental sulfur at the outlet of the reactor in the TPD of 2-naphthalenethiol, 2-(methylthio)thiophene, and *p*-tolyl disulfide further suggests that the •SH radical is formed in these cases. It is worth noting that the initial bond cleavage temperature of C$_{ar}$—S is 280 °C, which is 65 °C higher than that of the C$_{al}$—S bond. This order agrees with the bond energies determined by
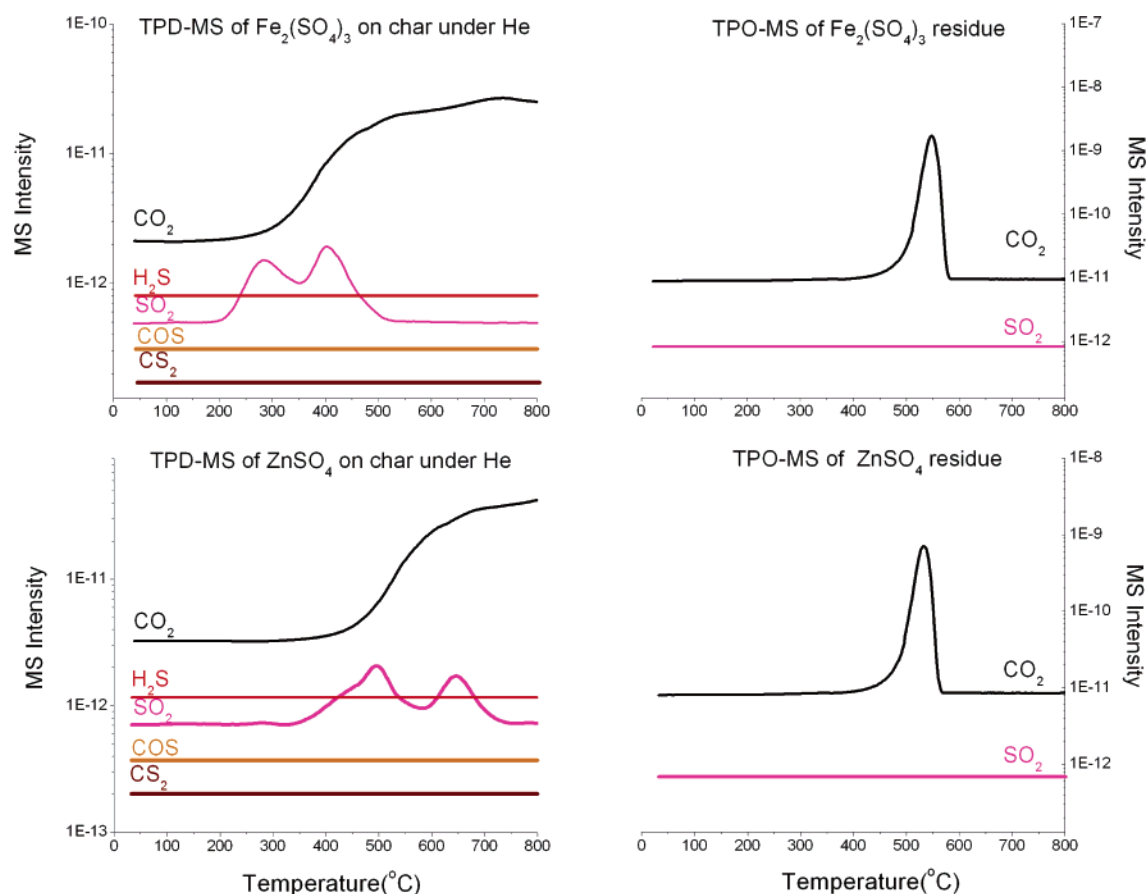
FIGURE 9. TPD-MS/TPO-MS analysis of Fe$_2$(SO$_4$)$_3$ and ZnSO$_4$ loaded on the char.

density functional theory calculations, 210.8 kJ/mol for C$_{al}$—S and 330.8 kJ/mol for C$_{ar}$—S.

Behavior of Dibenzothiophene. TPD-MS and TPO-MS profiles (Figure omitted) of dibenzothiophene (Figure 1) are very different from the five sulfur compounds already discussed but similar to that of the char in Figure 2. In addition, white dibenzothiophene crystal is found at the outlet of the reactor, indicating vaporization of dibenzothiophene during the TPD. Clearly, no bond cleavage occurs and no radical is generated in the TPD. The absence of an SO$_2$ peak in TPO indicates that no sulfur is transformed into the char during the TPD. This phenomenon indicates that the sulfur atoms in a compound cannot interact with and transfer into the char without the formation of the •SH radical.

On the basis of the TPD-MS and TPO-MS studies of the six organic sulfur compounds, it is certain that formation of the •SH radical is a key step to initiate reactions with the char and consequently results in sulfur transformation. However, it is not clear whether the gaseous sulfur compounds, such as H$_2$S, SO$_2$, and COS, formed from reactions of the •SH radical with the char are also responsible for the transformation of sulfur in the char. To clarify this possibility, more TPD-MS and TPO-MS studies were made on pyrite, FeS, and two inorganic sulfates.

Behavior of Inorganic Sulfur Compounds. TPD-MS and TPO-MS studies of FeS$_2$ and FeS mixed with the char were preformed under hydrogen to evaluate the role of H$_2$S in sulfur transformation. Figure 8 shows that, as expected, TPD results in the formation of H$_2$S in a temperature range of 420−850 °C for FeS$_2$ and 480−750 °C for FeS. The three well-defined H$_2$S peaks for FeS$_2$ suggest that the pyrite in the presence of the char and H$_2$ undergoes transformation to pyrrhotite and then to troilite (29) and then to elemental Fe, as evidenced by X-ray diffraction (XRD) analysis of the TPD

residue (not shown). It is important to note that the TPO-MS analysis made right after the TPD-MS analysis yields no SO$_2$ in the effluent. The absence of COS and SO$_2$ in the TPD and the absence of SO$_2$ in the TPO suggest that H$_2$S is formed from the reactions between FeS$_2$ and H$_2$ and that H$_2$S does not interact with the char under the conditions used. The TPD-MS, TPO-MS, and XRD analyses conducted on FeS gave results similar to those for FeS$_2$, which confirms that H$_2$S has no ability to react with the char to form sulfur structures in the char in the temperature range of 420−850 °C.

Figure 9 shows TPD-MS profiles of Fe$_2$(SO$_4$)$_3$ and ZnSO$_4$ impregnated on the char under helium. It is clear that TPD of these two compounds yields only SO$_2$ in the gas phase, from 200 to 530 °C for Fe$_2$(SO$_4$)$_3$ and from 330 to 750 °C for ZnSO$_4$, and no other gaseous sulfur compounds are formed. The TPO-MS analysis following TPD-MS shows no evolution of SO$_2$ for both sulfates. It is obvious that TPD of the sulfates mixed with the char does not involve the formation of •SH radical and that SO$_2$ formed from the decomposition of the sulfates does not react with the char to form sulfur structures in the char in the temperature range of 200−750 °C. These data indicate that SO$_2$ is not an intermediate in the sulfur transformation to the char.

Role of Hydrogen. Hydrogen has been reported to have significant effects on sulfur partitioning in thermal processing of coal (30−32). If the •SH radical is an important intermediate in sulfur transformation, hydrogen may have an effect on formation and reaction of •SH radicals. To gain insight on this subject, TPD-MS studies were carried out on the char and the benzyl sulfide-loaded char under a hydrogen atmosphere, followed by TPO-MS studies. Figure 10 shows that the TPD behavior of the char in H$_2$ is similar to that in He (Figure 2): gaseous sulfur compounds, benzene, and toluene are not detected in the reactor effluent. However,
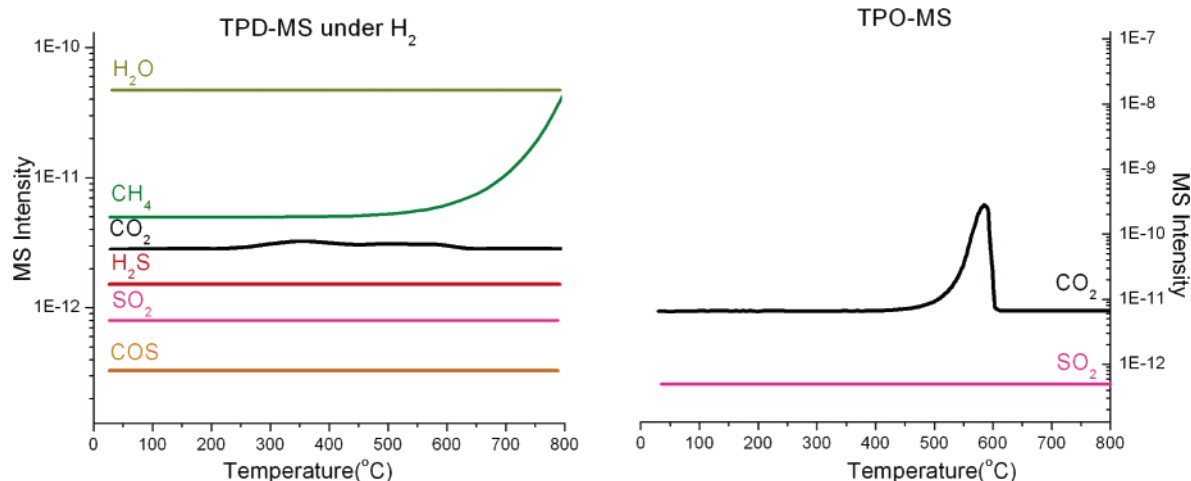
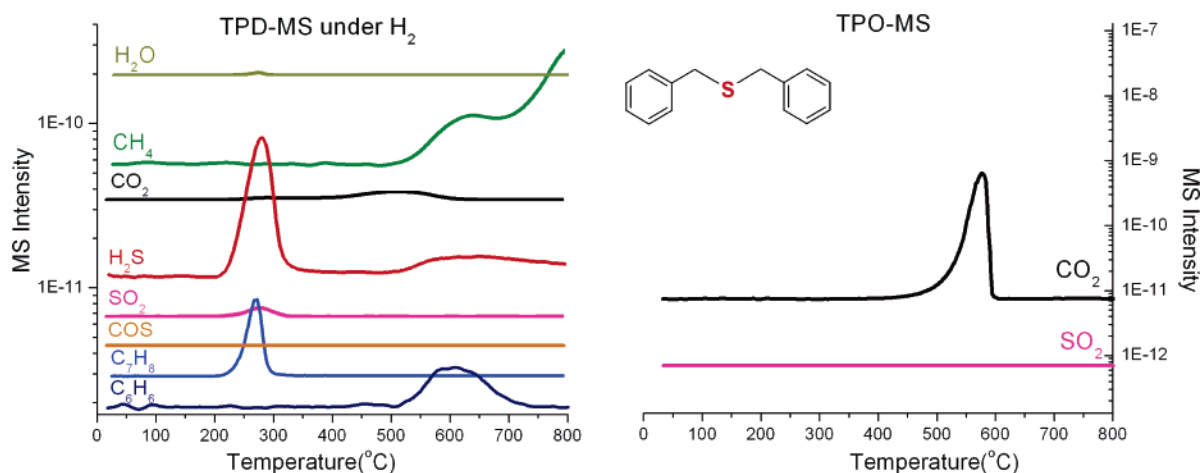FIGURE 10. TPD-MS in H_2/TPO-MS analysis of the char.

FIGURE 11. TPD-MS in H_2/TPO-MS analysis of benzyl sulfide loaded on the char.

increased CH_4 evolution and decreased CO_2 evolution in H_2, compared to that in He, indicate that H_2 does interact with the char and possibly modifies the char surface, especially at temperatures greater than 400 °C.

TPD-MS results for the char-supported benzyl sulfide under H_2 atmosphere and the corresponding TPO-MS results are shown in Figure 11. Similar to those in He (Figure 3), the TPD-MS spectra show toluene, H_2S, and SO_2 peaks starting at 215 °C and peaking at 270 °C. The absence of benzyl mercaptan in the gaseous product further suggests the key role of •SH in the sulfur transformation. The increased H_2S peak, the disappearance of the COS peak, and the reduced SO_2 peak show the effect of H_2 on stabilizing the •SH radical and inhibiting its reaction to form oxygen-containing sulfur compounds. The similarity in peak temperature and deviation in peak intensity suggest that H_2 has little effect on cleavage of C_{al}–S bond in benzyl sulfide but has an effect on reactions of the radicals formed. Furthermore, it is surprising to see that a broad benzene peak accompanied by a broad H_2S peak and a CH_4 peak, but not a toluene peak, appear in the temperature range 510−750 °C, which is very different from that in He. These seem to suggest that a large fraction of toluene generated from cleavage of C_{al}–S bonds can also be retained in the char in the presence of H_2, which then undergoes further cracking to yield benzene and CH_4, and that some of the sulfur structures formed in the char via the •SH radical at low temperatures undergo reactions at high temperatures to release H_2S, with the help of H_2.

The TPO-MS experiment performed after TPD shows no SO_2 release, which indicates that no sulfur structure is left

in the char. This behavior may indicate that H_2 stabilizes the radicals formed and modifies the char surface, which weakens the interactions between the radicals and the char and results in the formation of less stable sulfur structures in the char (compared to the sulfur structures formed in the He environment), which decompose at higher temperatures in TPD. It should be noted that elemental sulfur was also found at the outlet of the reactor during TPD, which confirms the generation of the •SH radicals through cleavage of C_{al}–S bonds in H_2.

Effect of Metals on Sulfur Transformation. As mentioned earlier, the chars of different ash contents result in different sulfur transformation behavior in TPD. This effect can be attributed to the effect of minerals. It is necessary, therefore, to understand the effect of various minerals commonly found in coal on the formation and reaction of •SH radicals. Figure 12 shows TPD-MS results, in He, of char samples preloaded with Na^+, K^+, Ca^{2+}, Fe^{2+}, Fe^{3+}, and Ni^{2+} irons and impregnated with benzyl sulfide. Clearly, the mineral ions have strong effects on the sulfur transformation, in terms of the C_{al}–S bond cleavage temperature and the reactions of •SH with the char.

Compared to the char impregnated with benzyl sulfide (see Figure 3) and to the samples load with other metal ions, the cleavage of the C_{al}–S bond on Na- and K-loaded chars occurs at a higher temperature, about 245 °C, and the gaseous products includes CS_2, which was found in our earlier work on a high-ash char (24). It is important also to note that the TPO-MS spectrum shows no SO_2 peak (data not shown). These suggest that the reactions of the sulfur radical with the
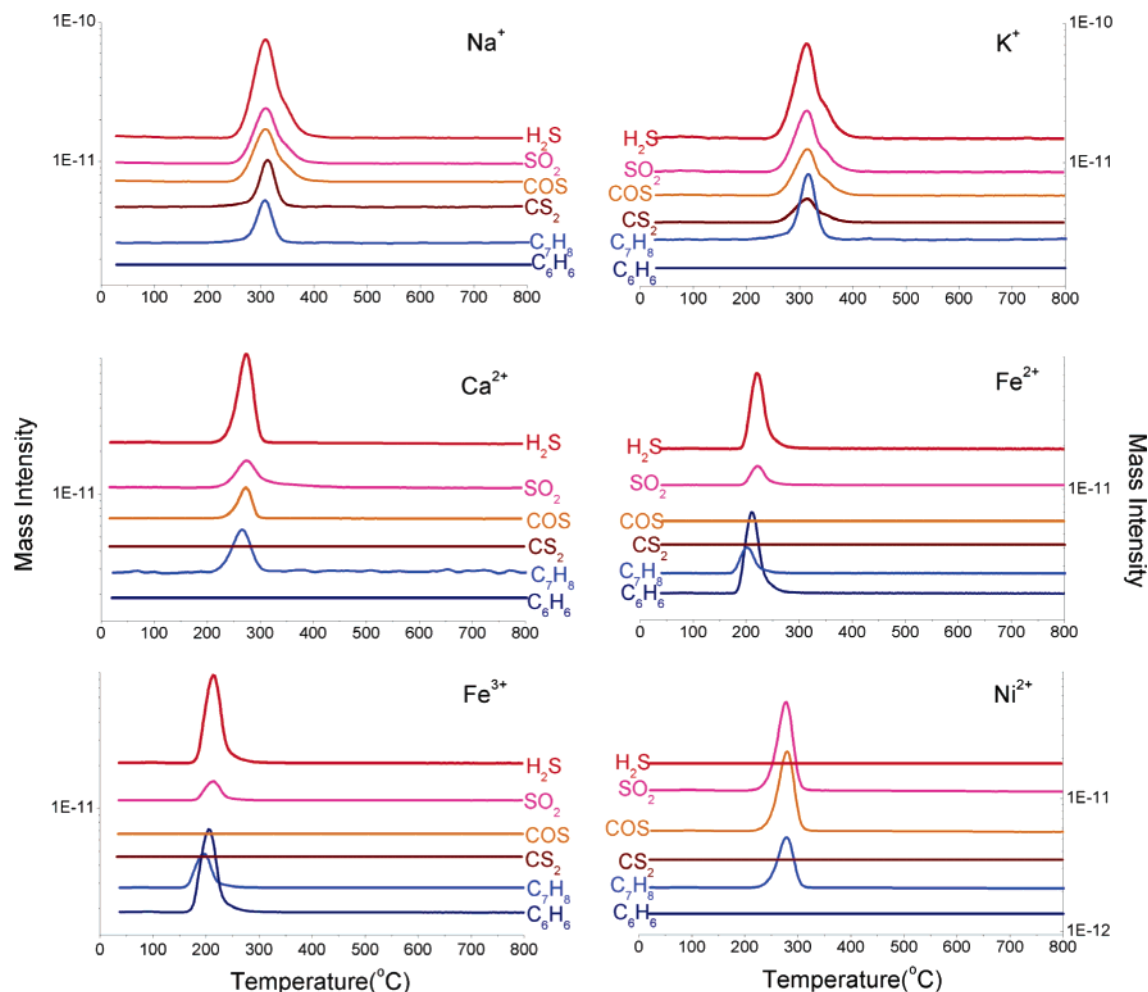
FIGURE 12. TPD-MS/TPO-MS analysis of benzyl sulfide loaded on the metal-laden char.

char yield only gaseous sulfur products and no sulfur structure is formed in the char in the presence of Na and K.

TPD-MS of benzyl sulfide impregnated on a Ca-loaded char shows the same behavior as that in Figure 3, including the formation of elemental sulfur, and the TPO-MS experiment shows the formation of SO_2 (data not shown). Clearly, Ca has little influence on the formation and reaction of sulfur radicals in the temperature range 210–310 °C, although it has been used extensively to adsorb H_2S and SO_2 in practice (*33, 34*).

TPD-MS of benzyl sulfide impregnated on Fe(II)- and Fe-(III)-loaded chars show different behavior in comparison to all the MS spectra presented so far: a low C_{al}–S bond cleavage temperature, 175 °C for Fe(II) and 160 °C for Fe(III); the formation of benzene; and the absence of COS in the product. The evolution of SO_2 in TPO-MS suggests the formation of new sulfur structures in the char. Apparently, Fe catalyzes the dissociation of C_{al}–S and C_{ar}–C_{al} bonds.

TPD-MS of benzyl sulfide impregnated on a Ni-loaded char is also different from the others. The most significant difference is the absence of H_2S in the product. Since the TPO-MS shows evolution of SO_2, Ni seems to alter only the reactions associated with hydrogen.

Clearly, different metals have very different effects on sulfur transformation in pyrolysis of benzyl sulfide impregnated on the char, and these effects are too complex to be elucidated on the basis of the data available in this paper. But these effects provide further evidence on the •SH-based mechanism for sulfur transformation and may open up new research areas and also stimulate development of new technologies for sulfur emission control.

Complex sulfur transformation behavior in pyrolysis of coal is uncoupled in this work. It is found that the secondary reactions responsible for sulfur transformation are initiated by formation of the •SH radical. The •SH radical is very active and able to acquire H, O, and C atoms from the char structure to form H_2S, SO_2, and COS, to polymerize into elemental sulfur, and to be retained in the char through reactions with the char structure. H_2S and SO_2 do not have such abilities. The reactions of the •SH radical with the char are influenced by the gas atmosphere and by the presence of minerals in the char. H_2 stabilizes the radicals formed, weakens their interactions with the char, and results in high H_2S evolution. Na and K in the char prevent the transformation of the •SH radical into the char and result in the formation of CS_2 in addition to other gaseous sulfur compounds. Ni prevents the formation of H_2S. Fe(II) and Fe(III) prevent the formation of COS and CS_2. The identification of the •SH radical as the key intermediate in sulfur transformation in coal is very important, which rationalizes the complex behaviors as understood presently in the literature.

Literature Cited

(1) Stock, L. M.; Wolny, R.; Bal, B. Sulfur distribution in American bituminous coals. *Energy Fuels* **1989**, *3*, 651–661.

(2) Majchrowicz, B.; Yperman, J.; Mullens, J.; Van Poucke, L. Automated potentiometric determination of sulfur functional groups in fossil fuels. *Anal. Chem.* **1991**, *63*, 760−763.

(3) Makishima, A.; Nakamura, E. Determination of Total Sulfur at Microgram per Gram Levels in Geological Materials by Oxidation of Sulfur into Sulfate with in Situ Generation of Bromine Using Isotope Dilution High-Resolution ICPMS. *Anal. Chem.* **2001**, *73*, 2547−2553.

(4) Calkins, W. H. The chemical forms of sulfur in coal: a review. *Fuel* **1994**, *73*, 475−484.

(5) Maes, I. I.; Gryglewicz, G.; Machnikowska, H.; Yperman, J.; Franco, D. V.; Mullens, J.; Van Poucke, L. C. Rank dependence of organic sulfur functionalities in coal. *Fuel* **1997**, *76*, 391−396.

(6) Renedo, M. J.; Fernandez, J. Preparation, Characterization, and Calcium Utilization of Fly Ash/Ca(OH)₂ Sorbents for Dry Desulfurization at Low Temperature. *Ind. Eng. Chem. Res.* **2002**, *41*, 2412−2417.

(7) Hayvanovych, V.; Pysh'yev, S. Desulfurization of Low-Rank Coal with High Sulfur Content is the First Stage of Coal Burning at Heat Electric Stations. *Energy Fuels* **2003**, *17*, 1186−1190.

(8) Miura, K.; Mae, K.; Shimada, M.; Minami, H. Analysis of Formation Rates of Sulfur-Containing Gases during the Pyrolysis of Various Coals. *Energy Fuels* **2001**, *15*, 629−636.

(9) Liu, Q. Y.; Liu, Z. Y.; Huang, Z. G.; Xie, G. Y. A honeycomb catalyst for simultaneous NO and SO₂ removal from flue gas: preparation and evaluation. *Catal. Today* **2004**, *93−95*, 833−837.

(10) Liu, Q. R.; Hu, H. Q.; Zhou, Q.; Zhu, S. W.; Chen, G. H. Effect of mineral on sulfur behavior during pressurized coal pyrolysis. *Fuel Process. Technol.* **2004**, *85*, 863−871.

(11) Wang, T.; Zhu, X. F. Sulfur transformations during supercritical water oxidation of a Chinese coal. *Fuel* **2003**, *82*, 2267−2272.

(12) Xu, W. C.; Kumagai, M. Sulfur transformation during rapid hydropyrolysis of coal under high pressure by using a continuous free fall pyrolyzer. *Fuel* **2003**, *82*, 245−254.

(13) Telfer, M.; Zhang, D. K. The influence of water-soluble and acid-soluble inorganic matter on sulphur transformations during pyrolysis of low-rank coals. *Fuel* **2001**, *80*, 2085−2098.

(14) Patrick, J. W. Sulphur release from pyrites in relation to coal pyrolysis. *Fuel* **1993**, *72*, 281−285.

(15) Yan, R.; Chin, T.; Ng, Y. L.; Duan, H.; Liang, D. T.; Tay, J. H. Influence of Surface Properties on the Mechanism of H₂S Removal by Alkaline Activated Carbons. *Environ. Sci. Technol.* **2004**, *38*, 316−323.

(16) Lin, L.; Khang, S. J.; Keener, T. C. Coal desulfurization by mild pyrolysis in a dual-auger coal feeder. *Fuel Process. Technol.* **1997**, *53*, 15−29.

(17) Mukherjee, S.; Borthakur, P. C. Effects of alkali treatment on ash and sulphur removal from Assam coal. *Fuel Process. Technol.* **2004**, *85*, 93−101.

(18) Soneda, Y.; Makino, M.; Yasuda, H.; Yamada, Q.; Kobayashi, M.; Kaiho, M. The effect of acid treatment of coal on H₂S evolution during pyrolysis in hydrogen. *Fuel* **1998**, *77*, 907−911.

(19) Ibarra, J. V.; Bonet, A. J.; Moliner, R. Release of volatile sulfur compounds during low-temperature pyrolysis of coal. *Fuel* **1994**, *73*, 933−939.

(20) Cernic-Simic, S. A Study of Factors That Influence the Behavior of Coal Sulfur During Carbonization. *Fuel* **1962**, *41*, 141−151.

(21) Attar, A. Chemistry, Thermodynamics and Kinetics of Reactions of Sulfur in Coal-gas Reactions: A Review. *Fuel* **1978**, *57*, 201−213.

(22) Kozowski, M.; Wachowska, H.; Yperman, J. Transformations of sulphur compounds in high-sulphur coals during reduction in the potassium/liquid ammonia system. *Fuel* **2003**, *82*, 1149−1153.

(23) Karaca, S.; Bayrak, R.; Gürses, A. Investigation of relation between both sulfur removal and adsorption capacity with surface morphology of a pyrolysed Turkish lignite. *Fuel* **2003**, *82*, 1013−1019.

(24) Xu, L.; Yang, J. L.; Li, Y. M. Liu, Z. Y. Behavior of organic sulfur model compounds in pyrolysis under coal-like environment. *Fuel Process. Technol.* **2004**, *85*, 1013−1024.

(25) Zhuang, Q. L.; Kyotani, T.; Tomita, A. DRIFT and TK/TPD Analyses of Surface Oxygen Complexes Formed during Carbon Gasification. *Energy Fuels* **1994**, *8*, 714−718.

(26) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Órfão, J. J. M. Modification of the surface chemistry of activated carbons. *Carbon* **1999**, *37*, 1379−1389.

(27) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 3rd ed.; J. Wiley & Sons: New York, 1962; pp 349−351.

(28) Bates, D. R., Rowe, B. R., Mitchell, J. B. A., Canosa, A., Eds.; *Dissociative Recombination*; NATO ASI Series; Plenum: New York, 1993; pp 1−10.

(29) Elsner, M.; Schwarzenbach, R. P.; Haderlein, S. B. Reactivity of Fe(II)-Bearing Minerals toward Reductive Transformation of Organic Contaminants. *Environ. Sci. Technol.* **2004**, *38*, 799−807.

(30) Sinha, R. K.; Walker, P. L. Desulfurization of Coals and Chars by Treatment in Various Atmospheres between 400 and 600 °C. *Fuel* **1972**, *51*, 329−331.

(31) Gryglewicz, G.; Rutkowski, P.; Yperman, J. Characterization of Sulfur Functionalities of Supercritical Extracts from Coals of Different Rank, Using Reductive Pyrolysis. *Energy Fuels* **2004**, *18*, 1595−1602.

(32) Westberg, H. M.; Bystrom, M.; Leckner, B. Distribution of Potassium, Chlorine, and Sulfur between Solid and Vapor Phases during Combustion of Wood Chips and Coal. *Energy Fuels* **2003**, *17*, 18−28.

(33) Matsuoka, K.; Abe, A.; Tomita, A. Suppression of SO₂ Emission during Coal Oxidation with Calcium Loaded by Hydrothermal or Hydration Treatment. *Energy Fuels* **2001**, *15*, 648−652.

(34) Grubor, B.; Manovic, V. Influence of Non-Uniformity of Coal and Distribution of Active Calcium on Sulfur Self-Retention by Ash—A Case Study of Lignite Kolubara. *Energy Fuels* **2002**, *16*, 951−955.