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Study on the Desulfurization Performance of N-Type and P-Type Semiconductor Pyrolysis Char Composite Catalyst

ABSTRACT

Ordos coal pyrolysis product roasted under 750^{o}C was used as desulfurization sorbents to investigate the effect of flue gas desulfurization performance of supported metal catalyst. There were 14 kinds of metal oxides from groups IA, IIA, VIB, VIIB, VIII, IB and IIIB chosen as active components to prepare metal oxide supported catalysts by equivalent volume impregnation method. And the mechanism of pyrolysis was studied. The similarities of desulfurization performance among the same group of metal oxides were related to the structure of their outer electrons. In addtion, the influence of transition metal oxides on the desulfurization performance was related to metal oxide semiconductor type. Finally, the influence of the VIII group oxide catalyst of iron (Fe), Cobalt (Co), Nickel (Ni) on the desulfurization performance showed the characteristics of diversity related to their d percentage (%).

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INTRODUCTION

Sulfur dioxide (SO_2) in flue gas causes severe air pollution and acid rain (*Chen Jun 2001*), which damages the environment and human health (*Cao Dongmei 2013*). Flue gas desulfurization technology is the most effective and widespread technology to control the discharge of SO_2 at present (*Zhou Yuxin and Liu Jianzhang 2007*). Carbon-based material dry removal is superior among this. Desulfurization, denitrification and recycle of sulfur resources could be achieved without secondary pollution such as wastewater. But the costs of its operation and activated carbon adsorbent in carbon-based material itself are high (*Zhang 2010, Li et al. 2007, Ciesla and Schuth 1999, Zhang and 2006*).

Thus it is very necessary to develop a cheaper, better desulfurization sorbent. Pyrolysis char is cheap and it is both an excellent adsorbent and a good catalyst, even as catalyst carrier because there are abundant pore structure in it and a lot of oxygen-containing functional groups on its surface. However, its catalytic activity is not high enough. After loading process, the catalytic activity will be greatly improved. In this study, pyrolysis char was selected as desulfurization sorbent (*Zhang and Chen 2014*) to prepare metal oxide loaded catalyst by equivalent lume impregnation. Currently, local and international

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studies are mainly focused on individual metal and oxide catalysts' impacts on desulfurization, while there are less systematic studies on the impacts of each ethnic groups on desulfurization performance especially transition metal catalysts in group VIII (*Ruan et al. 2000, Deng et al. 2006, Li Deqi, Guo and Li 2011, Fang at al. 2006*), *Zhang et al.* (*2013*), *Li and Guo* (*2012*), *Yue et al.* (*2006*). The effect of different active component selected from 14 kinds of metal oxide catalysts on desulfurization performance and the mechanism of pyrolysis were studied in this paper.

MATERIALS AND METHODS

Catalyst preparations

Lignite from Erdos was used to prepare the pyrolysis char at 750^{o}C under a stream of nitrogen; this was used as the carrier. Metallic oxides from different groups were then selected as activated component (**Table 1**). Fourteen kinds of metallic nitrate, all analytical commercial reagents, were combined to make the steeping liquor. Then metal oxide loaded catalysts were prepared via equivalent volume impregnation. The amount of metal oxide precursor required elemental metal content was calculated according to the load amount of metal which is 10% (mass fraction), and the catalyst particle size is 20 to 40 mesh. This means that “The loading amount of precursor of metal oxide was 10% with the metal elemental content.

Steps for catalyst preparation

The inhomogeneity metal oxide as an active component is needed and the metal load type catalyst for desulphurization experiment, was prepared, followed by screening of the optimal active component. Then the pyrolysis coke was sieved to uniform particle size (20 ~ 40 mesh) and was set aside afterwards. When the grams of nitrate (metal oxide precursor amount calculated on metal elemental content) configuration metal nitrate solution is 50 ml, load of 10% was computed and then the solution is poured to the volumetric flask. The corresponding nitrate solution with pyrolysis tar was mixed in the dry boiler, and steeped for 24 h. Then the steepd solution was dried up with pyrolysis tar mixture (there is already a big part of the solution by adsorption) using micro heat. Moreover, the dry type load was stir-fried under the metal oxide catalysts in an oven with a temperature of 120^{o}C for 40 min. Lastly, the material was into the muffle furnace at 450^{o}C for 4 h, which is also supported the metal oxide catalysts.

Table 1. The selection of active component.

IA	IIA	VIB	VIIB	VIII			IB	IIB
Na K	Ca Sr	Cr Mo	Mn	Fe	Co	Ni	Cu Ag	Zn Cd

Catalyst activity evaluation

The experiment was conducted in a fixed bed adsorption column with constant temperature. Catalyst was placed in a quartz tube whose inner diameter is 20 mm and length is 60 cm, heated in a tube furnace (**Figure 1**).

RESULTS AND DISCUSSION

Selecting the activated component

The condition for preparing 14 kinds of metallic oxide catalysts are as follows: metal loading was 10%, by calcination temperature was 450^{o}C, and calcination time was 4h. The influence of different active components in the process of desulfurization was also studied. In addition, desulfurization rates were compared very closely to determine which has the better performance.

There was an improvement on the desulfurization performance of different loading metal oxide of pyrolysis char compared with the pyrolysis char without loading (**Figure 2**).

The desulfurization performance was affected by elements in different main groups. Sodium (Na) and potassium (K) in the main group IA had the better desulfurization performance than calcium (Ca) and strontium (Sr) in the main group IIA. The desulfurization rate reached 70% at around 2.76 min, 2.73 min, and 2.21 min, 2.48 min, respectively. The catalyst had better desulfurization performance with active components in the group VIII, such as transition metal Fe, Co, and Ni. The

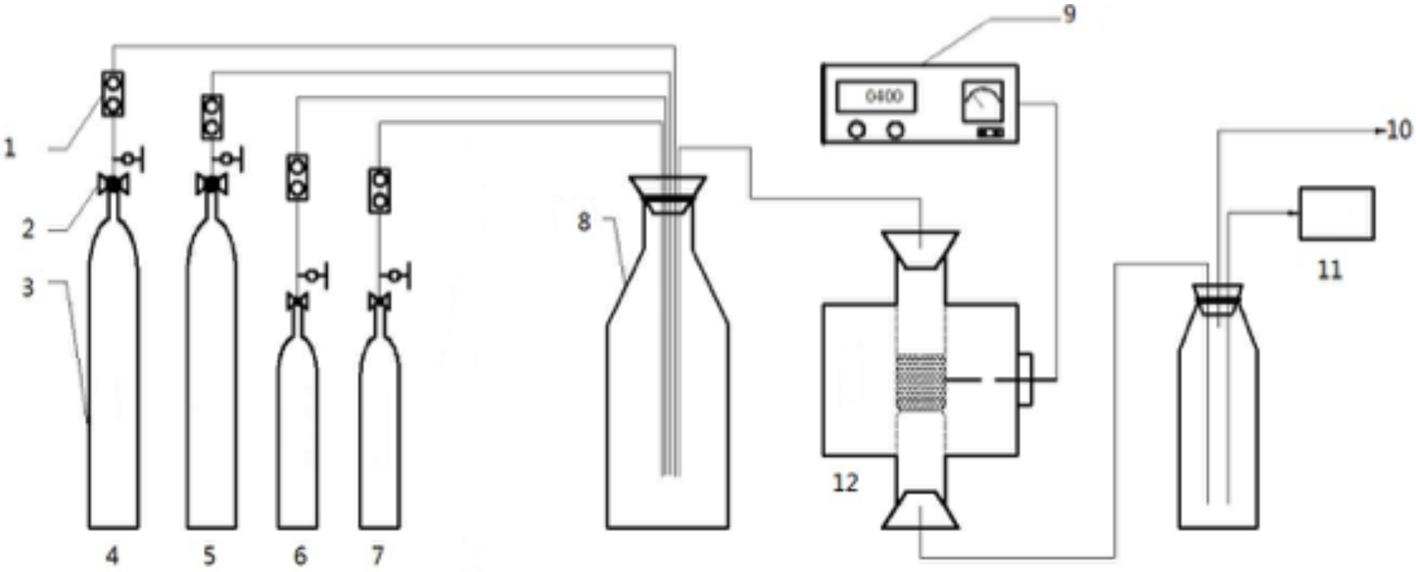


Figure 1. The test device for catalyst performance (1. gas flow meter; 2. relief valve; 3. high pressure steel; 4. oxygen; 5. nitrogen; 6.sulfur; 7. ammonia; 8. mixed gas cylinders; 9. tube furnace control instrument; 10. gas emission; 11. hand-held gas analyzer; 12. tube furnace).

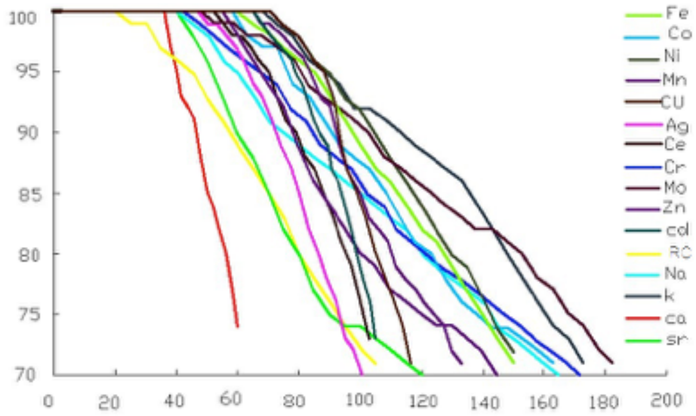


Figure 2. The performance of different metal loaded catalyst on flue gas desulfurization.

Fe_xO_y/AC catalyst had the longest maintained time with the desulfurization rate of 70% at 2.88 min. The elements in Sub-group such as molybdenum (Mo), chromium (Cr), zinc (Zn), and cadmium (Cd) had better performance than manganese (Mn) in group IB and copper (Cu), silver (Ag) in group IB, and the times with the desulfurization rate was 70% at 3.11 min, 2.78 min, 2.68 min, 2.55 min, 2.21 min, 2.08 min, and 1.60 min, respectively.

Activity evaluation of the catalyst

When alkali metal in group IA worked as activated component, the desulfurization rate was better than the raw coke, and when Na and K worked as activated component, the time with desulfurization rate above 70% were 2.73 min and 2.76 min, respectively (**Figure 3**). But with the shorter penetration time of SO_2, there is only one electron in the outermost layers of the alkali metal elements that broughtabout the stronger activity in the process. Along with the increase of the number of nuclear charge, the atomic radius also increased, the attraction of outer electrons decreased, the beta topic capacity gradually enhanced, and the metal reactivity gradually increased.

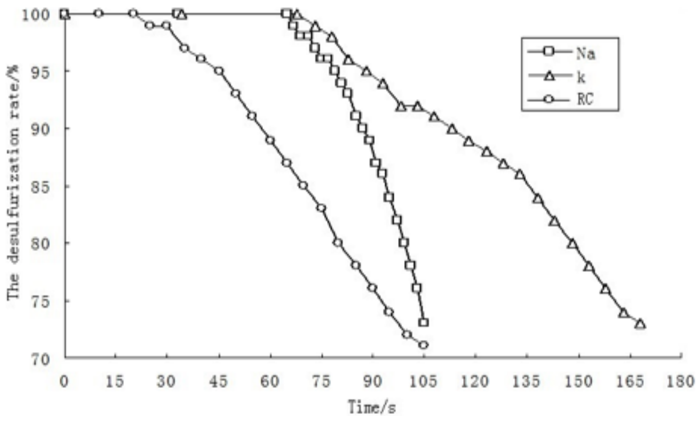


Figure 3. The performance of metal loaded catalyst of the IA elements on flue gas desulfurization.

Thus, the desulfurization rate rapidly decreased when SO_2 penetrated with subsequent fast reaction with alkali metal which created sulphate. When alkali metal in group IIA worked as activated component, its desulfurization rate was better than raw coke, and when Ca and Sr worked as activated component, their time with desulfurization above 70% were 2.21 min and 2.48 min, respectively (**Figure 4**). When desulfurization rate was lower than 100%, the penetration of SO_2 time was shorter, especially for the metal of Ca, and the time of desulfurization dropped from 100% to 70% that took 42 seconds. The calcium oxide (CaO) and strontium oxide (SrO) are hardly soluble in water and created Gypsum ($CaSO_4$) with the form of a hydration crystal when reacted with SO_2. It can stop the SO_2 reaching into the surface of catalyst and could affect the desorption of SO_2. With respect to the desulfurization rate of the catalysts which loaded the transition metal Fe, Co, and Ni in group VIII as an active component has greatly improved compared with the raw coke catalyst (**Figure 5**). The penetration time of NiO/AC catalyst was the longest, and the Fe/AC's with the desulfurization rate of about 70% was the longest. The desulfurization performance of penetration time of catalyst order is: Fe/AC > Co/AC > Ni/AC. When it loaded the sub-group elements, such as Cu, Ag, and Mn, the desulfurization performance of pyrolysis coke catalyst did

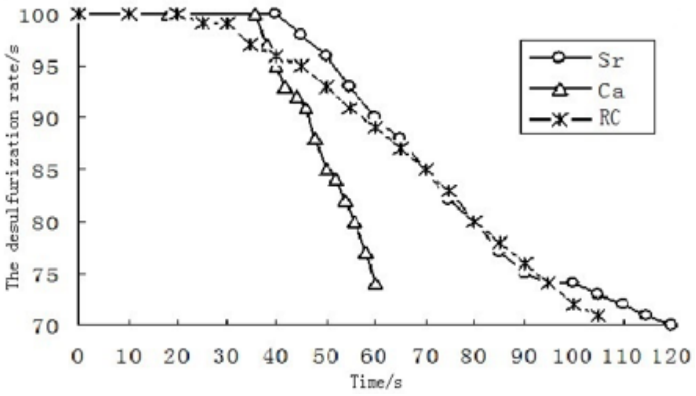


Figure 4. The performance of metal loaded catalyst of the IIA elements on flue gas desulfurization.

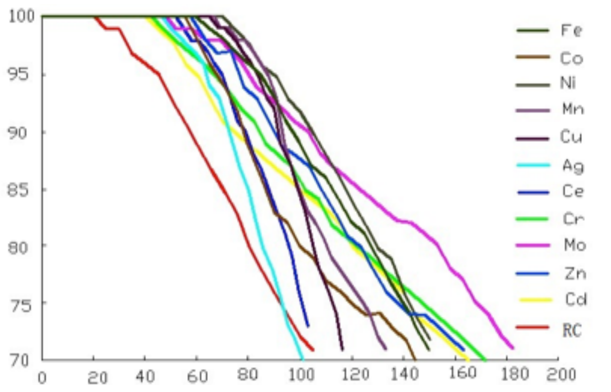


Figure 5. The performance of transition metal loaded Catalyst on flue gas desulfurization.

not improve significantly. The elements Cr and Mo in the group VIB had the better desulfurization effect than Zn and Cd (Group IIB), Mn (group VIIB) and Cu and Ag (group IB).

Analysis of mechanism of catalyst reaction

Relationships between the electron in the outermost layers arrangement and the catalytic activity of metal oxide catalyst. The catalysts had the similar desulfurization performance when loading the active component in the same main group, such as Na and K in group IA and Ca and Sr in group IIA that the atoms have the same number of electrons in the outermost layers (**Figures 3 and 4**). The catalyst loading with different atoms that have different number of electrons in the outermost layers in the group has very different desulfurization performance, this means that the outermost electrons of element and desulfurization rate has a certain relevance.

Electrons in the outermost layers of the transition metal elements in the same group. These have similar arrangement. A high degree of similarity about its desulfurization performance denotes that the arrangement of outermost electrons of transition metal and desulfurization catalyst activity has a certain relevance (**Figure 5**). However, there are also some differences between the elements in the same group in the desulfurization rate. For example, Cu and Ag in group IB works as active component with maintain time of the desulfurization rate at 100% for 1.08 min and 0.78 min, respectively. This is because Cu is a valence metal in which oxides can easily promote the formation N-type and P-type semiconductors during the process of roasting. In order to study the mechanism of metal oxide desulfurization performance of catalyst, the following study needs to do more detailed researches about the relationship between the type of transition metal oxide semiconductor and catalytic activity.

The relationship between the type of semiconductor and catalytic activity. Chromium (III) oxide (Cr_2O_3), zinc oxide (ZnO), silver oxide (AgO), and cadmium oxide (CdO) belong to the N-type semiconductor, and molybdenum oxide (MoO), manganese oxide (MnO), ferrous oxide (FeO), cobalt (II) oxide (CoO), nickel (II) oxide (NiO), and copper (I) oxide (Cu_2O) belong to the P-type semiconductor (**Figure 7** and **Table 2**). Under high temperature environment, the catalyst has the following reaction:

$$SO_2+O_2\xrightarrow{\blacklozenge\blacklozenge\blacklozenge}SO_3 \qquad (1)$$

With oxygen (O_2) as an electronic gas adsorbed in SO_2 during this process. In the N-type semiconductor, O_2 has a big electronegativity and it is easy to seize the electrons in the conduction band. As a result, the conductivity decreased with the oxygen pressure increasing and the number of free electrons in the conduction band was reduced. On the other hand, the negative electron shell covered on the surface of N-type semiconductor catalyst was not conducive to the transfer of electron, so the adsorption of oxygen on the surface was limited. However, in the P-type semiconductor, the O_2 as an acceptor impurity can accept the electrons in the filled band to increase the amount of holes. With an increase of oxygen pressure, conductivity increases and the adsorption of oxygen concentration increases on the surface of the P-type semiconductor.

Table 2. The semiconductor types of transition metal oxides.

The group	Element	Metal oxide	Semiconductor type
VIB	Cr	Cr_2O_3	N
	Mo	MoO	P
VIIB	Mn	MnO	P
	Fe	FeO	P
VIII	Co	CoO	P
	Ni	NiO	P
IB	Cu	Cu2O	P
	Ag	AgO	N
IIB	Zn	ZnO	N
	Cd	CdO	N

Therefore, the oxygen is adsorbed on the surface of catalyst and its concentration is getting higher during the process of the flue gas desulfurization. Higher oxygen concentration improves the reaction of SO_2 reacted with O_2 and generated sulfur trioxide (SO_3). Thus, the SO_2 concentration decreased and the purpose of flue gas desulfurization accomplished. Therefore, the P-type semiconductor catalyst has a better desulfurization effect than the N-type semiconductor catalyst.

The P-type semiconductor MnO in group VIB had

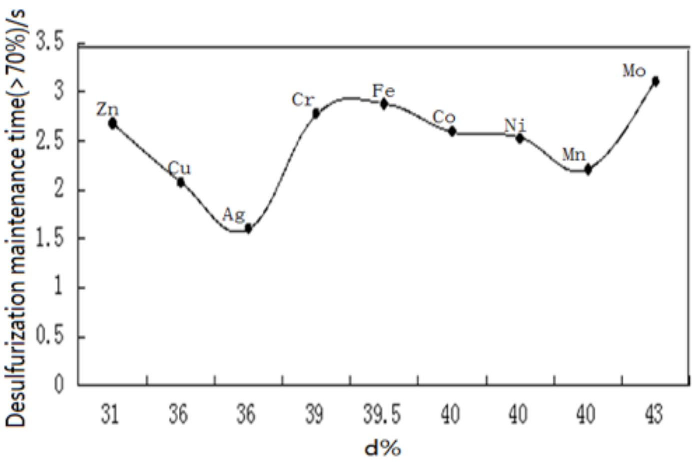
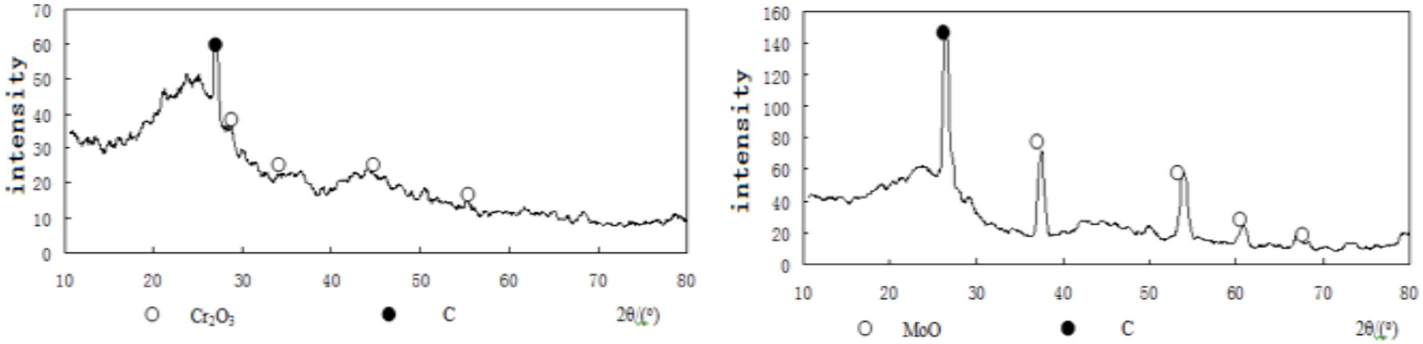
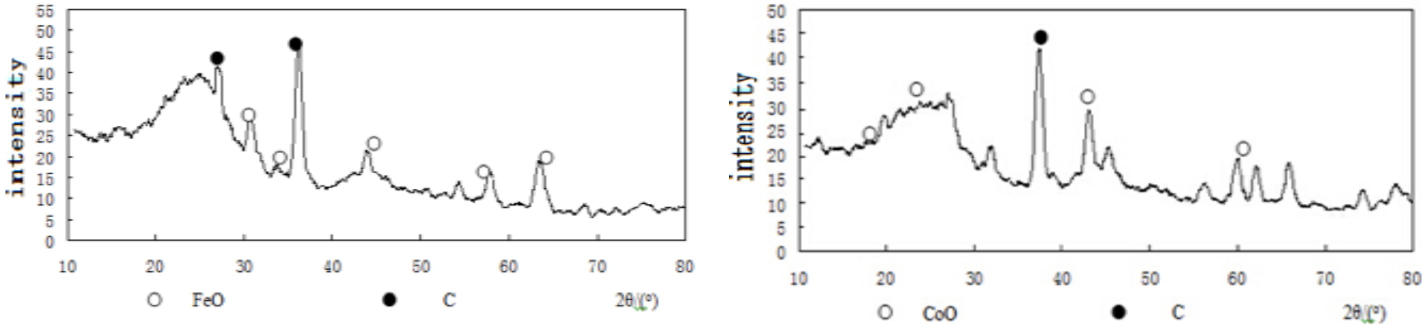


Figure 6. The relationship between the d% and catalytic activate.



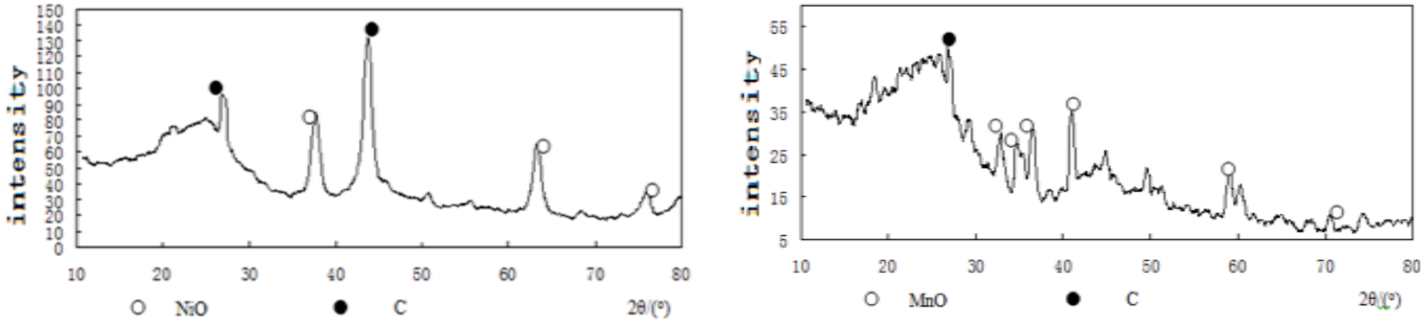
(a) XRD spectra of the metal catalysts for Cr_2O_3 / AC;

(b) XRD spectra of the metal catalysts for MoO/ AC;



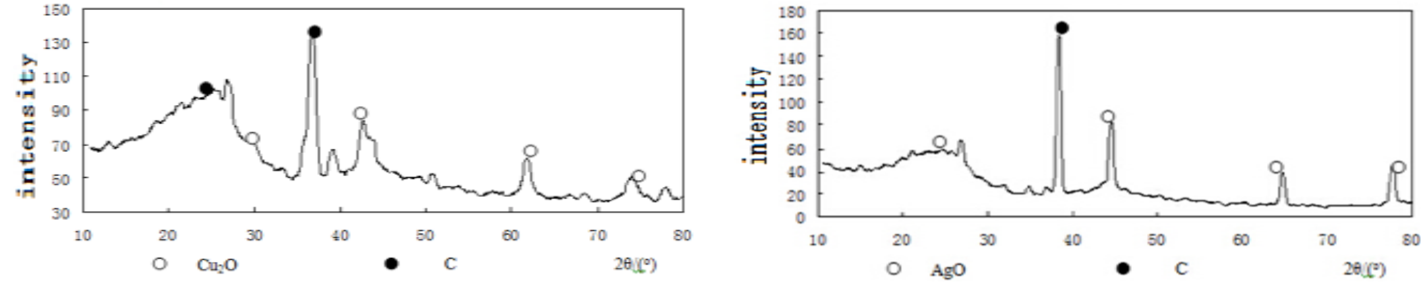
(c) XRD spectra of the metal catalysts for FeO/AC;

(d) XRD spectra of the metal catalysts for CoO/AC;



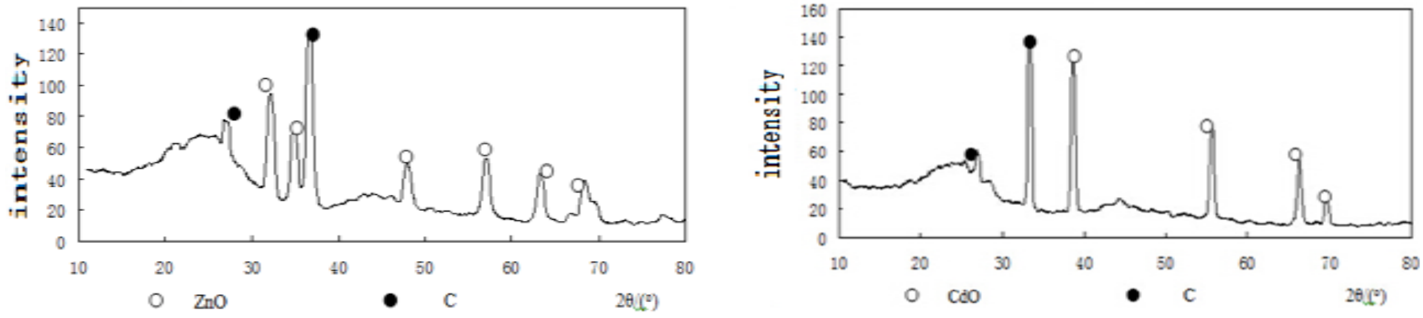
(e) XRD spectra of the metal catalysts for NiO/AC;

(f) XRD spectra of the metal catalysts for MnO/AC;



(g) XRD spectra of the metal catalysts for Cu_2O/AC;

(h) XRD spectra of the metal catalysts for AgO/AC



(i) XRD spectra of the metal catalysts for ZnO/AC;

(j) XRD spectra of the metal catalysts for CdO/AC

Figure 7. XRD spectra of the metal catalysts for different metal oxide.

the longer time of the desulfurization rate at 100% than N-type semiconductor Cr_2O_3. The Cu_2O in group IB had the longer time of the desulfurization rate at 100% than AgO as well as MnO and Cr_2O_3. The conclusion is consistent with the results of the experiment.

However, there are still some differences about the desulfurization rate between FeO, CoO, and NiO in group VIII as P-type semiconductors. It is due to the different percentage of their characteristic d (d %). To detail the impact of d% on the desulfurization rate, the following discussion is focused on elements in group VIII.

Relationship between the percentage of characteristic d (d%) and the catalytic activity.According to the Valence Bond theory, the transition metal atoms united through hybrid orbitals. Generally speaking, the hybrid orbitals are linear combination of the atomic orbital such as s, d and p and so on, and it can be called spd hybrid or dsp hybrid. The percentage of atomic orbitals of d in hybrid orbitals is called feature percentage of d and expressed in terms of d%. It is used as a characteristic parameter to connect catalytic activity of metal and other physical quantity. More electrons will be filled into the d energy band and electron holes will be decreased if the d% of metal increased. The d% and d electron holes are respectively related to chemisorption and catalytic activity of catalyst (**Table 3**). The mechanism of carbon-based catalyst is the ability of the combination between metal or metallic ion and adsorbates to be enhanced to improve the adsorption capacity of the activated carbon material for SO_2 (*Jin et al. 2006*).The more d holes, the stronger ability of combination between the loading metal ions and the absorbates, and the better subsequent adsorption effect. The d% in the group VIII are: Ni(40%), Co(40%), and Fe(39.5%). The d% of Mn in the group VIIIB is 40%, and the d% of Cu in the group-IB is 36% (**Table 3**). The catalytic activity of catalyst is better when the d% is in the range of 39%~40% (**Figure 6**). Metallic oxide catalysts with metals in group VIII such as Mo based catalyst has a better impact on desulfurization than metallic oxides catalysts in other groups, and this is accordance with the Valence Bond theory (**Figures 5** and **6**).

Analysis of catalyst XRD characterization

To examine the desulfurization mechanism of metal oxide catalyst, this study conducted the XRD analysis of the metal oxide catalysts and studied the law of desulfurization of metal oxides catalyst using the XRD characterization spectrogram. The XRD characterization spectrogram of catalysts with different transition metal oxides worked as active components (**Figure 7**). Specific analysis are as follows:

Table 3. The d percentage of metal bond of transition metal.

VIB	VIIB		VIII		IB	IIB
Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	39.5	40	40	36	31
Mo	-	-	-	-	Ag	
43	-	-	-	-	36	

There are characteristic peaks of the metal oxide except element C in the spectrogram. While the characteristic peak of metal oxide Cr_2O_3, FeO, CoO, MnO, and Cu_2O were not sharp, which means that these oxides dispersed evenly on the surface of carrier (**Figure 7**).

Moreover, the metal oxides like MoO, NiO, AgO, ZnO and CdO formed integrated crystal structure and their dispersion was uneven because their intensity of characteristic peaks were very strong and peaks appeared sharply. In addition, the metal oxides in the same group had different distribution uniformity on the surface of carriers, as well as the desulfurization rate.

Analysis of catalyst SEM characterization

The appearance pictures of raw coke and catalyst loading with Mo were magnified 1000 times and 3000 times, respectively, by the scanning electron microscope before and after they are sulphuretted (**Figure 8a to f**). There are significant pore structure on the surface of pyrolysis coke catalyst, but no obvious grain (**Figure 8a** and **b**).

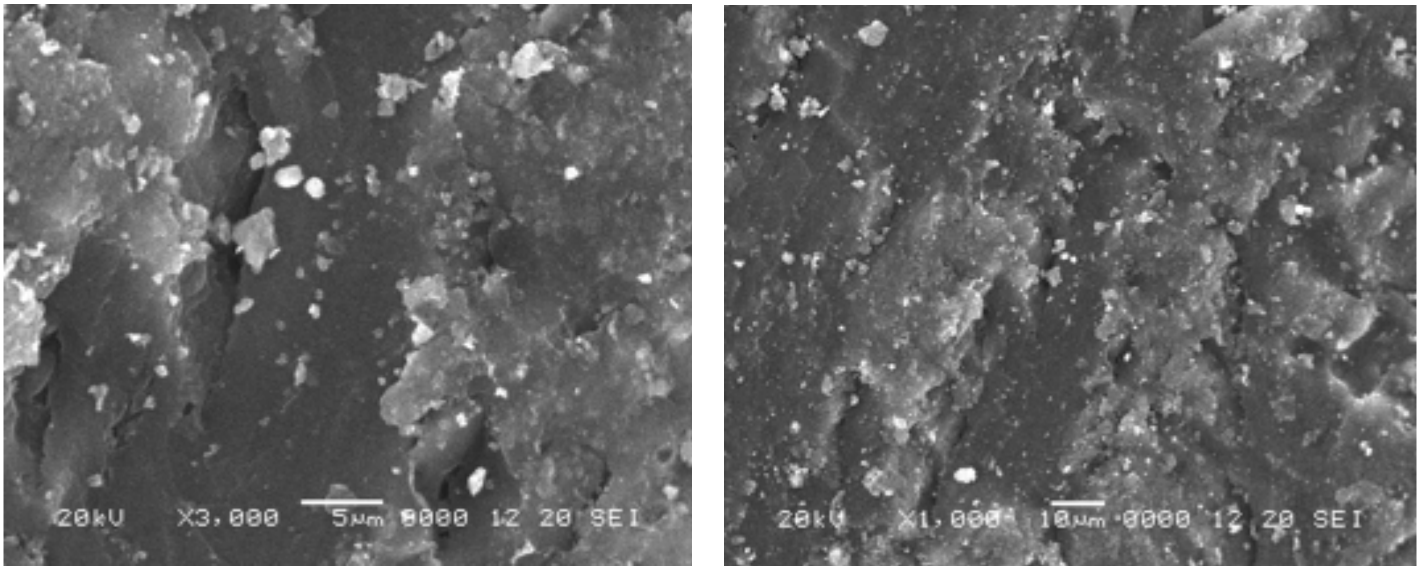
It can be noted that there were some dispersed particles and the porosities on the surface of pyrolysis coke were not obvious (**Figure 8c** and **d**) because there were some significant grains on the surface of catalyst supported with metal Mo before sulphuretted whose size and distribution were uniform.

The lamellar structure of catalyst loading with Mo was destroyed after the desulfurization experiment (**Figure 8e** and **f**). The size and distribution of grains were not uniform as before. In addition, the pore structure on the surface of the activated carbon was not of such significant as the previous.

CONCLUSION

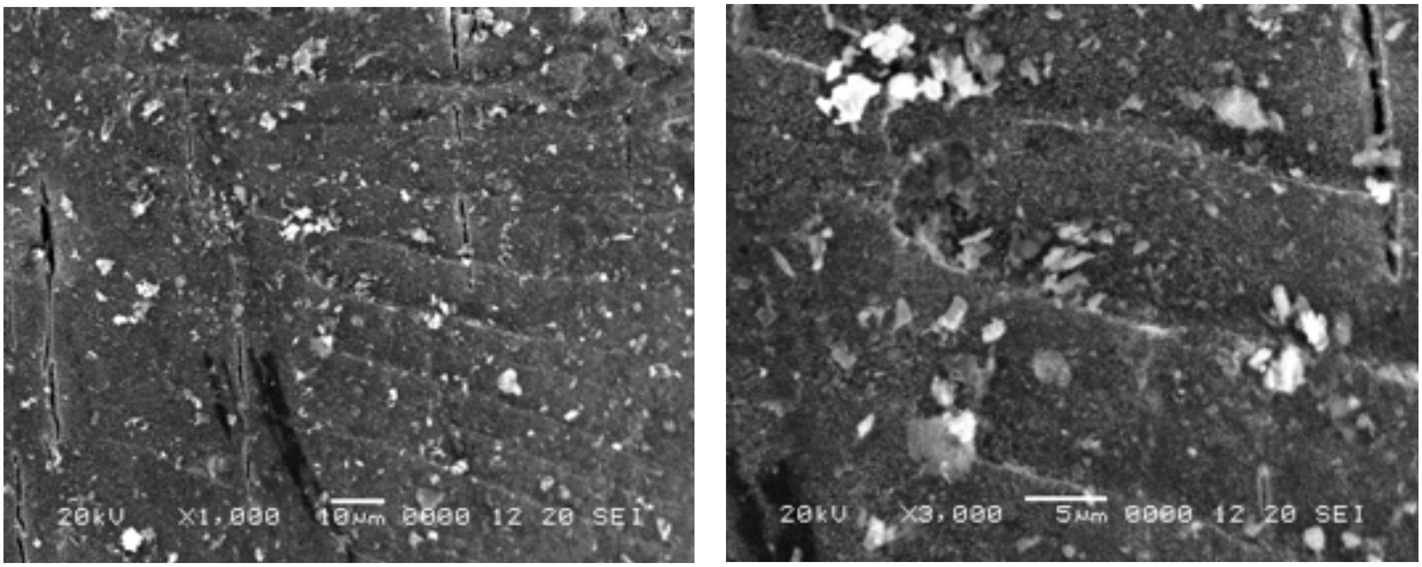
In this study, 14 kinds of metal oxides were chosen from groups IA, IIA, VIB, VIIB, VIII, IB and IIB as active components to prepare metal oxide supported catalyst by equivalent volume impregnation method.

Metal oxides in the same group showed similar desulfurization performance due to their structures of



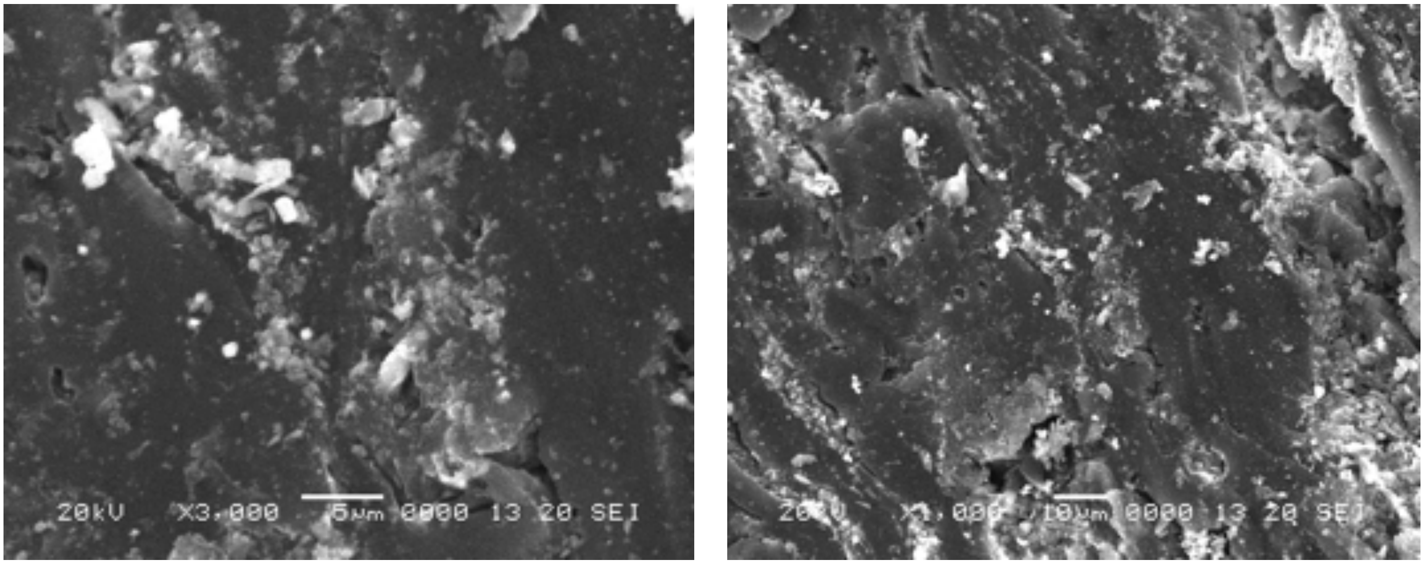
(a)The original coal surface topograph (1000 times)

(b)The original coal surface topography(3000 times)



(c)MoO sulfur/AC on former topography (1000 times)

(d)MoO sulfur/AC on former topography (3000 times)



(e)MoO/AC on sulfur topography (1000 times)

(f)MoO/AC on sulfur topography (3000 times)

Figure 8. SEM characterization of different catalysts.

electron in the outermost layers. The desulfurization performance was effected by transition metal oxides associated with the types of metal oxide semiconductor. The metal of oxides catalysts with the loading metals Fe, Co and Ni in group VIII showed different impacts on desulfurization performance due to the different d characteristic percentages (%).

REFERENCES

Cao Dongmei. 2013. SO_2 Pollution and its hazards and control technology in China. *Environmental Science Survey*, 32 (2): 73-74.

Chen Jun. 2001. An empirical research on the regional difference in China's coal consumption and pollution emission. *China Population, Resources and Environment*, 21(8): 72-79

CieslaU, SchuthF. 1999. Ordered mesoporous materials. *Micro Meso Mater*, 1999(27): 131-149

Deng Yiying, Bu Xuepeng, Ying Youju. 2006. Evaluation and characterization of ZnO-based sorbent for hot-gas desulfurization. *Journal of China Coal Society*, 31(02): 223-226

Fang Huibin, Zhao Jiantao, Wang Sheng. 2006. Preparation and mechanism of Fe-K/AC for catalytic oxidation of hydrogen sulfide. *Journal of Fuel Chemistry and Technology*, 40(1): 105-110

Jin Guangzhou, Zhu Jianhua, Ju Huliang. 2006. Preparation of molybdenum carbide catalyst and its hydrodesulfurization performance for thiophene. *Journal of Chemical Industry and Engineering* (China), 57(4): 799-804.

Li Deqi, Guo Shuqiang, Li Yulong. 2011. New Mn-based sorbents for high temperature coal gas desulfurization. *Coal Conversion*, 34(01): 13-17

Li Yuan, Zhang Xianglan, Xu Deping. 2007. Research on the mechanism of SO2 removal by activated carbon. *Coal Processing & Comprehensive Utilization*, 2007(2): 46-49

Li Yulong, Guo Shuqiang. 2012. Performance improvement of the supported ZnO/γ-Al2O3 sorbent. *Coal Conversion*, 2(35): 81-84

Ruan Guise, Feng xianjin, Gong weimin. 2000. Study on metal oxide support sorbents for desulfuration of flue gas. *Mining and Metallurgy*, 9(1): 99-102

Yue Jun, Liu Xiaoqin, Yao Huqing. 2006. Deep desulfurization performance of CuCl supported adsorbents. *Journal of Chemical Engineering of Chinese Universities*, 6(20): 81-84

Zhang Bin, Wang Zhanwen, Lu meili. 2013. Study on desulfurization properties of nickel sorbent loaded zinc ferrite. Hebei Enterprises, 2013, (3): 83-84

Zhang Lei, Zhang Xianglan, Zhang lei. 2006. The research on the effect of SO_2 removal property of activated semi-coke (carbon). *Journal of Environmental Management College of China*, 16(2): 71-72

Zhang Rui. 2010. Current status and prospect of dry flue gas desulfurization technologies based on activated carbon-base adsorbent. *Chemical Engineer*, 2010(10): 34-37

Zhang Sifang, Chen Hu. 2014. Research progress of metal sorbents for hot coal gas desulfurization. *Chemical Industry and Engineering Progress*, 33(6): 1373-1379

Zhou Yuxin, Liu Jianzhang. 2007. Current development situation of flue gas desulphurization technology abroad and home. *Chemical Engineer*, 145(10): 37-39

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