

Article

Study on the Relation between the Mn/Al Mixed Oxides Composition and Performance of FCC Sulfur Transfer Agent

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Abstract: A sulfur transfer agent in catalysts can effectively reduce the emission of SO₂ with minimum adverse effects on the catalytic cracking ability of the primary catalyst. In this paper, the composition and performance of sulfur transfer agents with different oxidative active components (such as Cu, Fe, Ni, Co, Ba, Zn and Cr) were prepared by acid peptization technique and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and N₂ adsorption-desorption technique. The relationship between the composition and performance of the new sulfur transfer agents was investigated and the regeneration and recycling of the agents were performed. The results indicates that copper is a very good desulfurization active component. Moreover, the presence of CO has no significant effect on the absorption ability of SO₂ by the sulfur transfer agent.

Keywords: fluid catalytic cracking; sulfur transfer agent; adsorption

1. Introduction

With the rapid developments of industries and the transportation sector in large cities all around the world, the emissions of the toxic sulfur oxide (SO_x, especially SO₂ and SO₃) gases have caused serious environmental pollution, such as atmospheric pollution [1–6]. For oil refineries, the sulfur oxide interacts with fumes in Fluid Catalytic Cracking (FCC) regeneration system and corrodes the regenerator and other equipment through sulfidation. Besides, sulfur oxides emitted outside may react with the water in the atmosphere and produce acid rain, which has significant adverse impacts on human beings, the ecosystem and infrastructure. In recent years, with the increase of sulfur content in the raw materials that FCC processed as well as the increasing restriction on the sulfur oxide emission by environmental regulations, to reduce the release of SO₂ in FCC regeneration flue gas has drawn significant attention and techniques have been developed [7].

Nowadays, oil refining companies mainly apply three different methods to control the emission of SO_x in FCC regeneration: hydrodesulfurization of raw materials, cleaning of flue gases and sulfur transfer agent technology [8–11]. Pretreatment of catalytic cracking raw materials by adding hydrogen can improve the feed-in cracking performance and product distribution, enhance the yield of light oil and processing ability of devices, reduce the yields of coke and dry gas, and eliminate effectively the sulfur oxide in feed-in materials. Nevertheless, it is very difficult to adopt this method in most small and medium-sized refining companies due to its high initial investments and operating costs. The cleaning methods for flue gas desulfurization in FCC equipment include such cleaning techniques as the wet-type one, semi-dry type one and dry-type one. Wet-type cleaning technique uses conventional

absorbents for SO_x removal, such as soda, sea water, or lime/limestone slurry, while dry-type or semi-dry type cleaning techniques use alkaline powder instead. Adding sulfur transfer agent into the FCC catalyst is the most cost-effective method without damaging the cracking performance of primary catalyst, oxidizing SO_2 into SO_3 , chemisorbs of SO_3 and forming stable sulfate on the additives, which are released as H_2S when circulated to the improved tubular reactor along with the primary catalyst. For the catalytic cracking reaction, the use of a sulfur transfer agent in large quantity may cause low conversion rate and yield, and increases non-selective hot cracking reaction. Thus, the amount of sulfur transfer agents shall not exceed 5% of the total amount of catalyst.

The research work on catalytic cracking sulfur transfer agents started in the 1960s and 1970s. The SO_x removal efficiency of early sulfur transfer agents was low for Al_2O_3 or MgO were used as rare earth carriers. The second generation of product carriers is alkaline earth metals spinels doping with Ce or V, which plays a good absorption performance of SO_x and which is easy to prepare, so it has been widely adopted in the industry. As early as 1971, Lowell *et al.* [1] calculated the thermodynamics of 47 types of metallic oxides absorbing sulfur dioxide and optimized 16 types among them, including cerium, aluminum and titanium, *etc.*; while magnesium sulfate was excluded due to its high decomposition temperature. However, only the possibility of sulfate thermal decomposition was considered, but not the possibility of regeneration of formed sulfate. Later, Baron *et al.* [12] further selected cerium, aluminum, nickel, iron and other metallic oxides. The research of Bhattacharyya *et al.* [13] found out the reduced desorption mechanism of oxidative adsorption of $\text{CeO}_2/\text{MgAl}_2\text{O}_4 \cdot \text{MgO}$, in which CeO_2 as an oxidant, is turned into SO_2 and SO_3 , and then reverted to Ce_2O_3 in reduction process. MgO , the active center, absorbs SO_3 creating MgSO_4 during oxidation-reduction process. Ce_2O_3 absorbs gas phase oxygen and is re-oxidized to CeO_2 . Polato *et al.* [14] studied the performance of Mn, Mg, Al-spinel, hydrotalcite-like compounds, as desulfurization catalyst in simulated FCC condition. The maximum absorption of SO_x occurs five minutes before the reaction, and propane has a poorer effect than hydrogen in regeneration condition. The experimental results indicates that manganese-containing spinel is a promising sulfur transfer agent. Wang *et al.* [15] focused on the preparation method based on magnesium aluminate spinel and the functions of different metallic elements (cerium, iron and vanadium, *etc.*) in the catalysts. In particular, the introduction of vanadium can improve sulfur absorption performance of the additive as well as the reduction of metallic sulfate. By improving the trial device in tube circulating fluidized bed, the author systematically investigated the device's influence of SO_2 content in flue gas and desulfurization capability of sulfur transfer agent, in the FCC reaction and regeneration operation condition closing to the practical cases.

In recent years, the development of sulfur transfer agent includes metallic oxide and spinel to mixed metallic oxides [7,16]. According to the literatures, sulfur transfer agent of magnesium aluminate spinel or magnesium aluminate spinel with rare earth has been developed in the past few years. Adding certain amount of vanadium oxide and cerium oxide will promote the oxidation susceptibility of sulfur transfer agent, while it will also increase the preparation, as well as damage the primary catalyst used in catalytic cracking device [2]. In this paper, we investigated the composition and performance of a sulfur transfer agent with different oxidative active components prepared by acid peptization technique [6] under conditions similar to those in the typical FCC units. In addition, this paper tries to discuss the relationship between the composition and performance of the new sulfur transfer agent as well as the CO 's influence on oxidative adsorption.

2. Results and Discussion

Different metallic oxides, such as cerium, copper, cobalt, vanadium, chrome and iron combining with hydrotalcite precursors by impregnation method or means of coprecipitation will have alkalinity and oxidation-reduction quality, leading to the best way of preparing spinel. By analyzing the report results of different researchers, the author find that none result systematically reports the adsorption capacity of sulfur transfer agent of metallic oxides. In the paper, taking pseudo-boehmite as aluminum

source, a series of mixed oxides precursor of M/MgAl type were prepared to apply acid peptization technique, then it was calcined to create sulfur transfer agent of mixed oxides to determine the adsorption capacity and reduction capacity of sulfur transfer agent of oxides and get cheaper oxidized active components.

2.1. Evaluation of Activity of Sulfur Transfer Agent

Figure 1a,b show the adsorption and desorption curves and pore size distribution diagram of sulfur transfer agents with different active components prepared by acid peptization technique. It can be seen from the adsorption and desorption curves that the uneven and irregular pore size distribution is still in typical mesoporous structure, and samples APG-1, APG-2, and APG-3 show level two adsorption steps under relative pressure of 0.45–1.0 p/p_0 , which should be capillary condensation of nitrogen in mesoporous under relatively low pressure. The isothermal adsorptions amount of samples APG-4, APG-5, APG-6, APG-7 are lower with less specific surface area. For the desulfurization reaction, a key factor is the surface area of sulfur transfer catalysts, which affects the desulfurization activity as large numbers of active sites locate at the surface of catalysts; the other one is its pore sizes, which determine whether gas can diffuse to crystal interior to contact more active sites. Table 1 is the pore parameters of different sulfur transfer catalysts. The pore size distribution curve (PSD, Figure 1b) reflects that pore size distribution is within mesoporous scope, with most probable apertures of 7.6 nm, 9.4 nm, 7.6 nm, 9.1 nm, 6.5 nm, 16.3 nm, 17.3 nm in order. The reason is that different active component impact on the pore structure.

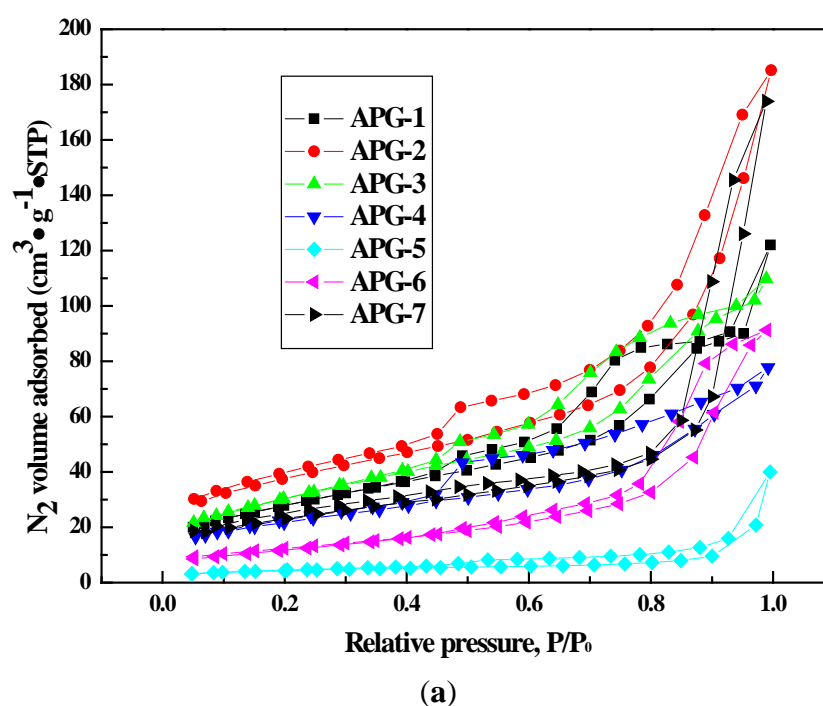


Figure 1. Cont.

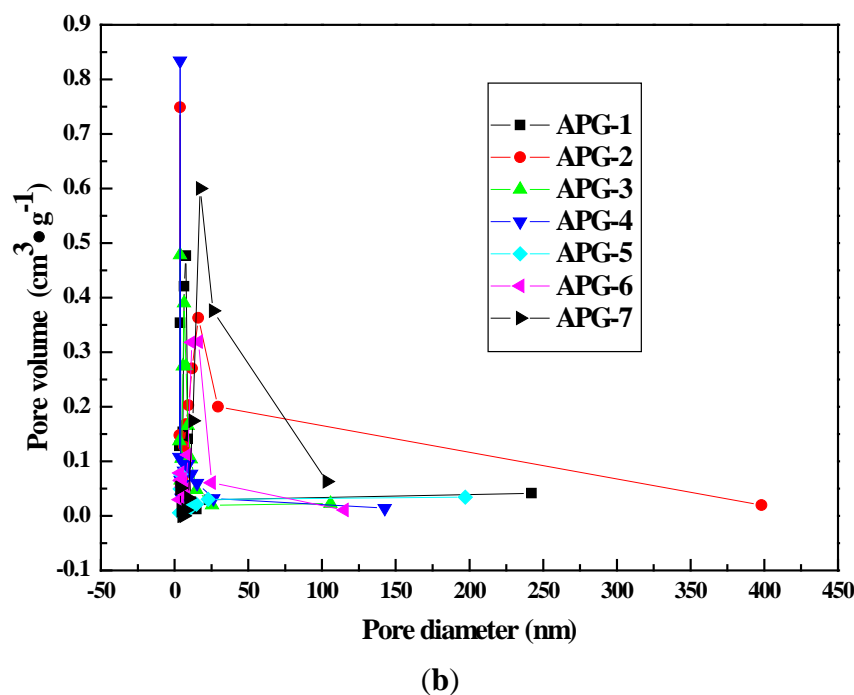


Figure 1. N₂ adsorption isotherms and pore size distribution of sulfur transfer catalysts with different metals. (a) Adsorption and desorption curves; (b) Pore size distribution diagram.

Table 1. Pore parameters of different sulfur transfer catalysts.

Samples	Most Probable Pore Size/nm	S _{BET} /m ² ·g ⁻¹
APG-1	7.6	143.6
APG-2	9.4	142.7
APG-3	7.6	143
APG-4	9.1	80.5
APG-5	6.5	86.3
APG-6	16.3	67.2
APG-7	17.3	80.8

As can be seen from XRD Figure 2, calcined in 700 °C, the former stratified structure collapses and forms weak Mg(Al)O [14] crystalline phase. As for APG-7 sample, MgCr₂O₄ and Mg(Cr, Al)O appear simultaneously, which is consistent with the results of C.M.S.Polato [2] calcined at 750 °C. The same part of APG-1 and APG-3 sample has a Mg(Al)O and spinel phase, while what is different is APG-1 has CuO crystalline phase but a structure containing nickel cannot be detected in APG-3, indicating that nickel has very good dispersion in APG-3. There are mixed oxides of cobalt and iron as well Mg(Al)O crystalline phase found in APG-2 and APG-4 sample. APG-5 and APG-6 sample appears BaAl₂O₄ and ZnAl₂O₄.

Infrared absorption signal in metallic oxides were distributed mainly in the intermediate infrared region and far infrared region [17]. Figure 3 shows the infrared spectroscopy of the composition and performance of sulfur transfer agent with different oxidative active components prepared by acid peptization technique. It can be seen that all the samples have very similar characteristics of infrared spectroscopy. After the thermal treatment, broad peak in 3500–3400 cm⁻¹ is –OH stretching vibration of H₂O that results from physical absorption of water [18]. The peak after 1000 cm⁻¹ [19] fingerprint region represents the M–O characteristic peak formed by some metal and oxygen of mixed oxides. The peak at around 1500 cm⁻¹ [19] is network structure in form of bridged bond formed by metal and

other metals using chemical bonds. The frequency of absorption band of infrared spectroscopy will change accordingly with the change of the system composition.

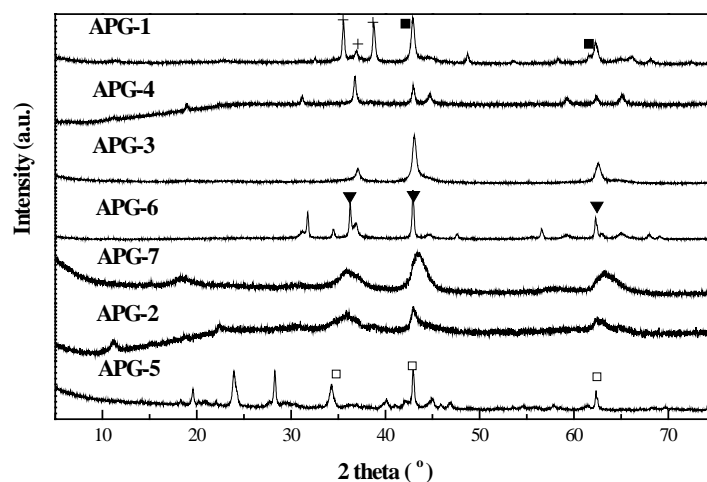


Figure 2. X-ray diffraction patterns of the mixed oxides derived from precursors after calcinating at 700 °C. +: CuO, ■: Mg(Al)O, ▼: ZnAl₂O₄, □: BaAl₂O₄.

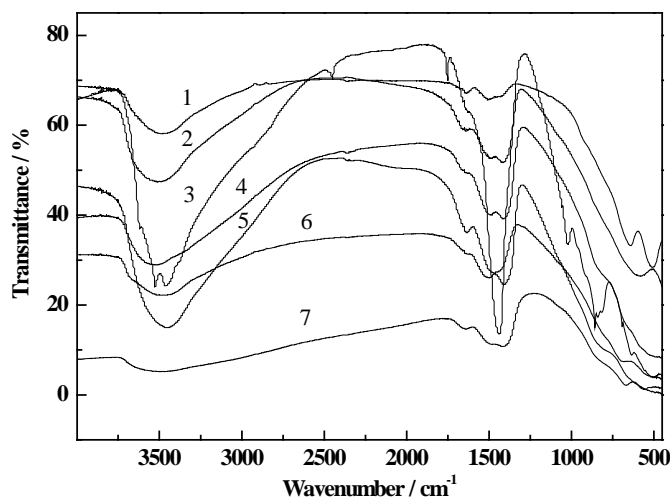


Figure 3. FT-IR spectra of the mixed oxides derived from precursors after calcinating at 700 °C. 1: APG-7; 2: APG-2; 3: APG-5; 4: APG-1; 5: APG-3; 6: APG-6; 7: APG-4.

Based on the analysis of above physical and chemical properties, desulfurization activity of the composition and performance of sulfur transfer agent with different oxidative active components have been studied after the samples are in 700 °C (Figure 4). It can be seen from Figure 4 that all sulfur transfer agents prepared by different oxidative active components have certain degree of oxidative desulfurization performance and the oxide removal of SO₂ is: APG-1 > APG-7 > APG-2 > APG-3 > APG-5 > APG-4 ≈ APG-6. The reason for significant desulfurization performance of APG-1 is that copper oxide is beneficial to SO₂ oxidation. Gabriele *et al.* [10,20] believes that functions of copper are reflected in following aspects: (1) copper can oxidize SO₂ into SO₃ to improve the efficiency; (2) SO₃ after chemical adsorption integrates with copper species to form sulfate; (3) the sulfate connecting with copper moves to adjacent active site of aluminum and forms sulfate connecting with aluminum, and the reduced copper rapidly regenerates through oxygen. Rodriguez *et al.* [21] suggested that by introducing Cr and Fe to MgO, the introduced metal are not wholly oxidized since they are in low

chemical state (Cr^{2+} , Fe^{2+}), so it is beneficial to form electronic state of low stability and promote the interaction with SO_2 .

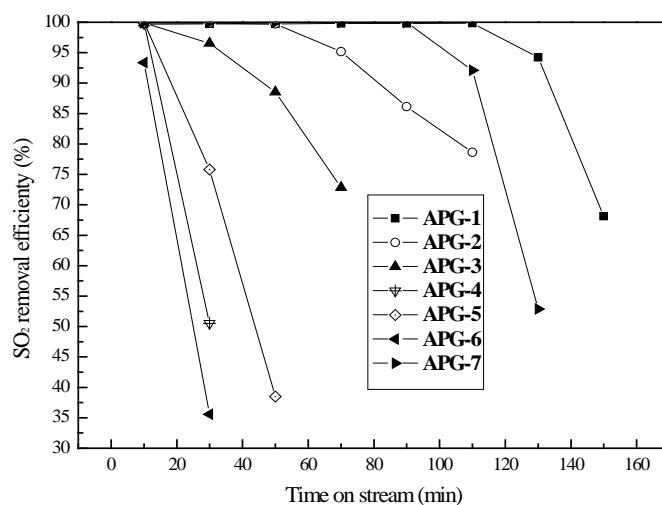


Figure 4. SO_2 pick-up efficiency of sulfur transfer catalysts with different oxidation active components.

Figure 5 is the XRD Figure of sulfur transfer agent with different oxidative active components after reaction. The spectrogram demonstrates that CuO phase and $\text{Mg}(\text{Al})\text{O}$ phase in APG-1 sample still exist, and new crystalline phase $\text{Cu}_{1-x}\text{Al}_x(\text{SO}_4)_{0.5}$ and MgSO_4 come out. The $\text{Mg}(\text{Al})\text{O}$ crystalline phase disappears in APG-7 and APG-2 samples but new crystalline phase MgSO_4 occurs. There is still $\text{Mg}(\text{Al})\text{O}$ phase in APG-4 and APG-6 samples but sulfate does not exist. Taking desulfurization performance analysis into account, on one hand, it demonstrates that magnesium oxide is the active site of SO_2 adsorption and forms magnesium sulfate; on the other hand, transition metal forms synergistic effect with magnesium and aluminum so that samples with copper have good desulfurization performance while samples with barium and cobalt have poorest desulfurization performance.

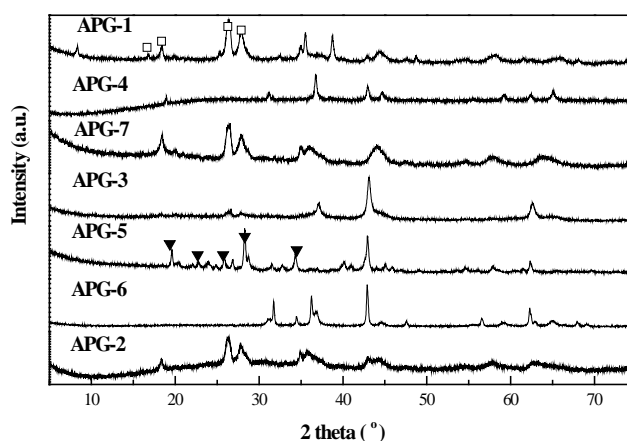


Figure 5. X-ray diffraction patterns of spent sulfur transfer catalysts with oxidation active components: \square : $\text{Cu}_{1-x}\text{Al}_x(\text{SO}_4)_{0.5}$; \blacktriangledown : MgSO_4 .

For the changes after adsorption desulfurization of samples after reaction, FT-IR is used to characterize the samples after adsorption SO_2 . It can be seen from Figure 6 that all samples after adsorption have stretching vibration absorption peak with $\text{S}=\text{O}$ double bond and $\text{O}-\text{S}-\text{O}$ single bond near 1140 cm^{-1} and 1020 cm^{-1} , respectively, indicating that the series of samples has active site that can adsorb or interact with SO_2 .

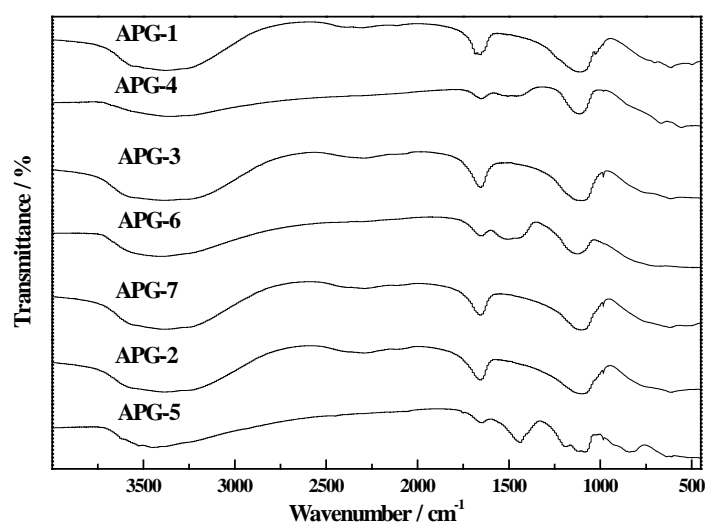


Figure 6. FT-IR spectra of spent sulfur transfer catalysts with different metals.

2.2. Thermogravimetry Reduction Analysis

DTU-2A TG-DTA analyzer is used to study the reduction and regeneration performance of sulfur transfer agent with different oxidative active components after reaction (Figure 7). As Figure 7 has shown to us, sulfur transfer agents with different oxidative active components can be restored and regenerated after the deactivation, and the differences on reduction temperatures in maximum reduction rate were different. Temperature in maximum reduction rate is among 400–630 °C and the orders of difficulty level of reduction are: APG-1 > APG-2 > APG-3 > APG-4 > APG-6 > APG-5 ≈ APG-7. Palomares *et al.* [22] showed that the reducibility of mixed oxides of copper, magnesium and aluminum after desulfurization was better than that of mixed oxides of cobalt, magnesium and aluminum after desulfurization, because that CuS is easier to be reduced than CoS, which is consistent with the result of the reducibility of APG-1 > APG-4. Wang *et al.* [15] supposed that iron participating in forming sulfate should produce more oxygen vacancy in reduction process, which is helpful in adsorbing oxygen and thus enhance the desulfurization performance after reduction. Kim *et al.* [9] studied the change of reduction and regeneration performance after different transition metals were introduced in Mg/La/Al mixed oxides. The result indicated that the orders of reduction and regeneration capacity of propane were: V > Ce > Fe > Cr, which is consistent with the result of APG-2 > APG-7. As can be seen from Table 2, for the APG-1 sample, the weight loss peak appeared twice, the initial reduction temperature was relatively low, and the temperature for reaching the maximum reduction rate was low.

Table 2. Analyzed results of spent sulfur transfer catalysts' reduction performances.

Item	Sample							
	APG-1	APG-2	APG-3	APG-4	APG-5	APG-6	APG-7	
Starting gravimetric temperature (°C)	280	275	350	400	490	436	480	
Final gravimetric temperature (°C)	700	704	650	570	640	704	690	
First weight loss ratio (%)	21.26	33.99	21.26	11.44	7.42	12.77	27.76	
Second weight loss ratio (%)	32.55	-	-	-	-	12.99	-	
Total weight loss ratio (%)	53.81	33.99	21.26	11.44	7.42	25.76	27.76	
Max reduction rate (%)	0.55	0.56	0.39	0.32	0.23	0.38	1.02	
Temperature in Max reduction rate (°C)	407	416	499	490	579	577	627	

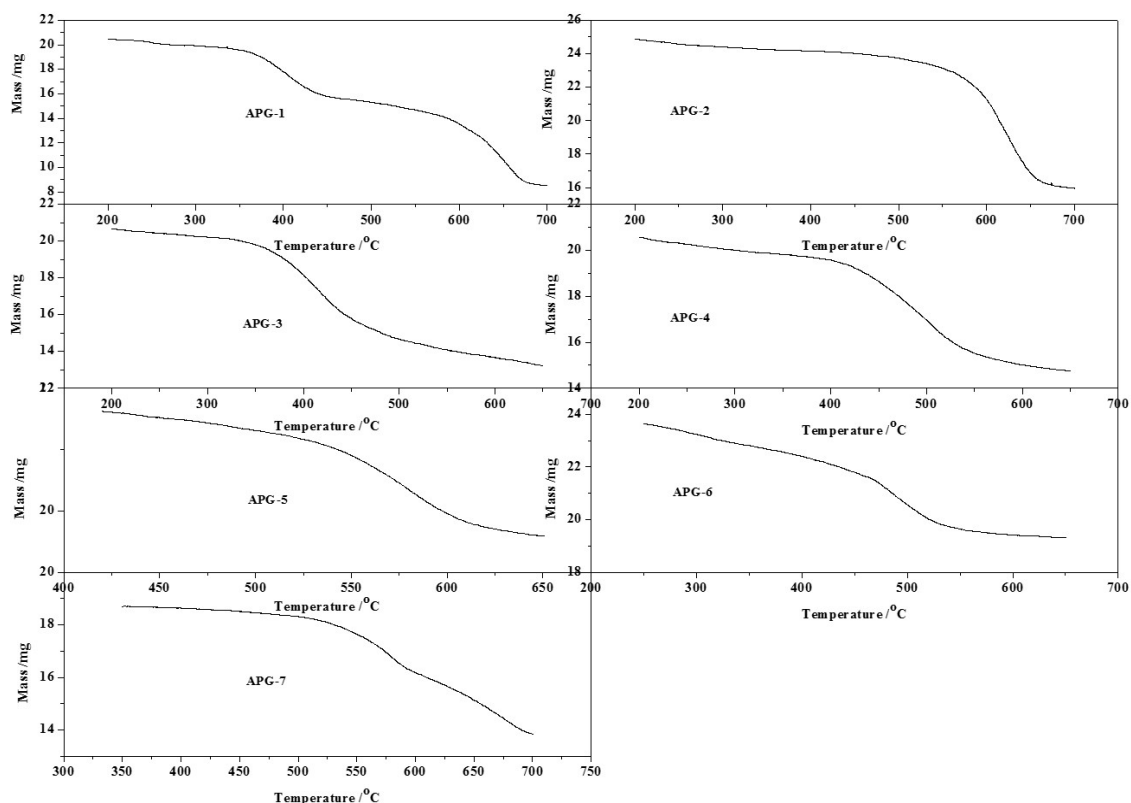
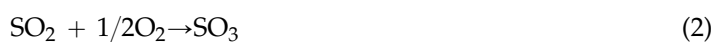


Figure 7. Reduction performances of spent sulfur transfer catalysts with different metals.

2.3. CO's Influence on Oxidative Adsorption

CO₂, CO and SO_x form in FCC regenerator, and it is important to investigate the change of sulfur transfer agent by simulating CO atmosphere. In order to study on the CO's influence on oxidation and adsorption desulfurization, different sulfur transfer agents were selected to compare the changes in O₂, CO₂ and SO₂ in mixed CO atmosphere. The mixed gases are: 10 vol. % of CO₂, 8 vol. % of CO, 7.6 vol. % of O₂ and the rest of N₂.

The reactions may occur in the regenerator are as follows:



It can be seen from Table 3 that CO has no significant influence on the oxidation and adsorption desulfurization [23], CO₂ content in mixed gas showing the trend of increasing first and then decreasing with reaction, whilst O₂ decreases first and then increases with reaction. Therefore, it can be referred that change takes place in reaction of step Equation (1). It may be because the metallic oxides in the sulfur transfer agent are both an adsorption center and oxidization center that adsorb oxygen to gather on their surface and form oxygen species, and then adsorb SO₃ and CO to their surface. Oxidation reaction between CO and active oxygen species creates CO₂, while SO₃ forms metal sulfate. With the process of reaction, metallic oxides gradually form metal sulfate, and the amount of metallic oxides decreases, then the degree of reaction Equation (1) decreases and the production amount of CO₂ reduces. Along with the reduction reaction Equations (1) and (2), the O₂ content increases, basically meeting the experimental data rule.

Table 3. The adsorption of SO₂ in presence of carbon monoxide.

Samples	Gas	Cycles				
		0	1st, 20 min	2nd, 20 min	3rd, 20 min	4th, 20 min
APG-1	O ₂	7.6	5.4	5.5	7	7.8
	SO ₂	1900	6	6	215	941
	CO ₂	10	11.8	11.7	10.6	9.9
	CO	8	6.2	6.3	7.4	7.8
APG-3	O ₂	7.6	4.5	7.5	8	-
	SO ₂	1900	5	462	1082	-
	CO ₂	10	12.4	10.2	9.7	-
	CO	8	5.6	7.8	7.6	-
APG-4	O ₂	7.6	4.9	8	-	-
	SO ₂	1900	7	1113	-	-
	CO ₂	10	12.1	9.8	-	-
	CO	8	5.9	7.9	-	-
APG-7	O ₂	7.6	4.8	5.2	7.7	8
	SO ₂	1900	12	7	258	1011
	CO ₂	10	12.2	11.9	10	9.5
	CO	8	5.8	6.1	7.9	8

Concentration unit: O₂, CO₂, CO (vol. %), SO₂ (ppm).

2.4. Cycles Tests

The regeneration performance of sulfur transfer agent is also one of the most important indicators to evaluate its overall performance. In the catalytic cracking process, the sulfur transfer agent and the main catalytic cracking catalyst respectively conduct their own reaction and regeneration. In this study, APG-1 was tested for six times for its reaction-regeneration performance, and the results are shown in Figure 8. It can be seen that, after the deactivation of the sample APG-1, the desulfurization effect of regenerating agent remained unchanged. With the increase of recycling, especially after recycling for four times, the activation of sulfur transfer agent declined gradually. Obviously, the regeneration efficiency did not change significantly. From the Figure 8, however, the regeneration efficiencies of other samples were relatively low compared with that of APG-1.

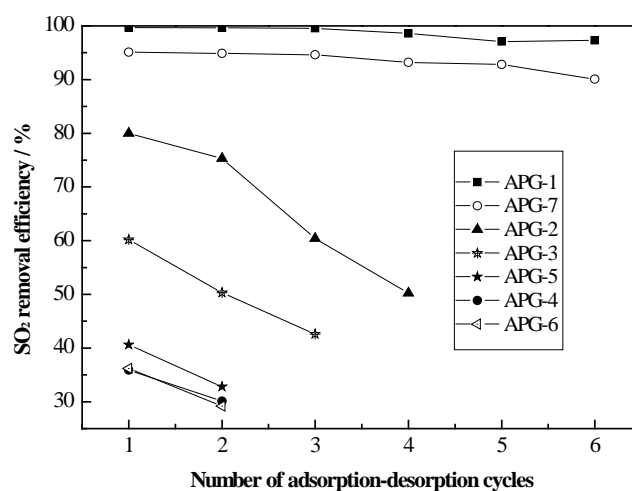


Figure 8. SO₂ adsorption-desorption cycles on different samples.

3. Experimental Section

3.1. Preparation of Sulfur Transfer Agents

According to Jiang's procedure [6], firstly, pseudo-boehmites was added to the beaker slowly, and we then poured in proper amount of distilled water, and stirred the solution for 3–5 min. Second, we took hydrochloric acid and added it to stirred seriflux drop by drop. After uniform gel was formed, added it to 65 °C water bath and adjusted pH to appropriate range; took out the gel and added to manganous nitrate, and then stirred the solution evenly. Then took copper nitrate, ferric nitrate, nickel nitrate, cobalt nitrate, barium nitrate, zinc nitrate and chromic nitrate and added to the gel respectively and stirred the solution sufficiently in 2 h. After that, placed it in oven to dry for 8 h in 140 °C, and then to muffle of 700 °C for roasting for 2 h, and then grinded the product and screened the grains by 80–120 meshes, and thereby obtained sulfur transfer agents for reserves. The sulfur transfer agents produced were named respectively APG-1, APG-2, APG-3, APG-4, APG-5, APG-6 and APG-7. As Table 4 has shown.

Table 4. The different oxidative active components in the different samples.

Samples	APG-1	APG-2	APG-3	APG-4	APG-5	APG-6	APG-7
oxidative active components	Cu	Fe	Ni	Co	Ba	Zn	Cr

3.2. Analysis and Characterization

X' Pert PRO diffractometer (X'Pert Pro MPD, PANalytical B.V., Almelo, Holland) is used to measure the crystal structure of sample, and scanning electron microscope (QUANTA200, Micromeritics instrument Corp, Atlanta, GA, USA) to analyze the morphology and particle size of the sample. Fourier infrared analyzer (NEXUS, Thermo Nicolet, Waltham, MA, USA) is used to analyze the framework vibration of the sample. DTU-2A TG-DTA (Beijing Yuanbo Technology Co., LTD, Beijing, China) is used to analyze the phase change of sample in the reduction process.

The fixed bed micro-reactor is used to evaluate the performance of sulfur transfer agent. Figure 9 is the experimental facility of fixed-bed micro-reactor unit. First of all, weigh a certain amount of sample and add it to the reactor, and then increase the temperature to the temperature of oxidized adsorption in the flow of nitrogen; secondly, respectively control the amount of SO₂ and air entering the reactor. Gas entered from the top of the reactor and the flow rate was controlled by mass flowmeter. For oxidative adsorption of SO₂, a stream (220 mL/min) containing 1900 ppm SO₂, 19.1% (v/v) O₂ and 80.4% (v/v) N₂ was introduced into the catalyst bed at 973 K.

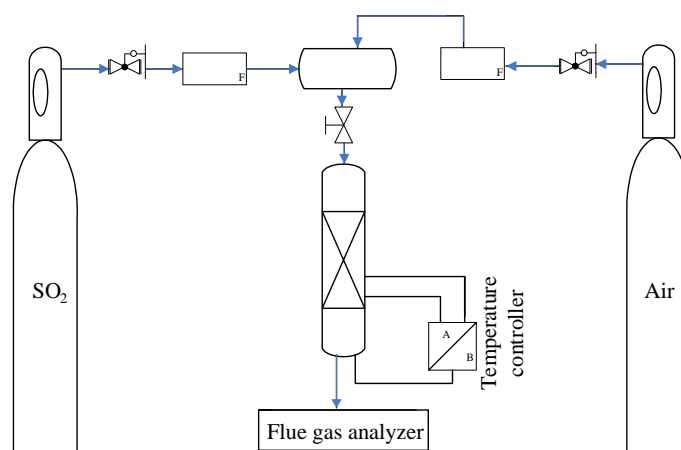


Figure 9. Experimental facility of homemade fixed-bed micro-reactor unit.

3.3. Data Processing

Activity of the catalyst is estimated using removal efficiency of SO₂ as:

$$E = (C_{v0, in} - C_{v, out})/C_{v0} \times 100\% \quad (4)$$

E is the Removal efficiency (%); $C_{v, out}$ is the Sulfur content in flue gas after adding sulfur transfer agent (ppm); $C_{v0, in}$ is the Sulfur content in flue gas before adding sulfur transfer agent (1900 ppm).

4. Conclusions

In order to solve the problems of expensive oxidative active components and damage to the primary catalyst, sulfur transfer agents with different oxidative active components prepared by acid peptization technique have been prepared to investigate the relationship of its composition and performance as well as explore CO's influence on oxidative adsorption. A comparison of sulfur transfer performance of different metal oxidative active components indicated that all sulfur transfer agents have oxidation desulfurization abilities, and the oxide removal capacity of SO₂ followed like this: APG-1 > APG-7 > APG-2 > APG-3 > APG-5 > APG-4 ≈ APG-6. Sulfur transfer agent with different oxidative active components can be restored and regenerated after the deactivation, and the differences on reduction temperatures in maximum reduction rate were different. Temperature in maximum reduction rate was in the 400–630 °C range and the reaction-regeneration performance followed like this: APG-1 > APG-2 > APG-3 ≈ APG-4 > APG-5 ≈ APG-6 > APG-7. In an anti-disturbance performance test of CO, the activity of sulfur transfer agent absorbing SO₂ does not change significantly.

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Author Contributions: R.J. and S.Y. conceived and designed the experiments; Y.Z. performed the experiments; R.J. and T.Z. analyzed the data; S.Y. contributed reagents/materials/analysis tools; R.J. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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