Original Research Paper

Study on the Application of CuO/Al$_2$O$_3$ Cordierite Ceramic Honeycomb Catalyst in Cleaning the Flue Gas for NO$_X$

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ABSTRACT

This paper introduces the current research status of denitration catalysts used in Selective Catalytic Reduction (SCR) technology, and assess the effects of a composite catalyst on the denitration performance of flue gas. Laboratory experiments were conducted to prepare a new composite catalyst, that is, CuO loaded on a honeycomb cordierite ceramic catalyst carrier with Al$_2$O$_3$ coating by the equivalent volume impregnation method. The orthogonal designed tests were used to study the effects on denitration performance caused by the changes of Al$_2$O$_3$ loading, calcination temperature and calcination time, obtain the optimum condition for the catalyst carrier preparation with the best denitration rate. Then the effects of CuO loading, calcination temperature and calcination time on denitration rate of the new composite catalyst were investigated. Results showed that: (1) As for catalyst carrier, significance of three factors that had effects on the flue gas denitration rate was in a sequence: loading of Al$_2$O$_3$ > calcination temperature > calcination time. (2) Calcined at 600°C for 4 hours with 3% of Al$_2$O$_3$ loading was the condition to prepare the composite carrier with the best denitration rate. (3) For the new composite catalyst, three noticeable increased-then-decreased trends of denitration rate change were presented with the increasing CuO loading, calcination temperature and calcination time. (4) Calcined at 450°C for 4 hours with 8% CuO loading was the condition to prepare the new composite catalyst with the best denitration rate.

INTRODUCTION

NOx emissions have been rapidly increasing during recent years, and have exerted a negative effect on the environment and even badly on human health, thus have drawn great attention from the whole world. SCR technology is one of the most economic and effective methods for NOx denitration, and the catalyst is the core of this technology. Honeycomb V$_2$O$_5$/TiO$_2$ is widely used as a catalyst in China now, but unsteady physical properties and high cost of V$_2$O$_5$ and TiO$_2$ have limited the application of the catalyst in industry scale (Liu et al. 2005, Zhou et al. 2002). Thus, studies on using non-metal oxide as active ingredients for catalysts are becoming research hotspots. Honeycomb cordierite ceramic is usually adopted as a catalyst carrier due to its big specific surface area (Yang et al. 2010, Nakahjima et al. 1996, Forzatti 2001), high mechanical strength, porosity and thermal stability (Lowell et al. 2001, Lin et al. 2003, Ye 2000, Macken et al. 1998). CuO with characteristic of excellence in selectivity, thermal stability, low cost and non-secondary pollution has presented a good potential for being carried on honeycomb cordierite ceramics with an Al$_2$O$_3$ coating to compose a new catalyst (Su et al. 2008, Liu et al. 2005, Macken et al. 2000, Ramis et al.. 1995).

MATERIAL AND METHODS

Preparation of composite carrier with Al$_2$O$_3$ coating: Honeycomb cordierite ceramic carrier was soaked with a variety of concentrations of solution for 24 h, stoved at 120°C for 40 min, and then calcined under certain conditions. Finally, the honeycomb cordierite ceramic carrier with Al$_2$O$_3$ coating was made.

Preparation of copper catalyst: A selected catalyst carrier with the best denitration rate from the above experiment was then soaked in copper (II) nitrate to prepare a honeycomb CuO/Al$_2$O$_3$ loaded cordierite ceramic catalyst by an equivalent-volume impregnation method. The volume of copper (II) nitrate needed was calculated from the loading of copper oxide. The loadings of copper oxide selected for this experiment were 1%, 3% and 5%; calcination temperatures were 350°C, 450°C, 550°C and calcination times were 3 hours, 4 hours and 5 hours.

The flow diagram of catalyst performance: This experiment was conducted following the steps: (1) Adjust the temperature controller to 105°C and connect a tube with a fixed amount of catalyst quartz to an intake tube. (2) Place the quartz tube into the hearth, and connect the outlet tube and

the flue gas analyser to a vitreous detecting bottle for detection. (3) Mix all of the original gases in a compound cylinder from the gas tank via a hose. Set the composition of the flue gas as follows: blanket gases 100 mL, 6% of oxygen, flow rate 60 mL/min, 2000 ppm of SO_2 flow rate 52.8 mL/min, and N_2 for the rest. (4) Open the hose clamp after setting the flow rate, then start the time and record the data every 30 seconds as soon as the analysis meter begins to change from 0 until the concentration of SO_2 is stable. (5) Calculate the desulfuration efficiency and the effective time of the compound carrier or the catalyst, draw charts and analyse the data. The catalyst was placed in a quartz tube whose inner diameter is 20 mm and the length is 60 cm, and heated by surrounding a tube furnace. The catalyst activity-rating device is shown in Fig. 1.

Characterization of catalyst: SEM and XRD techniques were used to characterize the catalyst.

RESULTS AND DISCUSSION

Effects of composite carrier with Al_2O_3 coating on denitration performance: Orthogonal designed test L9 (3^4) was used to find out the best conditions for the carrier preparation. The results and analysis of the tests are listed in Table 1. It can be seen that Group 4, Group 5 and Group 7 with 3% of Al_2O_3 loading calcined at 600°C for 4 hours, 3% loading calcined at 800°C for 5 hours and 5% loading calcined at 600°C for 5 hours, respectively, had good denitration rates.

It can be seen obviously from Table 1 that the loading of Al_2O_3, calcining temperature and calcining time all had effects on the denitration efficiency. According to the range analysis, the significance of these three factors' affecting the denitration rate were in a sequence as loading > calcination temperature > calcination time. Loading played the most important role in affecting denitration efficiency. Al_2O_3 could help with a good denitration rate, only when the load-

Table 1: Intuitive analysis table of orthogonal experiment.

Factors	Loading %	Calcination temperature, °C	Calcination time, h	Results
Group 1	1	600	3	0.315
Group 2	1	800	4	0.327
Group 3	1	1000	5	0.293
Group 4	3	600	4	0.455
Group 5	3	800	5	0.424
Group 6	3	1000	3	0.377
Group 7	5	600	5	0.405
Group 8	5	800	3	0.387
Group 9	5	1000	4	0.375
Average1	0.312	0.392	0.360	
Average 2	0.419	0.379	0.386	
Average 3	0.389	0.348	0.374	
Range	0.107	0.044	0.026	
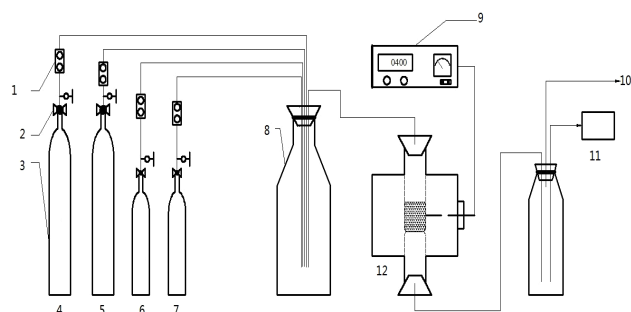
1. Gas flow meter; 2. relief valve; 3. high pressure steel; 4. oxygen; 5. nitrogen; 6. nitrogen monoxide; 7. ammonia; 8. mixed gas cylinders; 9. tube furnace control instrument; 10. gas emission; 11. hand-held gas analyzer; 12. tube furnace

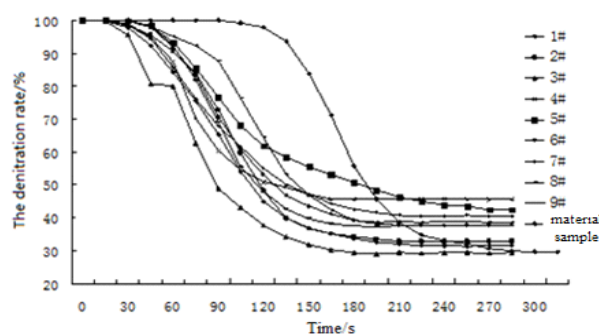Fig. 1: The test device of catalyst performance.

Fig. 2: The denitration rate of composite carrier under the different preparation conditions.
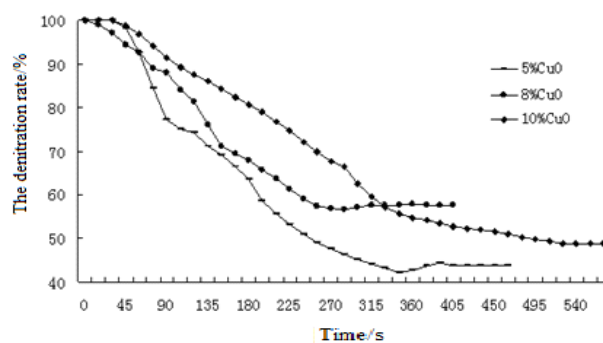

Fig. 3: The denitration rate of composite catalyst under the different CuO loadings.

ing of it was moderate. Too high loading may reduce the specific surface area of the carrier, and so the denitration efficiency as well.

Calcining temperature also had a big influence on the denitration rate. γ-Al_2O_3 was the aluminium oxide having catalytic effect. It was amorphous with the best activity and dispersibility only at temperatures of 200-600°C. When the
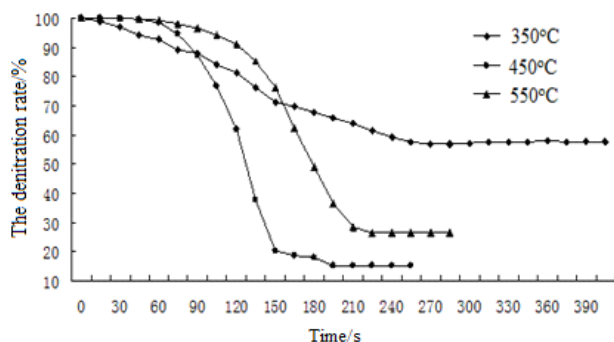
Fig. 4: The denitration rate of composite catalyst under the different calcination temperatures.
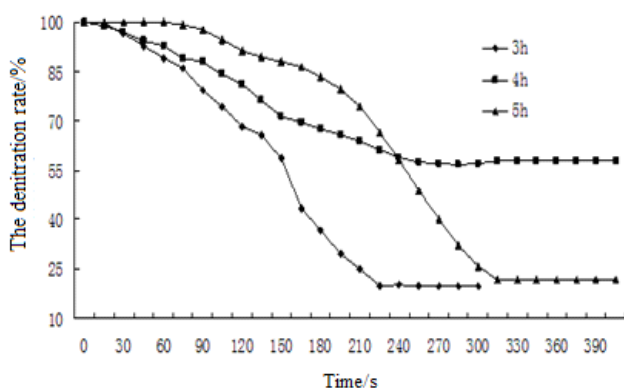

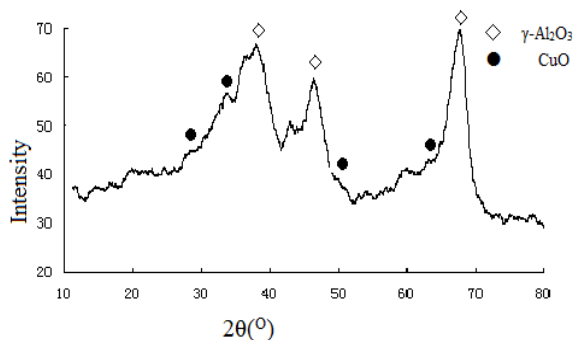Fig. 5: The denitration rate of composite catalyst under the different calcination time.

Fig. 6: XRD patterns of composite catalyst under the optimal preparation process.

temperature went up to 865°C, γ-A1$_2$O$_3$ would have a steady structure but lower activity and dispersibility. Also, the longer calcination time gave higher porosity to absorb ammonia appearing on the catalyst surface, and resulting in a higher denitration rate.

Effects of preparation conditions on denitration performance of composite catalyst

Effects of CuO loadings on catalytic activity: The prepared honeycomb CuO/Al$_2$O$_3$ catalyst were by the equivalent-volume impregnation method with loadings of 5%, 8% and 10% and separately calcined at 450°C for 4 hours. Then catalytic activities were assessed and shown in Fig. 2. As shown in Fig. 2, denitration performance changed greatly by different loadings. During 0~330 s, the denitration rate of the catalyst increased when the CuO loading was increasing. When the reaction was continued, the denitration rate reached the top with a loading of 8%. When the loadings were low, CuO formed smaller grains on the Al$_2$O$_3$ coating, and active sites were not enough to meet the reaction demands. With the increasing loadings of CuO, the catalyst had more active sites on it to gain a better denitration rate. However, Fig. 3 demonstrates that the denitration rate would not keep increasing only if the loading increased. The reason may be that too much loadings of CuO would lead to the formation of big CuO particles covering the surface of a carrier by many layers. Less active sites were available for denitration and specific surface area of the catalyst was also reduced with too high loadings. Thus, with a loading of 8%, the honeycomb CuO/Al$_2$O$_3$ cordierite ceramic catalyst would have the best catalytic activity.

Effects of calcination temperatures on catalytic activity: Adopted 8% as the loading according to the above result, calcined honeycomb CuO/Al$_2$O$_3$ cordierite ceramic catalyst at different temperatures (350°C, 450°C, 550°C) all for 4 hours. The assessments of catalytic activities are given in Fig 4. We could find that with the same loading and calcination time, denitration rate got a peak when calcination temperature was 450°C. The reason is that, copper nitrate as the active component wouldn't decompose until temperature reached 400°C or above it. At about 450°C, all kinds of organic amine templates in the catalyst carrier's pores were burned thoroughly, and in that way, active sites were easily formed on catalyst for denitration. However, when temperature reached more than 550°C, copper in the crystal lattice was losing, causing damages to the pore structure of the honeycomb cordierite ceramic. Some active sites for denitration were gone, and the catalyst activity was reduced.

Effects of calcination time on catalytic activity: Adopted 8% and 450°C as the loading and calcination temperature separately, prepared honeycomb CuO/Al$_2$O$_3$ cordierite ceramic catalyst with different calcination time. The assessments of catalytic activities are given in Fig. 5. As it was shown, calcination time had a profound influence on catalytic activity. After calcing for 4 hours, the denitration performance of a catalyst attained the break point, owing to the next two reasons. One was that copper nitrate would not decompose completely within the short calcination time so

(a) The SEM of cordierite honeycomb ceramics

(b) The SEM of composite carrier Al_2O_3

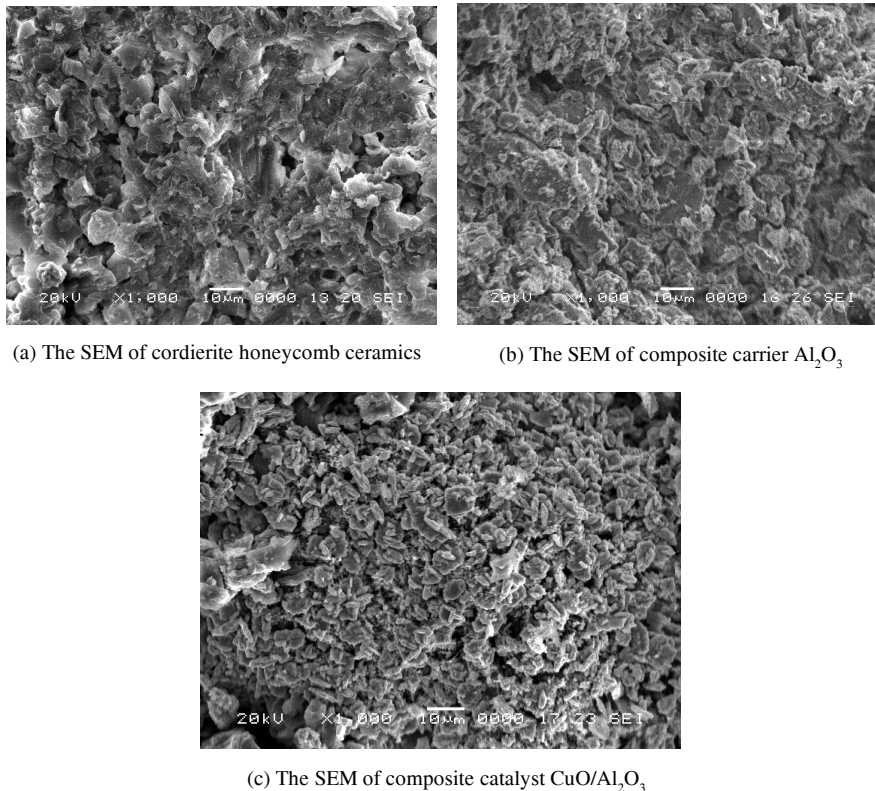(c) The SEM of composite catalyst CuO/Al_2O_3

Fig. 7: The SEM of composite catalyst.

that catalytic activity decreased, the other was that catalytic activity would decrease if the catalyst was calcined for too long time, because the catalyst could be coagulated and the copper in lattice could vaporize.

The characterization of catalyst

XRD characterization: The XRD image of the composite catalyst prepared is shown in Fig. 6. It was easy to find that diffraction peaks of copper oxide were wide and not sharp, which meant that copper oxides on the catalyst surface were well dispersed.

SEM characterization: The SEM images of the composite catalyst prepared in the optimal conditions are shown in Fig. 7. It could be inferred that the most of Al_2O_3 and CuO should be dispersed, which was in accordance with its catalytic effects. Thus, it was further demonstrated that loading of metals would enhance the denitration performance of the cordierite ceramic. The SEM images of the honeycomb cordierite ceramic, the Al_2O_3 composite catalyst carrier and the CuO/Al_2O_3 composite catalyst are shown in Fig. 7(a), 7(b) and 7(c), respectively. Comparing Fig. 7(c) to Fig. 7(a) and 7(b), particles on the catalyst surface were bigger and overlapped, and a layered structure was transformed into the cluster structure on the catalyst surface when CuO was added.

Comparing the obtained results with existing knowledge in the field, we found that most cordierite catalyst selected the cordierite as carrier directly. Although this method simplified the preparation procedures, but this technique did not use the coating layer, so the surface area of the prepared catalyst was too small, and the adhesion of active components was not strong. So, the disadvantages were not good for high flow velocity condition. In this paper, the experiment coated the alumina on the surface of cordierite firstly, and prepared the composite carrier, and then loaded the CuO on the composite carrier, this method will increase the activity of the catalyst, and improved the disadvantages of the traditional catalyst.

CONCLUSIONS

1. By coating cordierite ceramic surface with more Al_2O_3, denitration rate was increased and then gradually decreased. The optimum loading was 3%. Denitration rate presented a declining trend with the increase in the calcination temperature, the optimum temperature was 600°C. With prolonged calcination time, the denitration rate showed the same tendency as that of the Al_2O_3 coating, it increased and reached the best denitration rate after 4 hours of calcination, then started to go down.

2. In this experiment, the optimum condition for the preparation of a honeycomb cordierite ceramic catalyst carrier with Al$_2$O$_3$ coating was the loading of Al$_2$O$_3$ of 3%, calcined at 600°C for 4 hours.

3. For the denitration rate change of the honeycomb CuO/Al$_2$O$_3$ cordierite ceramic catalyst, there were the same noticeable increased-then-decreased trends with the increasing loading of CuO, calcination temperature and time. The breaking point happened at the loading of 3%, 450°C of calcination temperature and 4 hours of calcination time.

4. In this experiment, the optimum conditions for the preparation of honeycomb CuO/Al$_2$O$_3$ cordierite ceramic catalyst was with 3% loading of CuO, calcined at 450°C for 4 hours.

5. Characterization of this modified catalyst by XRD, SEM technology, the physical transition and denitration mechanism of the modified catalyst provided a reasonable theoretical foundation for the application of the SCR technology.

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1076