Catalytic reduction of SO$_2$ during combustion of typical Chinese coals

Yanhua Liu*, Defu Che, Tongmo Xu

School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Abstract

The catalytic effects of doping agents on SO$_2$ emission as well as the coal combustion behavior were investigated by thermogravimetry. All experiments were carried out in a flowing air atmosphere at a heating rate of 20 or 30 °C/min up to 1000 °C. The doping agents employed were NaCl, CaCl$_2$, FeCl$_3$, FeCl$_2$ and Fe$_2$O$_3$. The experimental results show that the agents added in coal reduce SO$_2$ emission of coal, with CaCl$_2$ being the most effective. The doping agents work with different mechanisms. The catalysis of NaCl, CaCl$_2$, and Fe$_2$O$_3$ promotes the reactions between SO$_2$ and the minerals in coal, and enhances the sulfur retention capacity of coal ash, thus decreasing SO$_2$ concentration in flue gas. They have weak effects on the combustion behavior of the coal. FeCl$_3$ and FeCl$_2$ have strong effects on coal combustion behaviour. They accelerate the combustion and improve the ignition of the char subsequently formed, increasing SO$_2$ concentration in flue gas in the region from 300 to 520 °C. However, they reduce the total amount of SO$_2$ emission during combustion. The reduction of SO$_2$ yield by FeCl$_3$ and FeCl$_2$ mainly results from the Fe$_2$O$_3$ created from them at high temperatures.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfur dioxide; Doping agent; Thermogravimetry

1. Introduction

The study on the emissions from coal combustion is still of significant interest due to the contribution of these pollutants to rain acidification, global warming and depletion of stratospheric ozone layer [1,2]. How these pollutants are considerably reduced is still challenging the scientists and the engineers all over the world although much effort has been made and various practical technologies have been employed in industries more

---

* Corresponding author. Tel.: +86-292660443; fax: +86-292668789.
  E-mail address: yhliu@xjtu.edu.cn (Y. Liu).

efficiently than ever over the past decades. Lowering the flame temperature and decreasing the oxygen supply in combustion systems are the common methods for minimizing the NO_X emission from coal combustion since thermal NO formation is very temperature-dependent [3], adding absorbents such as limestone or dolomite to the combustion process is a familiar way to reduce SO_2 emissions, and besides, catalysis concept has been introduced in combustion process due to the successful removal of pollutants by metal catalysts from flue gas before the emissions go in to the atmosphere [4–7].

Thermogravimetry has been widely used to study the combustion characteristics of coal, and a great amount of literature is available. In addition, it has been also used to investigate the behaviors of absorbents through the measurement of emission, and some valuable conclusions have been drawn [8–10]. In this paper, the catalytic effects of doping agents on the coal sulfur release as well as the coal combustion behavior have been studied by thermogravimetry. The doping agents employed are NaCl, $CaCl_2$, $FeCl_3$, $FeCl_2$ and FeO_3. The chlorides are chosen because they are important components in municipal solid waste (MSW) and have significant effects on the emissions during co-combustion of coal and MSW [11–13]. Although $FeCl_3$ and $FeCl_2$ are probably not constituents of MSW, they are selected in the study because they are usually employed as catalysts during coal utilizations [14–19]. Fe_2O_3, which is an important component in coal ash and can be formed by oxidizing $FeCl_3$ and $FeCl_2$ at high temperatures, is picked because it can be used to compare the effects of Fe ion in different compounds.

2. Experimental

2.1. Procedure and product analysis

All experiments were carried out on a thermogravimetric analyzer (made in China). The experimental equipment consists of a reactor, a weight detector (TG), a differential weight-analyzer (DTG), a differential thermal analyzer (DTA) and gas analyzer. A sample basket loaded with coal of 20 mg was placed into the reactor and then heated in a flowing air from room temperature to 1000 °C at a constant heating rate of 20

Table 1
Proximate and elemental analysis for the studied coal (wt.%, as received basis)

Proximate		Ultimate	
Moisture	2.5	Carbon	48.37
Ash	37.73	Hydrogen	2.86
Volatile	14.30	Nitrogen	0.86
Fixed carbon	45.47	Oxygen	4.73
		Sulfur	3.04
		Sulfates	0.55
		Pyrites	1.67
		Organic sulfur	0.82

Table 2
Size distribution for the studied coal

Particle size (μm)	Distribution (wt.%)
< 50	31.6
50–57	37.7
58–70	10.4
71–90	12.4
91–110	4.3
111–180	2.8
181–280	0.4
>280	0.4

°C/min or 30 °C/min. The flow rate of the air was 60 cm^3/min. The TG, DTG, and DTA data of sample versus time were recorded with a recording instrument. The concentrations of SO_2, NO and CO in flue gas were detected by an on-line gas analyzer (made in Germany) at the gas exit. The detection principle is based on chemical absorption. The concentrations of SO_2, NO and CO are expressed in volumetric fraction. The errors of SO_2, NO and CO measurements determined by repeated runs were within ± 5%.

2.2. Sample preparation

The parent coal used in this study is a pulverized coal for power plants from Tongchuan mine of China. The proximate analysis and elemental analysis data are shown in Table 1, the size distribution in Table 2, and the ash analysis in Table 3, respectively. The agents used are NaCl, $CaCl_2$, $FeCl_3$, $FeCl_2$ and Fe_2O_3, which are dry and ground into the fines less than 40 μm in advance. Each agent is mixed directly with the coal powder at room temperature and the dose rate is 6% by weight. The relatively higher percentage than in practice is chosen in order to elucidate the mechanism. Totally six samples are prepared including a parent coal sample for comparison. Each mixture (sample) is stirred well and kept airproof in a glass container overnight at room temperature before being combusted.

Table 3
Ash analysis for the studied coal (wt.%)

SiO_2	48.92
Al_2O_3	32.36
Fe_2O_3	6.7
CaO	3.47
MgO	0.55
K_2O	0.16
Na_2O	2.80
SO_3	2.83
TiO_2	1.18

3. Experimental results

3.1. The emission behavior of NO, CO and SO_2 from the parent coal

In Fig. 1, the data of NO, CO and SO_2 emissions versus temperature from the parent coal at a heating rate of 30 °C/min show the distinctions among coal nitrogen, sulfur and carbon. The curve for NO is of a single peak with asymmetry, and the peak does not appear until the temperature is elevated over 750 °C, which indicates that it is relatively more difficult for coal nitrogen to be released than coal sulfur.

A great amount of previous research has shown that the release of coal nitrogen during combustion is strongly dependent on the nitrogen functionalities in coal molecular structure. According to the investigation completed by XPS by the authors, the dominating nitrogen functionalities of the studied coal are pyridinic and pyrrolic nitrogen, and there are less quaternary nitrogen and nitrogen oxides [20]. It is concluded therefore that pyridinic and pyrrolic nitrogen are harder to be oxidized and subsequently released in NO. Compared to that of CO and SO_2, both the volumetric fraction and the total yield of NO are observed to be the lowest, which is due to the low content of coal nitrogen, only 0.86% by weight for the studied coal (Table 1).

CO is a dominant product and shows a peak at 600 °C corresponding to the temperature at which coal char is burnt severely, and a shoulder around 500 °C corresponding to the temperature at which volatile is burnt.

SO_2 shows a different behavior. It is easily formed and released at a lower temperature level. More than half of the yield was observed at lower than 600 °C. One possible explanation for the behavior of coal sulfur is the weak thermal stability of pyrite [21] and its content in the coal. The content of pyrite in the used coal is fairly high (see Table 1).
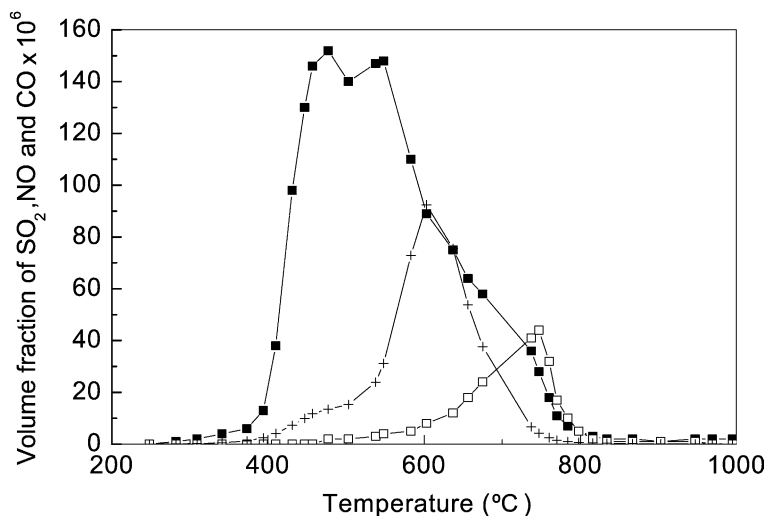

Fig. 1. SO_2, NO and CO emissions of the parent coal at 30 °C/min. ■, SO_2; □, NO; +, CO/25.

The SO_2 emission curve shows two distinct peaks and a shoulder around 480, 570 and 690 °C, respectively, which suggests that SO_2 originates from different source. The same trends have been also found in the case at a heating rate of 20 °C/min. Compared to CO data, a great deal of SO_2 is produced during the volatile combustion while NO is mainly formed during char combustion process.

3.2. The effects of doping agents on SO_2 emission

The percentages of removed SO_2 from the flue gas by doping agents added with 6% during combustion at 20 min and 30 °C/min are given in Fig. 2, calculated based on the entire SO_2 yield produced by 20 mg parent coal. The data show that all the agents used have reduced the coal sulfur release. The most efficient agent is $CaCl_2$. By adding $CaCl_2$
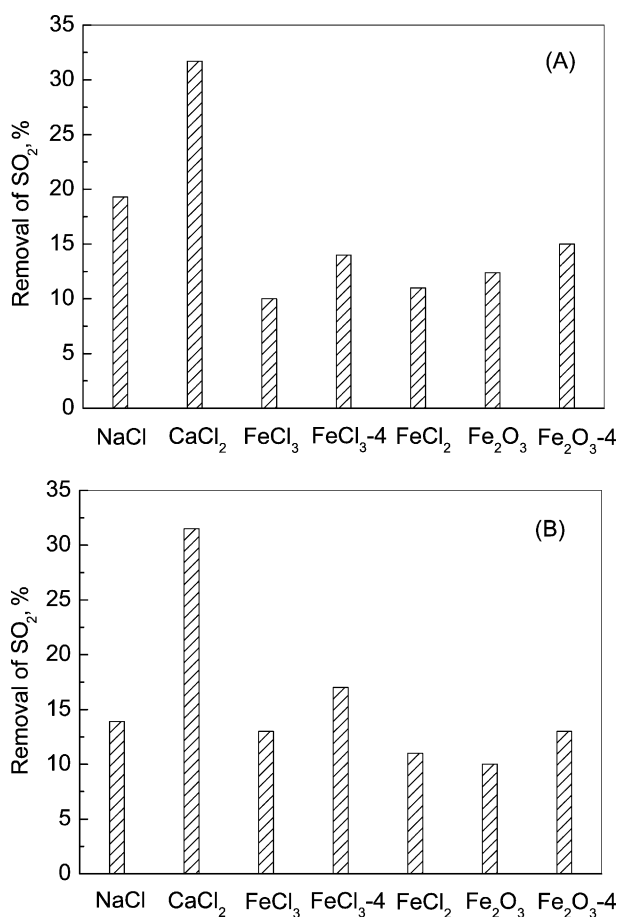

Fig. 2. Removal of SO_2 from the flue gas by addition of doping agents: (A) 20 °C/min; (B) 30 °C/min; $FeCl_3$-4: 4% dose rate of $FeCl_3$; Fe_2O_3-4: 4% dose rate of Fe_2O_3.

into coal, SO_2 emission is decreased by 32% either at 20 or 30 °C/min. In Fig. 2, the removal of SO_2 from the flue gas by $FeCl_3$ and Fe_2O_3 with dose rate of 4% by weight in coal, known as $FeCl_3$-4 and Fe_2O_3-4, respectively, is also given for comparison. It can be seen that better reduction ratios have been achieved with $FeCl_3$ or Fe_2O_3 addition of 4% to the studied coal than the addition of 6%.

The instantaneous SO_2 concentrations in flue gas against temperature are given in Figs. 3 and 4 for the coals with and without doping agents at 20 and 30 °C/min, respectively. Fig. 3 shows the effects of NaCl and $CaCl_2$ on SO_2 emission. In the presence of NaCl and $CaCl_2$ although SO_2 concentration in flue gas is decreased, the peak and shoulder
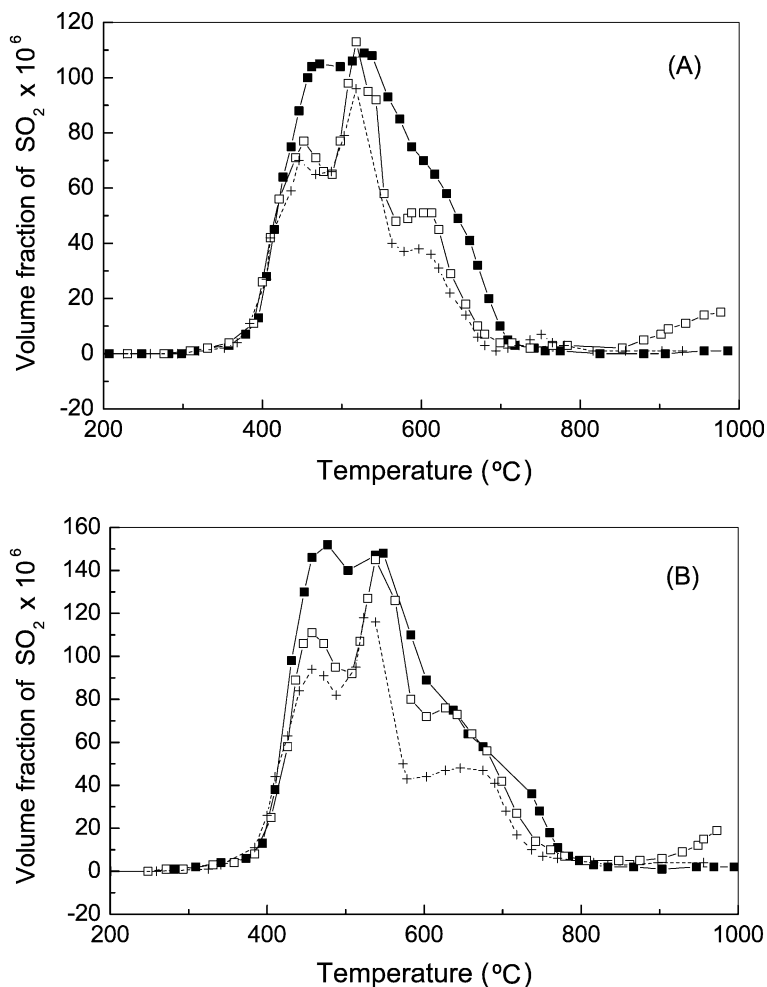

Fig. 3. Effects of NaCl and $CaCl_2$ on SO_2 emission: (A) 20 °C/min; (B) 30 °C/min. ■, Parent coal; □, doped coal with NaCl; +, doped coal with $CaCl_2$, quantity added: 6% by weight.
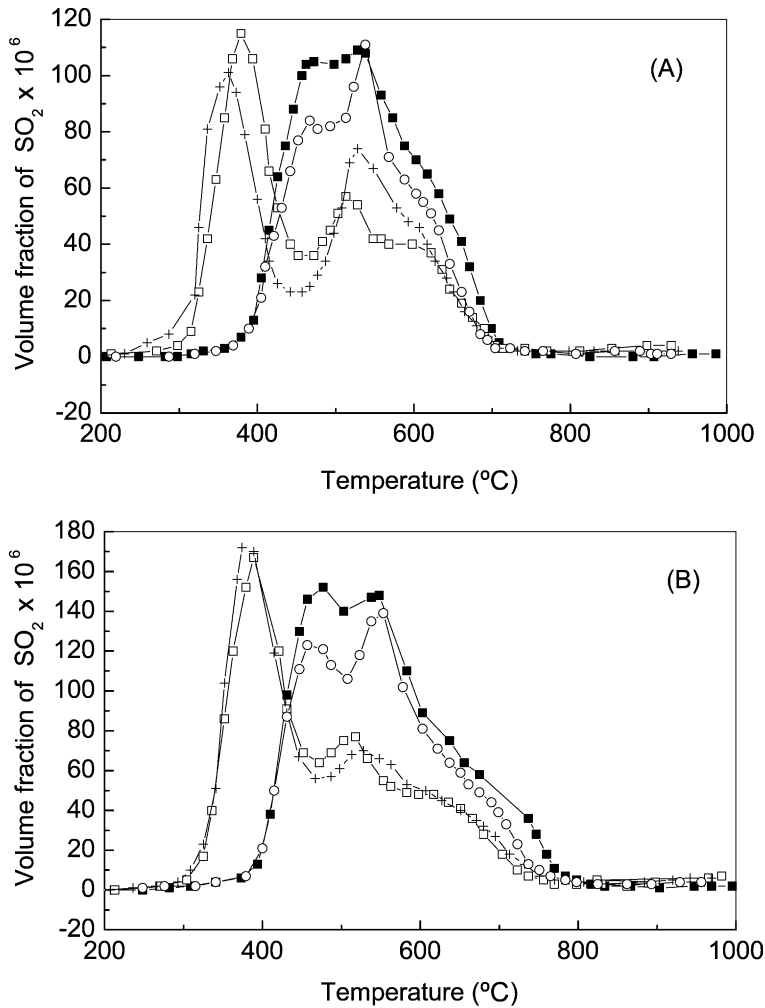
Fig. 4. Effects of FeCl$_3$ and FeCl$_2$ and Fe$_2$O$_3$ on SO$_2$ emission: (A) 20 °C/min; (B) 30 °C/min. ■, Parent coal; □, doped coal with FeCl$_3$; +, doped coal with FeCl$_2$, ○, doped coal with Fe$_2$O$_3$, quantity added: 6% by weight.

temperatures for the parent coal, at which a peak or a shoulder appears on SO$_2$ curves are almost unchanged. They remain nearly 450, 550 and 650 °C at 30 °C/min heating rate.

Additionally, it should be pointed out that the temperature range in which SO$_2$ concentration is reduced by adding NaCl is below 800 °C. When the temperature is elevated over 850 °C, an increased SO$_2$ is detected again in flue gas. This phenomenon was also observed and the mechanism was discussed in our previous work [12]. However, no such phenomenon has been observed in the presence of CaCl$_2$, which illustrates that the mechanism for SO$_2$ retention by CaCl$_2$ is somewhat different from that by NaCl.

Fig. 4 shows the effects of FeCl$_3$, FeCl$_2$ and Fe$_2$O$_3$ on SO$_2$ emission. In the presence of FeCl$_3$ and FeCl$_2$, the most noticeable feature is that all the peaks or the shoulders on

SO$_2$ curves of the parent coal are moved to the lower temperature side with distinct step sizes. In other words, the temperatures at which a peak or a shoulder appears are decreased. The biggest step size occurs to the leftmost peak no matter what heating rate is taken in the experimental conditions. In the case which the heating rate is 30 °C/min, the temperature of the leftmost peak, which appears at 450 °C on SO$_2$ curve for the parent coal, is decreased by about 100 °C and besides, it is remarkable that FeCl$_2$ has an effect similar to FeCl$_3$. Additionally, although the calculations in Fig. 2 show that both FeCl$_3$ and FeCl$_2$ reduced the total sulfur release, the SO$_2$ profiles in Fig. 4 show that they really promoted SO$_2$ concentration in flue gas at the range lower than 400 °C. Despite the possession of Fe ions, Fe$_2$O$_3$ shows different effects on SO$_2$ concentration
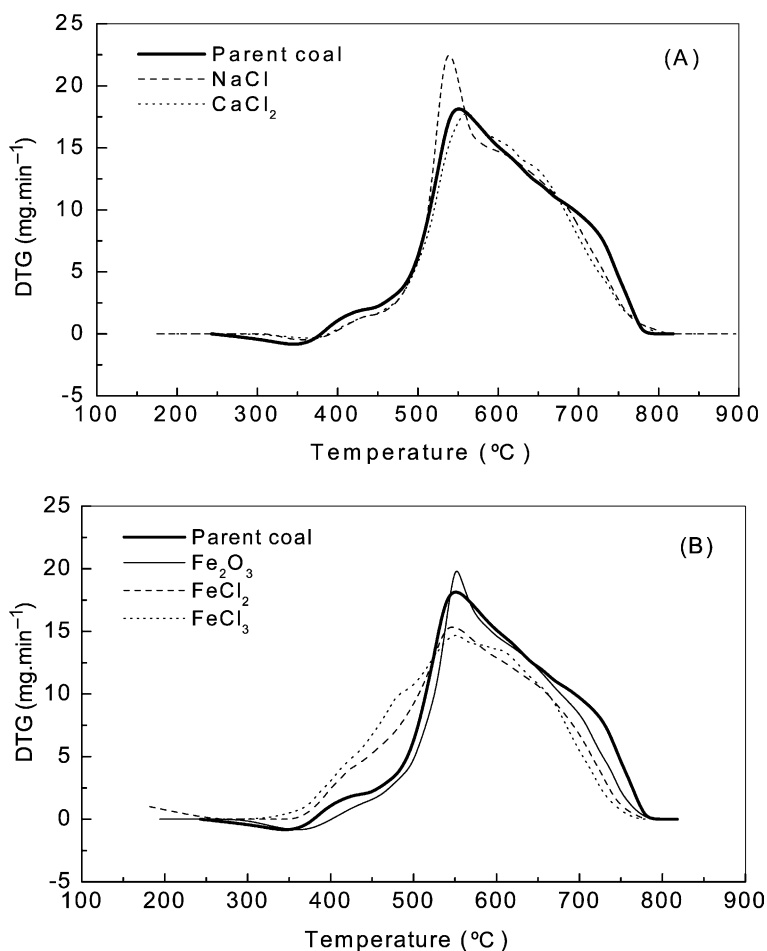

Fig. 5. DTG curves for parent coal and those doping with agents at 30 °C/min: NaCl and CaCl$_2$; (B) Fe$_2$O$_3$, FeCl$_2$ and FeCl$_3$.

profile from $FeCl_3$ and $FeCl_2$. SO_2 profile of the coal added with Fe_2O_3 shown in Fig. 4 reveals that Fe_2O_3 has a weak effect on the peak temperatures as NaCl or $CaCl_2$ has, while it decreases the coal sulfur release. There exist different mechanisms for the doping agents to capture SO_2 anyway.

3.3. The effects of doping agents on combustion characteristics

In Fig. 5, the data of DTG are shown for the coal samples with and without doping agents at 30 °C/min. In the presence of NaCl (Fig. 5A) and Fe_2O_3 (Fig. 5B), the severe variation of the DTG profile appears in the neighborhood of the peak, while the profile of DTG is not considerably changed due to the addition of NaCl, $CaCl_2$ or Fe_2O_3 in the
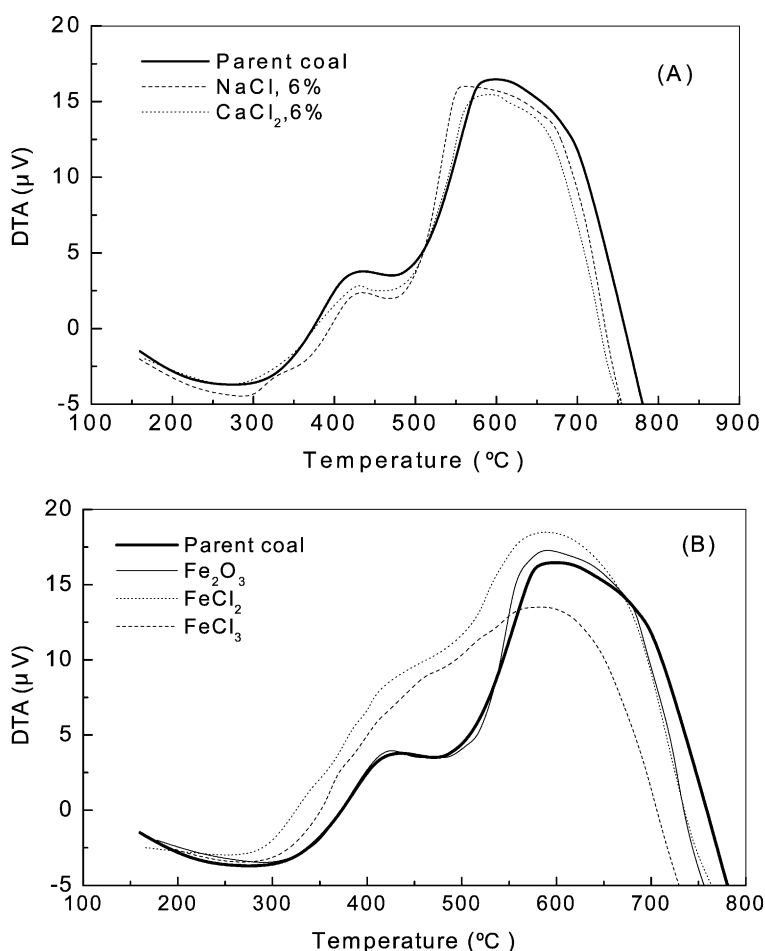

Fig. 6. DTA curves for parent coal and those doping with agents at 30 °C/min: (A) NaCl and $CaCl_2$; (B) Fe_2O_3, $FeCl_2$ and $FeCl_3$.

temperature range less than 520 °C. The weak change of DTG on the low temperature side
(< 520 °C) indicates that NaCl, CaCl$_2$, and Fe$_2$O$_3$ have insignificant effects on the rate of
burning or combustion behavior of the studied coal under 520 °C. Nevertheless, it can be
found that FeCl$_3$ and FeCl$_2$ have significant effects on the DTG envelope according to the
data in Fig. 5B). When the coal is doped with FeCl$_3$ or FeCl$_2$, its DTG data are evidently
increased in the range between 300 and 520 °C, which indicates that iron chlorides
improve the rate of burning of the studied coal. The increased DTA data between 300 and
550 °C shown in Fig. 6B) indicate the increase of heat release from enhanced combustion
process and prove the contribution of FeCl$_3$ or FeCl$_2$ to the coal combustion. There are
clearly two peaks on DTA curve of the parent coal. They correspond to the stage for
volatile to be burnt and the ignition of the resultant char. That the addition of FeCl$_3$ or
FeCl$_2$ increases DTA values in the stage means that the combustion of the volatile is
accelerated and the ignition characteristic of the resultant char is improved during coal
combustion process.

By the way, the data of DTA in the presence of NaCl, CaCl$_2$ and Fe$_2$O$_3$ are also shown
in Fig. 6, which is consistent with DTG. Additionally, the data of DTG and DTA at 20 °C/
min operating condition show a similar trend to the data obtained at 30 °C/min.

4. Discussions

It has been known that not all of the total sulfur in coal is emitted as gas species after coal
combustion is completed, no matter how the coal is burnt. Part of the sulfur will be retained
as solid compounds in ash due to neutralization of alkaline components of the parent coal.
In Chinese coals, most of the calcium are present as calcite or dolomite [22]. They are
rapidly decomposed to produce lime when the temperature is over 600–700 °C [23]:

$$CaCO_3 \Leftrightarrow CaO + CO_2 \tag{R1}$$

$$CaMg(CO_3)_2 \Rightarrow CaO + MgO + 2CO_2 \tag{R2}$$

The porous CaO and MgO produced from these reactions will be converted subsequently
into CaSO$_4$ and MgSO$_4$ to result in sulfur retention:

$$CaO + SO_2 + \frac{1}{2}O_2 \Rightarrow CaSO_4 \tag{R3}$$

$$MgO + SO_2 + \frac{1}{2}O_2 \Rightarrow MgSO_4 \tag{R4}$$

While the temperatures are low enough, the calcination reaction is thermodynamically
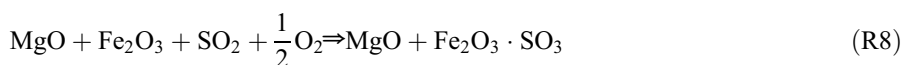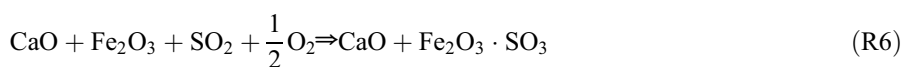disfavored and the limestone reacts with SO$_2$ by a direct mechanism [8]:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \Rightarrow CaSO_4 + CO_2 \tag{R5}$$

NaCl or $CaCl_2$ present in coal, we believe, can promote the reactions between SO_2 and the minerals (Eqs. (R3–5)), and enhances the sulfur retention capacity of coal ash and then decrease SO_2 concentration in flue gas [12].

According to Matsukata et al. [13], Delmon and van Houte in 1978 reported that a slight amount of $CaCl_2$ (2 wt.%) on $CaCO_3$ promoted SO_2 absorption in the temperature range of 573–908 K. By TEM, they observed that the morphology on $CaCO_3$ crystals was dramatically altered to form large aggregates and voids by the addition of $CaCl_2$. Similarly, in our experiments, $CaCl_2$ reduced SO_2 emission. NaCl has the same effect as $CaCl_2$. At high temperature level, the alkali chlorides will be oxidized to metal oxides and HCl will be generated at the same time. In the presence of HCl, SO_2 absorption by limestone in coal will be accelerated. With scanning electron microscopy (SEM), Matsuka et al. [13] found that large voids were formed on the surface of limestone in the presence of HCl. $CaCl_2$ is the most effective agent to suppress SO_2 emission among the agents used. The reasons are probably that the metal oxides also absorb SO_2. One mole of Ca consumed captures 1 mol of sulfur while 1 mol of Na captures 1/2 mol of sulfur.

NaCl and $CaCl_2$ have a weak effect on the coal combustion behavior, but $FeCl_3$ and $FeCl_2$ have a strong effect on it as mentioned above. They enhance the combustion of the volatile and improve the ignition of the resultant char during combustion, as well as rates of the combustion reactions between 300 and 520 °C, including those reactions between oxygen atom and sulfur from organic functionalities and pyrite. The enhancement increases SO_2 concentration in flue gas at the temperature range lower than 420 °C. Whereas, when the temperature is elevated high enough, $FeCl_3$ or $FeCl_2$ is decomposed. Then Fe_2O_3 is generated in air atmosphere as well as HCl, both of which are beneficial to SO_2 absorption.

Though Fe_2O_3 has a week effect on DTG, DTA, i.e. Fe_2O_3 has no catalysis on the combustion behavior of the coal, it really diminishes the emissions of SO_2. Fe_2O_3 may directly catalyze the reactions between SO_2 and the mineral substances in coal ash. The possible overall reactions are the following:

$$CaO + Fe_2O_3 + SO_2 + \frac{1}{2}O_2 \Rightarrow CaO + Fe_2O_3 \cdot SO_3 \tag{R6}$$

$$CaO + Fe_2O_3SO_3 \Rightarrow CaSO_4 + Fe_2O_3 \tag{R7}$$

$$MgO + Fe_2O_3 + SO_2 + \frac{1}{2}O_2 \Rightarrow MgO + Fe_2O_3 \cdot SO_3 \tag{R8}$$

$$MgO + Fe_2O_3SO_3 \Rightarrow MgSO_4 + Fe_2O_3 \tag{R9}$$

In one word, the catalysis of $FeCl_3$ and $FeCl_2$ on coal combustion leads to a rise of SO_2 concentration in flue gas in the relatively low temperature range. $FeCl_3$ and $FeCl_2$ are oxidized into Fe_2O_3 while the temperature is elevated high enough. Fe_2O_3 formed or doped has promoted the absorption reactions of SO_2 as listed above. That is why, the total SO_2 yield was reduced with the addition of $FeCl_3$ and $FeCl_2$. Jagtap [15] studied catalytic effect of $FeCl_3$ either inherent or deliberately added. They found that the degree of

desulfuration was observed to be strongly dependent on the $FeCl_3$/coal ratio, and increases as the ratio increases.

Although all additives used may reduce the release of coal sulfur, these treatments reduced the heating value of the coal and increased its chlorine content. Nevertheless, the investigation will be of value to the field of co-combustion of coal and MSW.

5. Conclusions

The addition of the agents in coal can reduce the coal sulfur release. $CaCl_2$ is the most effective one among the agents used. The doping agents work with different mechanisms. The catalysis of NaCl, $CaCl_2$ and Fe_2O_3 promotes the reactions between SO_2 and the minerals in coal, and enhances the sulfur retention capacity of coal ash and then decreases SO_2 concentration in flue gas, however, they have a weak effect on the combustion behavior of the coal. $FeCl_3$ and $FeCl_2$ have a strong effect on coal combustion behavior. They accelerated the combustion rate in the region between 300 and 520 °C and improved the ignition of the char subsequently formed, as far as increase SO_2 concentration in flue gas at the temperature region, while they reduces total sulfur release. The reduction of total sulfur release by $FeCl_3$ and $FeCl_2$ mainly results from the catalysis of Fe_2O_3 created by them at high temperature.

Acknowledgements

References

 [1] M. Kozlowski, L.L. Maes, H. Wachowska, et al., Fuel 78 (1999) 769.
 [2] J.C. Calvert, Pure and Applied Chemistry 69 (1997) 1.
 [3] K.M. Thomas, Fuel 76 (1997) 457.
 [4] Y. Ohtsuka, Z. Wu, E. Furimsky, Fuel 76 (1997) 1361–1367.
 [5] M.J. Illan-Gomez, E. Raymundo-Pinero, A. Garcia-Garcia, et al., Applied Catalysis B: Environmental 20 (1999) 267.
 [6] Z. Wu, L. Xu, Z. Wang, Z. Zhang, Fuel 77 (1998) 891.
 [7] Z. Wu, Y. Sugimoto, H. Kawashima, Fuel 80 (2001) 251.
 [8] E. Alvarez, J.F. Gonzales, Fuel 78 (1999) 341.
 [9] K. Ceylan, H. Karaca, Y. Onal, Fuel 78 (1999) 1109–1116.
[10] G. Matuschek, A.A. Kettrup, Journal of Analytical and Applied Pyrolosis 51 (1999) 223.
[11] B. Courtemanche, Y.A. Levendis, Fuel 77 (1998) 183.
[12] Y. Liu, D. Che, S. Hui, T. Xu, Journal of Xi'an Jiaotong University 34 (2000) 42.
[13] M. Matsukata, K. Takeda, T. Miyatani, K. Ueyama, Chemical Engineering Science 51 (1996) 2529.
[14] N. Ikenaga, H. Taniguchi, A. Watanabe, et al., Fuel 79 (2000) 273.
[15] S.B. Jagtap, Coal Fuel Processing Technology 43 (1995) 227.
[16] K. Asami, Y. Ohtsuka, Industrial and Engineering Chemistry Research 32 (1993) 1631.

[17] Q. Zhu, J.M. Jones, K.M. Thomas, Carbon 35 (1997) 855.

[18] Y. Ohtsuda, T. Watanabe, K. Asami, H. Mori, Energy & Fuels 12 (1998) 1356.

[19] R. Boncukcuoglu, M.M. Kocakerim, H. Ersahan, Fuel Processing Technology 38 (1994) 31.

[20] Y. Liu, D. Che, Y. Li, S. Hui, T. Xu, Journal of Xi'an Jiaotong University 35 (2001) 95.

[21] S.P. Middleton, J.W. Patrick, A. Walder, Fuel 76 (1997) 1195.

[22] C. Sheng, M. Xu, J. Zhang, Y. Xu, Fuel Processing Technology 64 (2000) 1.

[23] J.V. Ibarra, J.M. Palacios, A.M. Andres, Fuel 68 (1989) 861.