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## Catalytic effects of Na , Ca , Fe and their composites on NO-char reaction in the presence of SO<sub>2</sub>

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**Abstract** : Catalytic effects of Na , Ca , Fe and their composites on NO-char reaction in the presence of SO<sub>2</sub> were investigated by Temperature Programmed Reaction ( TPR ) technique. The catalytic activity order of three metals is Fe > Ca > Na in the same conditions. SO<sub>2</sub> may participate in the oxygen-transfer process to influence the metal catalytic effect in NO-char reaction. For three types of metal loaded catalysts , effects of SO<sub>2</sub> concentration on their catalytic activities are different. The catalytic activity of Na loaded char is influenced most by the SO<sub>2</sub> concentration. 2% Na or Fe loaded chars and 3% Ca loaded char have the highest NO conversion activity in the presence of SO<sub>2</sub>. Na-Fe and Na-Ca composite catalysts have higher catalytic activity. Synergistic effect of Na-Ca and Na-Fe may be responsible for the high NO conversion activity of these bimetallic catalysts in the presence of SO<sub>2</sub>.

**Key words** : NO-char reaction ; SO<sub>2</sub> ; metal catalytic activity ; composite catalyst

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There is a worldwide increasing concern about the air pollution from nitrogen oxides during coal combustion. NO<sub>x</sub> is one of the main contributors to acid rain , and N<sub>2</sub>O is a greenhouse gas and depletes the ozone layer indirectly. Great effort has been made for economical and effective reduction of NO<sub>x</sub> to harmless N<sub>2</sub>. The emission level of NO during coal combustion is affected by many factors , including the coal-N content , the combustion conditions and the inorganic impurities in coal. Moreover , it has been recognized early that NO-char reaction is one of the most important reactions in reducing NO during coal and/or char combustion<sup>[1~4]</sup> , and many researches<sup>[5~12]</sup> also found that metals such as K , Ca , Na and Fe have catalytic effects on NO-char reaction. It was found that the use of bimetallic catalysts , combining potassium with transition metals , presents a synergetic effect ; the activity of the bimetallic catalysts is higher than the sum of the activities of the monometallic catalysts<sup>[13,14]</sup>. The synergistic catalytic effect of Na-Fe composite in the NO-char reaction has been also observed in O<sub>2</sub>/Ar atmosphere<sup>[15]</sup>. SO<sub>2</sub> , always present in exhaust gases , can modify the metal chemical state , and consequently affect the metal catalytic activity. Recently , in the presence of SO<sub>2</sub> the effect of mineral matter on NO-char reaction has been reported<sup>[16]</sup>. In this paper , working with the same experimental conditions used in the previous work<sup>[16]</sup> , we extend our study to a more complex composite catalyst system. Thus the aim of this study is to analyze ,

in the presence of SO<sub>2</sub> , the catalytic behavior of some metals and their composites during NO reduction by carbon. The paper will also compare the NO reduction results with those found in the absence of SO<sub>2</sub>. For this purpose , some metals Na , Fe , Ca and metal combinations supported on a demineralized coal char , have been studied as catalysts.

### 1 Experimental

Longkou lignite with a particle size of 0.25 mm ~ 0.125 mm was used in this study. Demineralization of Longkou coal was performed by concentrated HF and HCl. After demineralization it was devolatilized in a quartz fluidized bed reactor ( i. d. 50 mm ) at 950 °C for 30 min in N<sub>2</sub> atmosphere. The ash content of prepared char ( denoted as LK-de ) is 0.42% ( dry basis ) , and the elemental analysis ( daf basis ) is : C : 92.9% ; H : 0.68% ; S : 0.30% ; N : 2.55% ; and O : 3.48% ( by difference ).

Metal nitrate solutions of Fe , Ca , Na with calculated concentration were prepared. Nitrates were loaded on the prepared char by impregnation method at 60 °C. Then , the sample was dried for 5 h at 110 °C , and calcined 30 min at 900 °C in Ar. The prepared catalyst is denoted as LK-de-xM , in which M represents the metal loaded , and x represents weight percentage of metal in the catalyst. Several metal composite catalysts are prepared by co-impregnation method as the similar condition. The composite catalyst is denoted as LK-de-( xM-yN ) , in which M and N

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represent the metal loaded, and  $x$  and  $y$  represent weight percentage of metal in the catalyst.

The NO-char reaction was carried out in a quartz fixed bed reactor (i. d. 20 mm) with a fused quartz disk in the center of the reactor to hold the reactant. Before the NO reduction experiment the char and the metal loaded chars were preheated at 900 °C for 30 min in Ar. After the temperature was cooled down to 400 °C, Ar was switched to Ar/NO/SO<sub>2</sub> or Ar/NO. The inlet concentrations of NO and SO<sub>2</sub> were  $560 \times 10^{-6}$  (v/v) and  $800 \times 10^{-6}$  (v/v), respectively, unless otherwise stated. When the gas concentration reached to the stable level, temperature programmed reaction (TPR) was performed at the heating rate of 5 °C/min to the final temperature of 900 °C. The weight loss of chars in all runs is less than 5% in this work.

## 2 Results and discussion

### 2.1 Effect of SO<sub>2</sub> on metal catalytic activities in NO-char reaction

Catalytic effects of Fe, Ca and Na metals on NO-char reaction in the presence of SO<sub>2</sub> by TPR are shown in Figure 1. It can be seen that complete NO reduction temperatures of metal loaded chars shift to lower temperature, and activities of metal loaded chars are all higher than that of the original char. The catalytic activity order of three metals is Fe > Ca > Na. However, without considering the influence of SO<sub>2</sub>, Zhao et al.<sup>[5,15]</sup> found that the catalytic activity order is Na > Fe > Ca for NO-char reaction in various atmosphere, and Na is more effective on reducing NO than Fe at low temperature (< 670 °C), while it is opposite at high temperature. From these results it can be concluded that SO<sub>2</sub> atmosphere has great influence on the catalytic activity of Na for NO conversion. Previous research<sup>[13,17]</sup> has concluded that catalytically active matters can catalyze the reaction of NO-char effectively because they can accept oxygen from NO to form M<sub>x</sub>O<sub>y</sub>(O) and then transfer oxygen to the active sites of char to form CO or CO<sub>2</sub>. According to this theory, it can be deduced that SO<sub>2</sub> may participate in the oxygen-transfer process in two ways to influence the metal catalytic NO-char reaction. One way is that SO<sub>2</sub> may block the formation of the important intermediate M<sub>x</sub>O<sub>y</sub>(O) and the other is that SO<sub>2</sub> may hinder the oxygen transfer from the intermediate to the active sites of chars. This influence is much more significant for Na loaded chars than others because of its strong alkalinity, which may cause the reaction between Na active sites and SO<sub>2</sub> relatively easy.

To further understand the effect of SO<sub>2</sub> in NO-char reaction, TPR profiles of original and Fe loaded chars are compared in Figure 2. For the original char, NO conversions in the presence and absence of SO<sub>2</sub> are almost the same at the low temperature range, and a small increase of the NO conversion is observed at the high temperature in the presence of SO<sub>2</sub>, which may be attributed to the thermodynamically spontaneous oxidation reaction of SO<sub>2</sub> to SO<sub>3</sub> by NO at high temperature<sup>[18]</sup>. For the Fe loaded char, NO conversions in the presence of SO<sub>2</sub> are lower than those in the absence of SO<sub>2</sub> in the whole temperature range, which may also because that SO<sub>2</sub> participates in the oxygen-transfer process in NO-char reaction and decreases the oxygen-transfer ability of Fe.

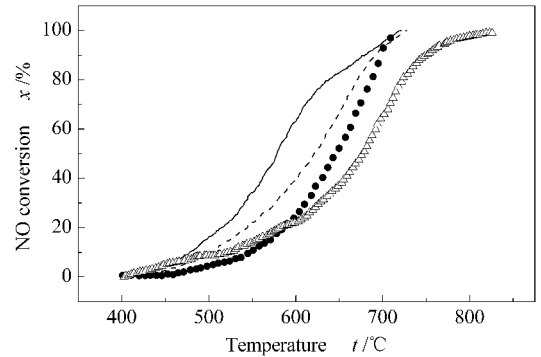


Figure 1 NO conversions over original and Fe(1%), Ca(1%) or Na(1%) loaded chars in the presence of SO<sub>2</sub>  
— LK-de-Fe; --- LK-de-Ca; ● LK-de-Na; △ LK-de

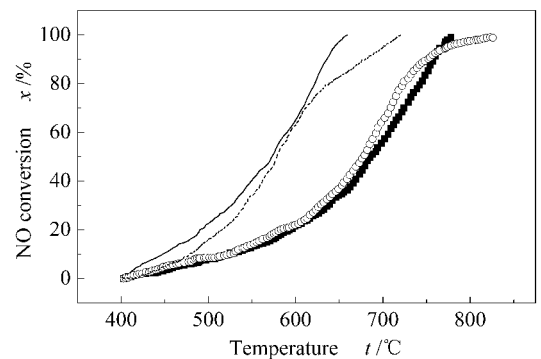


Figure 2 TPR profiles of catalytic activities of original and Fe loaded chars in the presence and absence of SO<sub>2</sub>  
— LK-de-1Fe; --- LK-de-1Fe; ■ LK-de; ○ LK-de

### 2.2 Effect of SO<sub>2</sub> concentration on NO-char reaction

Figure 3 shows catalytic activities of three metal loaded catalysts in NO-char reaction at SO<sub>2</sub> concentrations of  $80 \times 10^{-6}$  (v/v) and  $800 \times 10^{-6}$  (v/v). For three types of metal loaded catalysts, effects of SO<sub>2</sub> concentration on their catalytic activities are dif-

ferent. For LK-de-1Fe catalyst, the effect of  $\text{SO}_2$  concentration is complex. At low temperature (below  $570^\circ\text{C}$ ) NO conversions of LK-de-1Fe are a little higher in  $800 \times 10^{-6}$  (v/v)  $\text{SO}_2$  than those in  $80 \times 10^{-6}$  (v/v)  $\text{SO}_2$ , while at high temperature (above  $570^\circ\text{C}$ ) the situation is opposite and high  $\text{SO}_2$  concentration suppresses the NO conversion over LK-de-1Fe remarkably. For LK-de-1Ca catalyst,  $\text{SO}_2$  concentration has little effect on the NO conversion below  $570^\circ\text{C}$ , but above this temperature the negative effect of  $\text{SO}_2$  on the NO conversion is obviously especially in the high  $\text{SO}_2$  concentration. For LK-de-1Na cata-

lyst,  $\text{SO}_2$  concentration has great influence on its catalytic activity, and NO conversions in  $80 \times 10^{-6}$  (v/v)  $\text{SO}_2$  are all much higher than those in  $800\text{ppm}$  in the whole temperature range. From these results it can be drawn a conclusion that the catalytic activity of Na loaded catalyst in NO-char reaction is influenced most by  $\text{SO}_2$  atmosphere, which also provides an explanation of why the catalytic activity order of three metals in NO-char reaction is  $\text{Fe} > \text{Ca} > \text{Na}$  in the presence of  $\text{SO}_2$ , while in the absence of  $\text{SO}_2$  the catalytic activity order is  $\text{Na} > \text{Fe} > \text{Ca}$ .

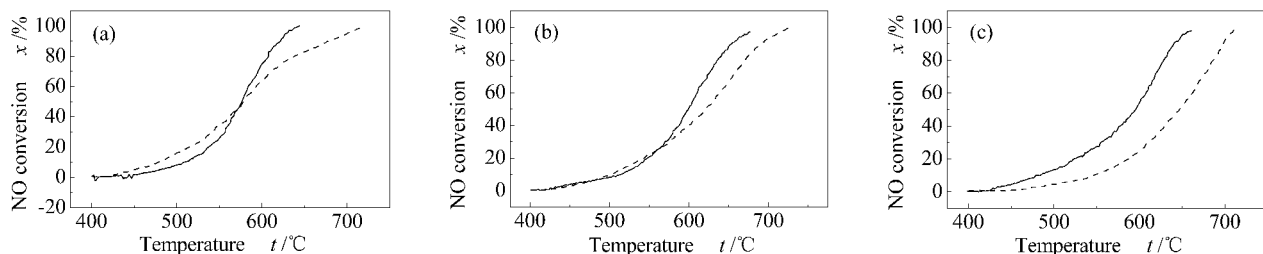


Figure 3 Effect of  $\text{SO}_2$  concentrations on the catalytic activities of catalysts

- (a) — LK-de-1Fe- $80 \times 10^{-6}$  (v/v); --- LK-de-1Fe- $800 \times 10^{-6}$  (v/v)  
 (b) — LK-de-1Ca- $80 \times 10^{-6}$  (v/v); --- LK-de-1Ca- $800 \times 10^{-6}$  (v/v)  
 (c) — LK-de-1Na- $80 \times 10^{-6}$  (v/v); --- LK-de-1Na- $800 \times 10^{-6}$  (v/v)

**2.3 Effect of metal loading amount on NO-char reaction** The effect of metal loading amount (1% ~ 3%) on NO-char reaction in the presence of  $\text{SO}_2$  was also studied by TPR, as shown in Figure 4. It is obvious that the activity of catalyst depends on not only the metal loading amount, but also the type of metal loaded. With increasing loading amount of

Fe and Na, 2% metal loaded catalysts have a maximum catalytic activity in the whole temperature range. However, Ca loaded catalysts show the different activity tendency compared with Fe and Ca loaded catalysts, which have the highest activity as the Ca loading amount is 3%.

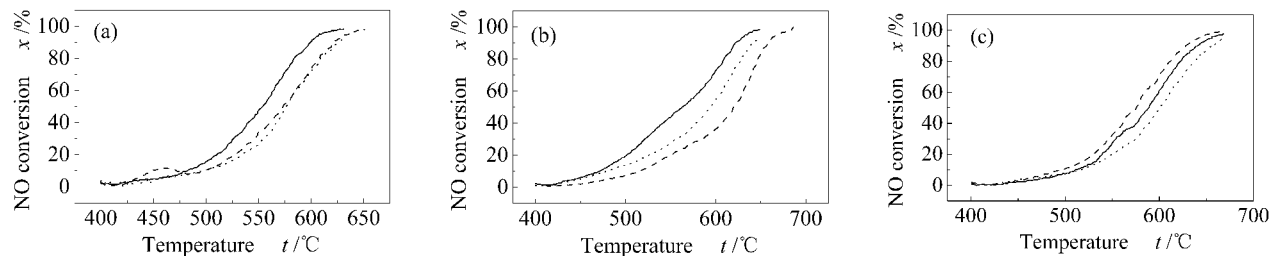


Figure 4 Effect of metal loading amounts on NO-char reaction in the presence of  $\text{SO}_2$

- (a) ... LK-de-1Fe; — LK-de-2Fe; --- LK-de-3Fe  
 (b) ... LK-de-1Na; — LK-de-2Na; --- LK-de-3Na  
 (c) ... LK-de-1Ca; — LK-de-2Ca; --- LK-de-3Ca

## 2.4 Catalytic activities of composite catalysts

Based on the results discussed above, it can be concluded that the presence of  $\text{SO}_2$  have difference influences on catalysis characteristics of Na, Ca and Fe loaded chars in the NO-char reaction. It would be very interesting to evaluate the influence of  $\text{SO}_2$  on the catalytic activity of composite catalysts. Several

Na, Ca and Fe bimetallic or trimetallic catalysts have been prepared with the total metal loading amount of 1% remaining unchanged while simultaneously varying the relative contents of Na, Ca and Fe. Activities of composite catalysts in NO reduction by TPR in the presence of  $\text{SO}_2$  are shown in Figure 5. It is found that the activity of composite catalyst is very complex

and varies with the component of the catalysts and the reaction temperature. For LK-de-( 1/2Ca-1/2Na ) and LK-de-( 1/2Fe-1/2Na ) composite catalysts , complete NO conversion temperatures are a little lower than those of mono-metallic catalysts ( Na , Ca or Fe ) , which clearly indicates that Na-Fe and Na-Ca composite catalysts have higher catalytic activity. Results in Figure 5( a ) show that the NO reduction activity of LK-de-( 1/2Ca-1/2Na ) composite catalyst is higher than that of LK-de-1Ca above 600 °C , and higher than that of LK-de-1Na in the whole temperature range. Figure 5( b ) shows that the reaction temperature has great influence on the activity of Na-Fe composite catalyst. It is interesting to see in Figure 5 ( c ) that the activity of Ca-Fe composite catalyst is almost the same as that of Ca mono-metallic catalyst ,

and lower than that of Fe mono-metallic catalyst. Ilan-Gomez et al<sup>[14]</sup> found that bimetallic catalysts , combining potassium with transition metals , present a synergetic effect ; the activity of the bimetallic catalysts is higher than the sum of the activities of the monometallic catalysts in the NO-carbon reaction. Thus , as in the same family with K , Na combining with transition metals may also have the synergetic effect to promote the NO-carbon reaction. Synergistic effect of Na and Ca or Fe during reaction may be responsible for the high catalytic activity of Na-Ca or Na-Fe bimetallic catalysts. Obviously , it is not strange to see the low catalytic activity of LK-de-( 1/2Fe-1/2Ca ) composite catalyst because of without the synergetic effect of Na.

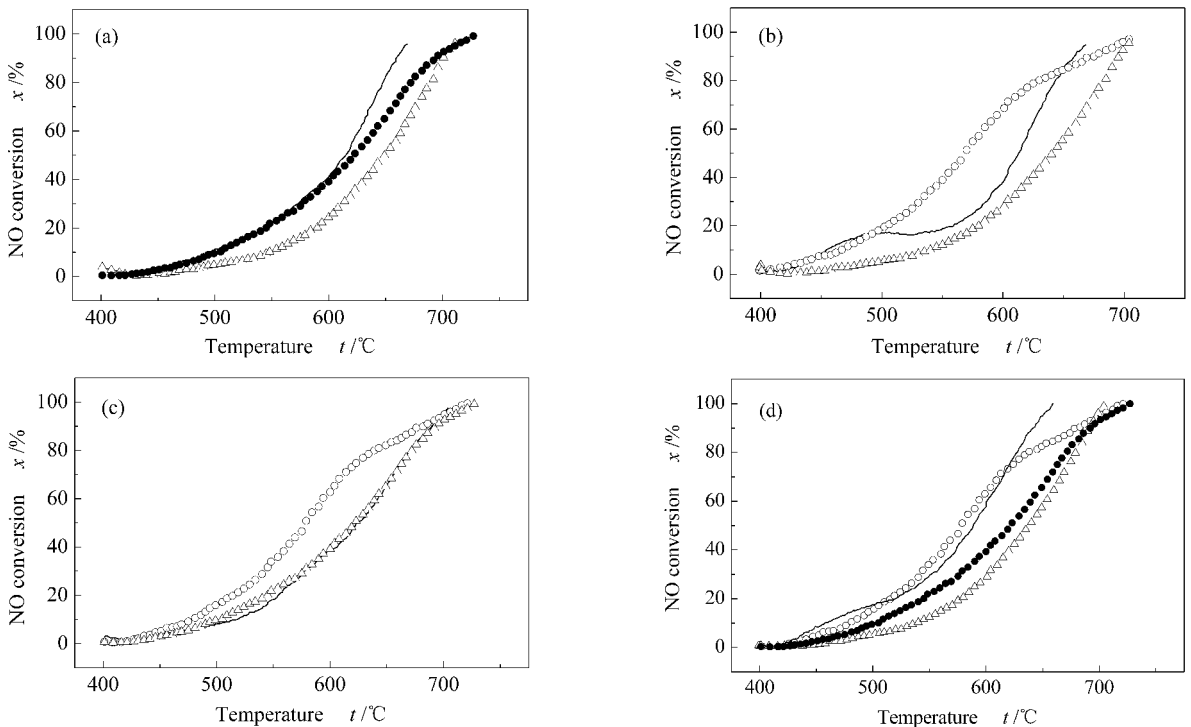


Figure 5 Effect of composite catalysts on NO-char reaction in the presence of SO<sub>2</sub>

( a ) — LK-de-( 1/2Ca-1/2Na ) ; ● LK-de-1Ca ; △ LK-de-1Na

( b ) — LK-de-( 1/2Fe-1/2Na ) ; ○ LK-de-1Fe ; △ LK-de-1Na

( c ) — LK-de-( 1/2Fe-1/2Ca ) ; ○ LK-de-1Fe ; △ LK-de-1Ca

( d ) — LK-de-( 1/3Na-1/3Fe-1/3Ca ) ; △ LK-de-1Na ; ○ LK-de-1Fe ; ● LK-de-1Ca

To further verify the synergetic effect , a Na-Ca-Fe trimetallic catalyst LK-de-( 1/3Na-1/3Fe-1/3Ca ) was prepared and tested in the NO-char reaction in the presence of SO<sub>2</sub> , as shown in Figure 5( d ). If there was not the synergetic effect in the trimetallic catalyst , its catalytic activity would be certainly lower than the catalytic activity of LK-de-1Fe which has the highest catalytic activity among three monometallic

catalysts in the NO-char reaction. However , below 620 °C the catalytic activity of the trimetallic catalyst is almost the same as that of LK-de-1Fe , and above this temperature its catalytic activity is higher than any monometallic catalysts'. The complete NO reduction temperature of trimetallic catalyst also shifts to lower temperature. It clearly demonstrates that the synergetic effect exists without doubt.

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## SO<sub>2</sub> 存在下钠、钙、铁及其复合物对 NO-半焦反应的催化作用

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摘 要 : 采用程序升温还原技术 , 在 SO<sub>2</sub> 存在气氛下 , 对钠、钙、铁及其复合物的 NO-半焦催化反应性能进行了研究。结果表明 , 在相同条件下三种金属对 NO-半焦反应的催化活性顺序为 : Fe > Ca > Na。SO<sub>2</sub> 可能通过参与氧传递过程来影响金属对 NO-半焦反应的催化活性。SO<sub>2</sub> 的浓度对负载三种不同金属半焦催化活性的影响是不同的。SO<sub>2</sub> 浓度对负载钠半焦的催化活性影响最为显著。在 SO<sub>2</sub> 存在气氛下 , 负载 2% 钠或铁和负载 3% 钙的半焦具有高的 NO 转化活性。在 SO<sub>2</sub> 存在气氛下 , 钠 - 钙和钠 - 铁二元金属复合催化剂的活性较高 , 这可能是由于这两种金属间存在协同作用的缘故。

关键词 : NO-半焦反应 ; SO<sub>2</sub> ; 金属催化活性 ; 复合催化剂

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