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Experimental analysis of removal of SO_2 and NOx for nano Mg-Al composite oxides

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Nano Mg - Al composite oxides were prepared through the solid state reaction synthesis method and molten salt synthesis method respectively, and efficiencies of desulfurization and denitrification were tested at the same time under the condition of flue gas, to find the optimal proportion of the material, and to investigate the adsorption mechanism of Mg-Al composite oxides. It was found that the more proportion of Mg, the efficiencies of desulfurization and denitrification are better. The removal efficiencies of the sample prepared by the molten salt synthesis method are better than that prepared by solid state reaction synthesis method. The sample, in which Mg/Al molar ratio is 4:1, has the best removal efficiency with molten salt method. The highest removal efficiency of SO2 can reach 100%, and the highest removal efficiency of NOx can reach 71%, whose time can maintain 150 min. It showed that the whole adsorption processes are controlled by surface adsorption reaction, and the internal diffusion and outer diffusion play a secondary role.

Keywords：Mg-Al composite oxides, desulfurization & denitrification, adsorption process, molten salt synthesis method, Solid state reaction synthesis method.

AIMS AND BACKGROUND

In China, lime slurry was adopted to reduce emissions of SO_2 from coal-fired power plants, and production of desulfurization can be used for producing gypsum board. Selective catalytic reduction method was adopted to reduce emissions of NOx in coal-fired power plants, and N_2 and water generated by reaction of NOx with NH_3. Separately using the above two methods are difficult to achieve the ideal effect of desulfurization and denitrification at the same time. Many scholars are researching and developing of a new technology of simultaneous control of SO_2 and NOx emissions. Because of rich source and low cost, Mg-Al oxides as adsorbent or catalyst in removing acid gas (SO_2, NOx and CO_2) have great potential.

As catalyst or catalyst carrier, MgO, Al_2O_3, $MgAl_2O_4$ used for removal of SO_2 and NOx have been reported much [1, 2]. So far, the researches about Mg-Al oxides as sorbent used for flue gas desulfurization and denitrification is still less. Reducing the size and increasing the specific surface area are breakthroughs of desulfurization and denitrification by Mg-Al oxide [3, 4]. Nanoparticle has two important features, namely, surface effect and volume effect, which has a very important using value and good development potential in the optical, catalyst, sensors, and many other industries. Pereira HB et al. [9] studied catalytic ability of SO_x removal by $MgAl_2O_4$ loaded Mn. Centi G et al. [10] studied catalytic removal ability of SO_x by CuMgAl hydrotalcite. Fornasari et al. [11] studied the influence of different Mg/Al molar ratio on the catalytic efficiency of NOx removal. Also, application of nanometer materials in the air pollution governance also is essential to research.

In this paper, Mg-Al composite oxides were prepared with solid state reaction synthesis (SSR) method and molten salt synthesis (MSS) method. Morphology, structure and performance of Mg-Al composite oxides were tested and analytically compared, and simultaneous removal rate of SO_2 and NOx were tested under the condition of simulate flue gas. Also the mechanism of removing was analyzed, to understand the cause of the high efficient removing.

EXPERIMENTAL

Material preparation and characterization

The reagents used in the experiment are all from Sinopharm Chemical Reagent CO.Ltd. When samples were prepared by SSR synthesis process, MgO and Al_2O_3 were used as raw materials, weighing according to the stoichiometric ratio (Mg

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and Al mole ratio of 1:4, 1:6, 1:8, and 4:1, 6:1, 8:1), then were put in the muffle furnace, calcining at different temperatures 1300 ℃ for 8 h. After muffle furnace cooled to room temperature, powders were removed out and sieved, achieve the products [5]. When samples were prepared by MSS process, MgO and Al_2O_3 were mixed together with KCl as molten salt. MgO and Al_2O_3 of different mole ratio (4:1、6:1、8:1) were homogeneously mixed by using ball mill, and dried. The dried power was later mixed with molten salt; the salt/oxide weight ratio was kept at 20:1. The powder mixture was grinded for 2h using an agate mortar. Later the powder mixture was placed in an alumina crucible covered with an alumina lid, heated to 1150℃ and held for 4h or 8h. After muffle furnace cooling to room temperature, the reacted mass was repeatedly washed with deionized water and filtered to remove salts. Then the resulting oxide powders were oven-dried before further characterization [6].

The obtained solid product were characterized by X-ray diffraction on a Rigaku D/Max-RB diffractometer using Cu Kα radiation (40KV, 35mA) in the range between 20°and 80°2θ. Fig.1and 2 gives the XRD patterns of samples synthesized with different mole ratio of Mg and Al. The Fig. 1 and Fig. 2 showed that when the amount of Mg is more, the main number of adsorbent is MgO and $MgAl_2O_4$. When the amount of Al is more, the main number of absorbent is Al_2O_3 and $MgAl_2O_4$.

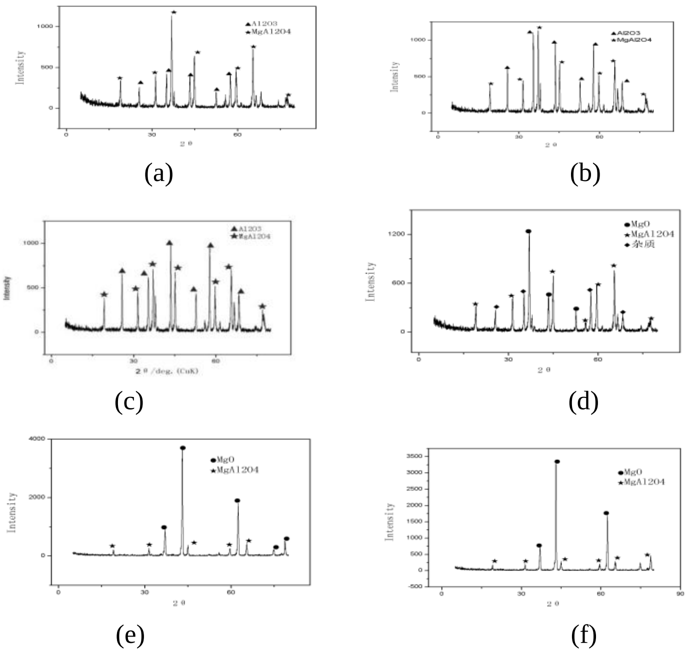

Fig.1. X-ray diffraction patterns of samples prepared by SSR with different Mg/Al mole ratio.

(a) 1:4; (b) 1:6; (c) 1:8; (d) 4:1; (e) 6:1; (f) 8:1.

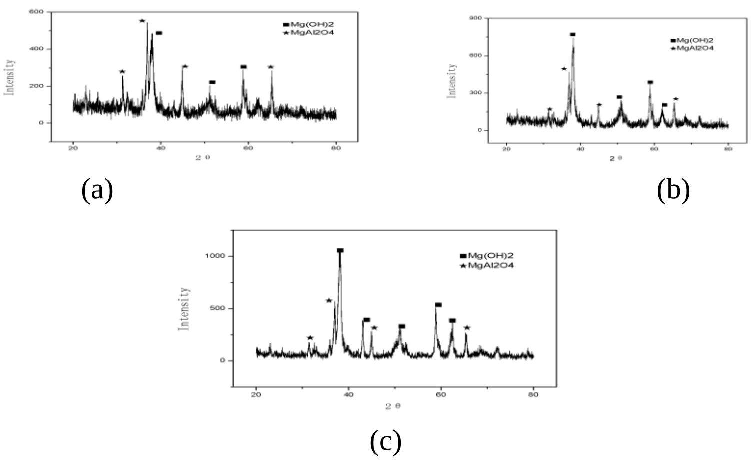

Fig. 2. X-ray diffraction patterns of samples prepared by MSS with different Mg/Al mole ratio.

(a) 4:1; (b) 6:1; (c) 8:1.

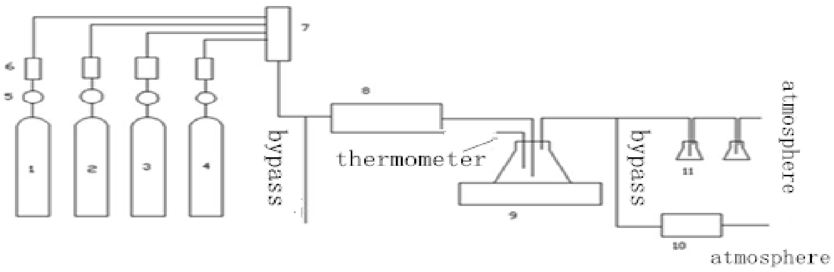

Fig. 3. The experiment system. 1. SO_2+N_2; 2.NO+N_2; 3. pure N_2 ; 4. compressed air; 5. pressure valve; 6. rotameter; 7. gas mixer;8. heater; 9. reactor ; 10. flue gas analyzer; 11. tail gas treatment.

Experiment for simultaneous desulfurization and denitrification

Fig. 3 shows the experimental system for removing SO_2 and NOx with the Mg-Al oxide slurry [7]. The slurry was set in a quartz tube reactor and heated to 30℃. High pure N_2, O_2 and the standard gas SO_2 and NO of 9% concentration separately enter from the high pressure cylinder into gas mixer. The mixed gas was heated to 120 ℃, and then flowed into the reactor. The amounts of SO_2 and NOx removed were calculated by subtracting the amounts of SO_2 and NOx after reaction from the total amounts of SO_2 and NOx in the initial gas. The gas after reaction was further treated by scrubber to remove the harmful gas. Then it was discharged into atmosphere [8]. The SO_2 and NOx gas concentration were adjusted to 1300 ppm and 900 ppm respectively. The total flow of mixed gas is 500 ml. SO_2 and NOx in the mixed gas were quantified by the 350-pro flue gas analyzer.

RESULTS AND DISCUSSION

As is shown in Fig.4, in the samples prepared by SSR, when the number of Mg is more than Al, the removal rates of SO_2 and NOx are not high. The removal rates of SO_2 and NOx reach the maximum in 5 or 15 minutes. After reaching the maximum, the removal rate maintains under few time interval, and then the removal rate fell. As the proportion of Al_2O_3 in the adsorbent becomes more, the downward trend becomes bigger, and the removal effect is worse. Among the samples prepared by SSR, when Mg/Al Molar ratio is 1:4, the removal rate is best. The maximum SO_2 removal rate can reach 98.9%, maximum NOx removal rate 50%. And after 60 minutes, SO_2 removal rate fell to 76.4%, and NOx removal rate 41.7%. And when the number of Mg is more than Al in the samples prepared by SSR, the removal rates of SO_2 and NOx are better. The removal rate of SO_2 reach upon 90% in 5 minutes, and the maximum removal rate all can reach about 94%. This moment the maximum removal rate can maintain a long time and followed by a slow decline. When the Mg/Al ratio is 6:1, the removal rate is the best. The highest SO_2 removal rate can reach 99%, and the highest NOx removal rate can reach 45%. After 60 minutes, SO_2 removal rate fell by 3.4%, and NOx removal rate fell by 1.5%.When the same Mg/Al ratio f Mg - Al composite oxides were prepared by MSS, the removal effects of SO_2 and NOx is better than by SSR. The maximum removal rate can maintain a more long time. However removal rates of samples of same Mg/Al ratio prepared by SSR began to decline in 60 minutes. By using MSS, the removal rates of the sample in which Mg/Al ratio is 4:1 are the highest, which can reach 100% of SO_2 maximum removal rate, 71% of NOx, and the time interval stays for 150 minutes. It is known that the high-efficiency operation interval by MSS is 2.5 times by SSR.

Adsorption process generally includes three aspects: diffusion on particle surface, diffusion in internal pore of particle and adsorption reaction. Lagergren first order kinetic model describes diffusion on particle surface, namely the process of the adsorbate molecules diffusion is from the liquid phase to a solid surface. Lagergren secondary kinetic model describes the adsorption reaction. Weber - Morris equation describes the internal diffusion that considered a critical stage in the process of adsorption. The linear fitting result of Lagergren secondary rate equation is better. Linear correlation coefficient of Lagergren secondary rate equation is significantly greater than that of Lagergren first rate equation. It showed that the dynamic adsorption process follows the Lagergren secondary dynamic model.

The correlation coefficients of Weber - Morris equation are 0.97412 and 0.94803. Comparing with the two correlation coefficients of Lagergren secondary dynamic equation and Weber - Morris equation, the correlation coefficient of Lagergren secondary dynamic equation is larger. It reveals that in the whole process is dominated by adsorption reaction, and the diffusion between internal and surface is secondary.

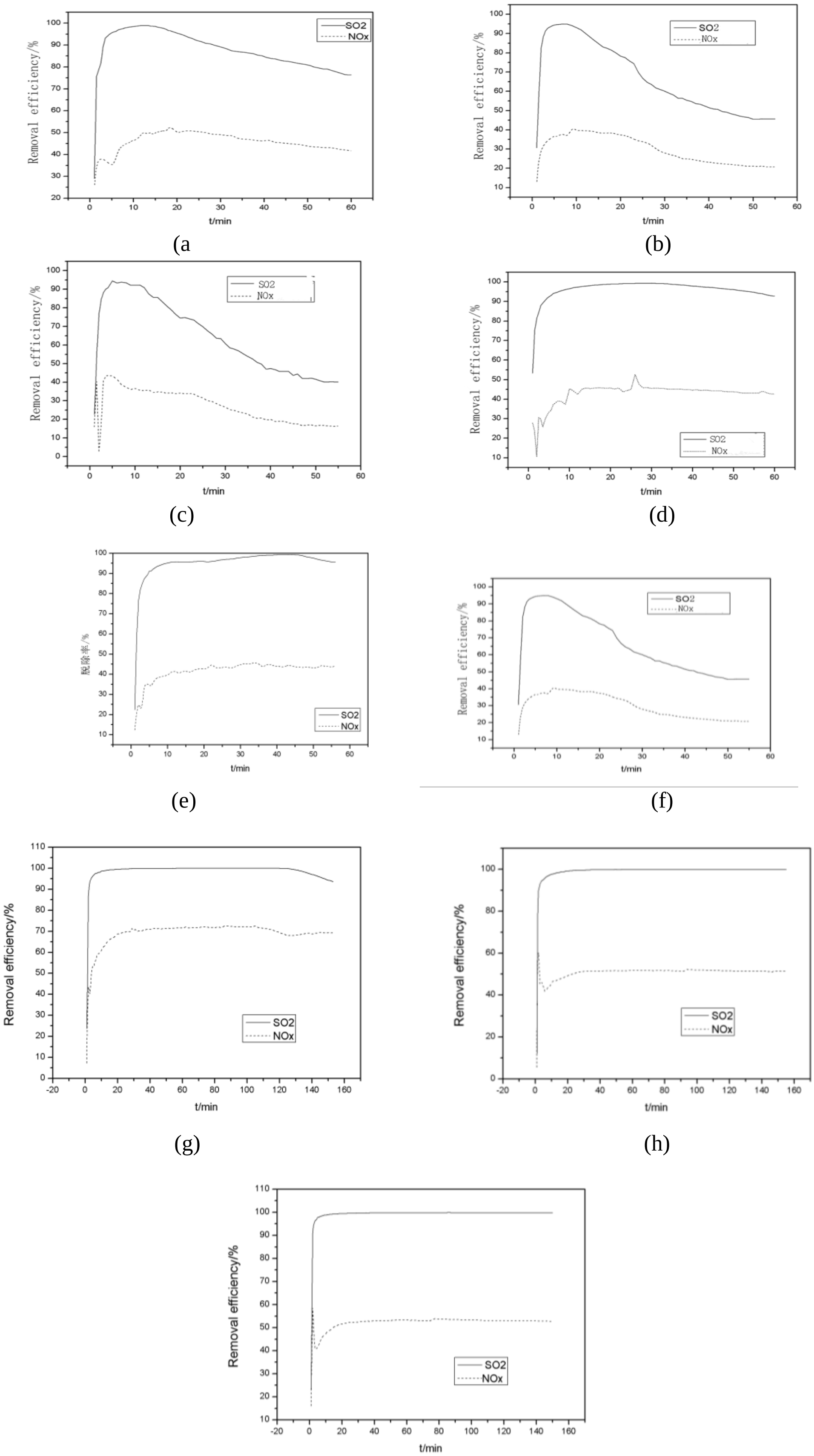

Fig. 4. The results of removal experiment of samples prepared by SSR (a, b, c, d, e, f) and MSS (g, h, i) (a)Mg/Al=1:4; (b)Mg/Al=1:6; (c) Mg/Al=1:8; (d)Mg/Al=4:1; (e) Mg/Al=6:1; (f) Mg/Al=8:1; (g) Mg/Al=4:1; (h)Mg/Al=6:1; (i)Mg/Al=8:1.

CONCLUSIONS

The Mg-Al composite oxides are prepared and characterized and simultaneous experiments of desulfurization and denitrification were done upon the condition of simulate flue gas of coal-fired powers.

For the samples prepared by SSR, when the number of Mg is more than Al, removal effects of SO_2 and NOx are much higher. The sample in which Mg/Al mole ratio is 6:1 has the best removal effect. The highest removal efficiency of SO_2 can reach 99%, and NOx reach 45%. After 60 minutes, SO_2 removal efficiency fell by 3.4% and NOx removal efficiency fell by 1.5%. When samples were prepared by MSS, the sample in which Mg/Al mole ratio is 4:1 has the best removal effect. The highest removal efficiency of SO_2 can reach 100% and that of NO_X can reach 71%. And the maximum removal efficiency can maintain 150 min. The maintain time is 2.5 times than that of samples prepared by SSR. Further research shows that the adsorption process is mostly controlled by adsorption reaction, and the particle diffusion between internal and inside is under the secondary action.

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