

Study on Mid-temperature SCR DeNO_x Catalyst under High SO₂ and CaO

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Abstract: This article introduce the performance of vanadium-titanium Middling temperature SCR DeNO_x catalyst, considering the factor NH₃/NO_x, SO₂ concentration, GHSV, O₂ concentration, H₂O concentration changes in high SO₂ and high CaO.

Keywords: Mid-temperature, DeNO_x, Catalyst; High SO₂, High CaO

1 INTRODUCTION

Chinese main energy resource is coal and fire power plant is the primary producer of NO_x. With the rapid development of economy, the environmental damage caused by coal-fired becomes more serious. The multiplex acid rain is mainly caused by the emission of SO₂ and NO_x of coal fire power plants and cement kilns. The Emission Standard of Air Pollutants for Coal-fired Plants implemented at 1st Jan, 2004, has greatly prompted the development of DeNO_x industry and the DeNO_x industry is becoming a highlight of environmental protecting industry.

The SCR technology (Selective Catalytic Reduction) is the most efficient method to control the emission of NO_x, which has been widely used in coal-fired plants of developed countries. However, in domestic, the commercial application of DeNO_x has just stepped out. The constitutes of coals in China vary drastically, and many coals contain high SO₂, high CaO, high ash, and contains of arsenic changes greatly. It is greatly different from the east area coal of America.[1]

So far, our country SCR DeNO_x equipment have applied alien technology entirely and what's more, We are short of the experience of pattern selection and operating of catalysts.

The core technology of SCR is the systemic design to maintain uniform distribution of smoke and fly ash in reactor.

It reported that (NH₄)₂SO₄ and CaSO₄ in smoke poisoned catalysts of SCR and reduced the efficiency of DeNO_x. Aiming at high SO₂ and high CaO ash in coals of China, this paper develops the DeNO_x experiments of Mid-temperature SCR catalyst in high SO₂ and high CaO condition. The research is a great help for the pattern selection of catalyst in domestic DeNO_x industry of coal fired plants.

2 EXPERIMENT

2.1 Experiment Set

It is used fixed tubular reactor to simulate the industry DeNO_x process. The reactor height is 1000 mm, inside diameter 45 mm, stainless steel, and outer part of set is heated by electricity. The height of fixed catalyst in reactor is 100 mm. The carrier gas is nitrogen of purity above 99% made by the membrane separation. SO₂, NO, liquid NH₃ and O₂ are loaded in steel cylinders. The gases are carried into reactor by gas in a certain proportion. The entrance region of reactor is equipped by two stage preheaters. Both preheaters and reactors have temperature controlled heaters. The entrance and exit of reactor have sample thief holes. The SO₂, NO_x concentration is analyzed by the KM900 handle gas analyzer (made by KANE inc, British).

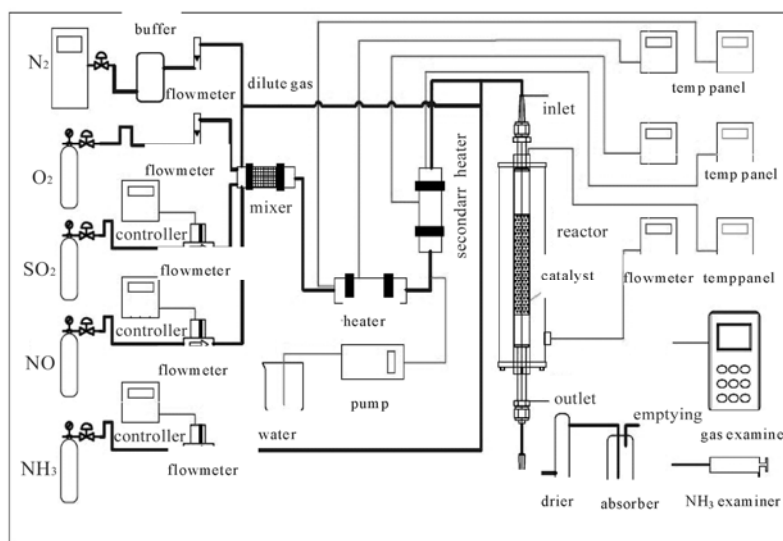


Fig. 1 Experiment Set

2.2 SCR Catalyst

This experiment use commercial catalysts to study their adaptability under high SO₂ and CaO. Two different fractures of catalysts are chosen in the test. One is called catalyst A (plate pattern), the other is called catalyst B (beehive pattern) in the following part.

2.3 Experiment Condition and Scope

In this experiment, investigated factors includes GHSV, temperature (T), NO_x, ratio of NH₃/NO_x, O₂, SO₂, H₂O, etc. All parameters' references and study scope are shown in Table 1.

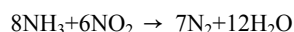
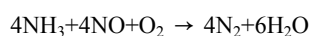
Table 1 All reference test conditions and study scope

Factor	Unit	Reference test condition	Study scope
GHSV	h-1	3000	2000-9000
T	°C	380	310-400
NO _x	ppm	400	200-800
NH ₃ /NO _x	1	0.8	0.6-1.0
O ₂	%	6	2-8
SO ₂	ppm	1500	0-2000
H ₂ O	%	8	0-12

3 RESULT AND DISCUSSION

3.1 SCR Reaction Character and Temperature Influence

At reference test conditions, we studied the reaction characters of the two different structure SCR catalysts and the temperature influence. The results were shown in Fig. 2. The DeNO_x process undergone a special temperature scope and a certain catalyst infection, and NO_x was deoxidized into N₂ and H₂O, the reaction process could be described as follows:



Because reaction described above is happened in the active exterior of catalysts, the micro porous character of catalysts largely determines the activity of catalysts.

From Fig. 2, we can see that both catalysts have a good performance on DeNO_x process with a wide reaction temperature scope between 300 °C and 400 °C. It is usual that catalysts have a high and stable DeNO_x efficiency at a relative stable temperature scope (360 °C–380 °C). But catalyst A keeps a high DeNO_x efficiency at interval temperature scopes (300 °C–320 °C, 380 °C–410 °C) Experiment results show both catalysts have a high DeNO_x efficiency at a wide temperature window(310 °C–400 °C).

3.2 Ratio of NH₃/NO_x Influence on DeNO_x

Ratio of NH₃/NO_x on DeNO_x efficiency has been studied under the smoke temperature 380 °C. The result is shown as Fig. 3. It shows that as the ratio of NH₃/NO_x increases, the DeNO_x efficiency accordingly increases. From catalytic chemical reaction equation, NO_x reacts with NH₃ in the terms of 1:1 (ratio of mol). In most cases, other chemical materials in the smoke related with the reaction is superfluous, thus the

injection amount of NH₃ is the most important chemical impetus in the chemical reaction. And because the smoke exists SO₂ etc acid substance, they would react with NH₃ at the same time. So the actual NH₃ consumption is appreciably more than calculated.

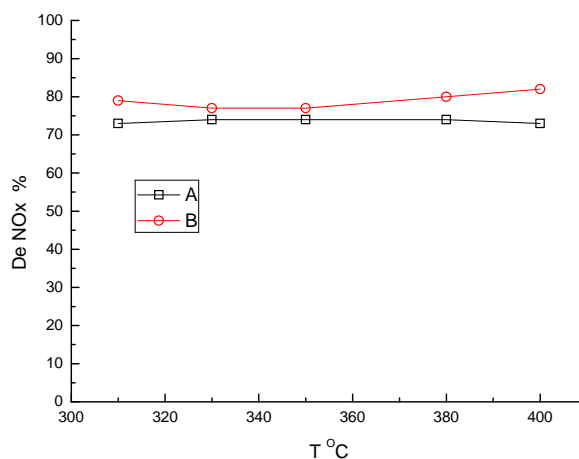


Fig. 2 Temperature Influence on DeNO_x

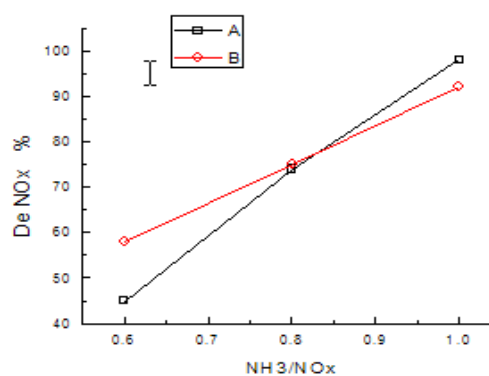


Fig. 3 Ratio of NH₃/NO_x on DeNO_x Efficiency

From the Fig. 3, we can see the ratio of NH_3/NO_x presents a linear relationship with the DeNO_x efficiency. To do linear regression and analysis of covariance of the two lines separately, we suppose the ratio of NH_3/NO_x is x , the DeNO_x efficiency is y , then gain a table (shown in Table 2).

2.3 GHSV on DeNO_x Efficiency

Effect of GHSV on DeNO_x efficiency is shown in Fig. 4. When the GHSV is 2000 h^{-1} – 6000 h^{-1} , both catalysts show a good performance of DeNO_x and the value is above 70%. The highest value is gained when the GHSV is about 3000 h^{-1} . In actual application, the GHSV value is chosen between 2000 h^{-1} and 6000 h^{-1} , considering there is enough residual catalysts to keep the system at a high DeNO_x efficiency when part of catalysts lose activity.

Table 2 Relationship between the ratio of NH_3/NO_x and the DeNO_x efficiency

Catalytic type	Line equation	Analysis of covariance
A	$y=132.5x-33.667$	$R_2=0.997$
B	$y=85x+7$	$R_2=1$

Notes: Constrained by the experiment condition, the conclusion above only be considered for engineering application.

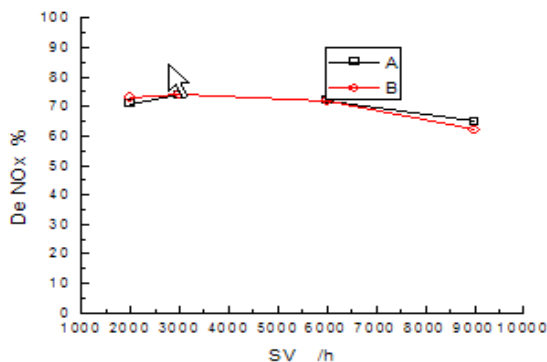


Fig. 4 GHSV on DeNO_x Efficiency

2.4 NO_x Concentration on DeNO_x Efficiency

The effect of initial NO_x concentration on DeNO_x efficiency has been investigated and the result is shown in Fig. 5. We can see that a little increase of initial NO_x concentration induces a slightly decrease efficiency. This tendency conforms to the analysis of reaction kinetics. As initial NO_x concentration increases, reaction velocity increases accordingly, but the DeNO_x efficiency decreases a bit. It demonstrates that the whole catalyst activity has a dominate effect in the reaction.

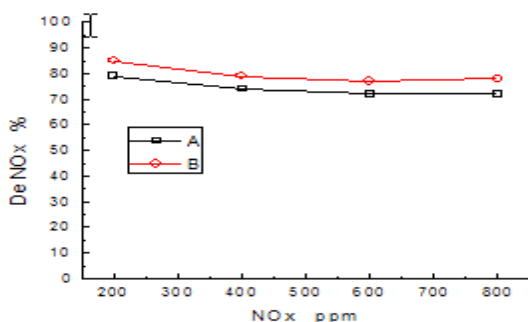


Fig. 5 NO_x Concentration on DeNO_x Efficiency

2.5 O_2 Concentration on DeNO_x Efficiency

At reference test condition, O_2 concentration on the DeNO_x efficiency has been investigated and the result is shown in Fig. 6.

From the catalytic reaction equation $4\text{NH}_3+4\text{NO}+\text{O}_2\rightarrow 4\text{N}_2+6\text{H}_2\text{O}$, O_2 is an indispensable substance in the reaction. Existence of O_2 prompts the reaction of NH_3 and NO [4–6] and perhaps that O_2 accelerates the transform process of NO into NO_2 . O_2 is often enough for the catalytic reaction in the smoke and the residual O_2 may oxides NH_3 and thus the DeNO_x efficiency reduces slightly. But on the whole, O_2 concentration change has little effect on the efficiency for the both catalysts.

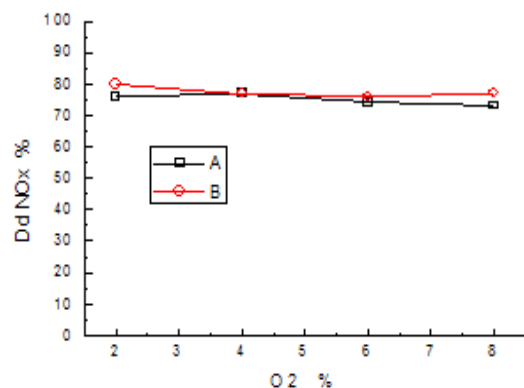


Fig. 6 O_2 Concentration on DeNO_x Efficiency

2.6 SO_2 Concentration on DeNO_x Efficiency

SO_2 concentration on DeNO_x efficiency is investigated at reference condition test. The result is shown in Fig. 7 and it shows SO_2 has a negative effect on the DeNO_x efficiency.

In this experiment, the smoke temperature is high (380°C) and the resultant $(\text{NH}_4)_2\text{SO}_4$ conglutinates on the catalysts' surface not easily, so the efficiency does not reduce apparently. It shows that both commercial catalysts have a good resistance against high SO_2 .

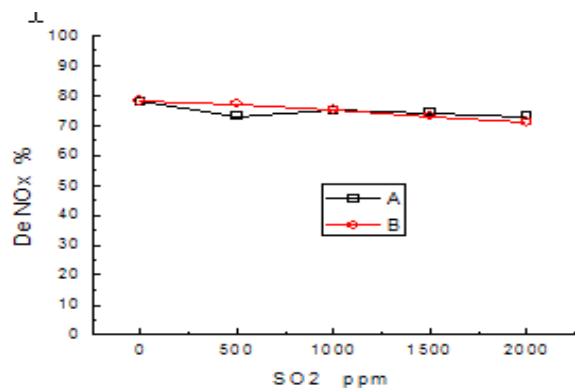


Fig. 7 SO_2 Concentration on DeNO_x Efficiency

2.7 H₂O concentration on DeNO_x efficiency

H₂O concentration on DeNO_x efficiency has been studied and the result is shown in Fig. 8. A bit increase of smoke humidity has no poisoned effect on the catalysts' performance. It reported that liquid H₂O (condensed or unvaporized), had a negative effect on DeNO_x efficiency.[7] Perhaps H₂O has a competitive adsorption with reaction substance (NH₃ and NO) and thus but not poisons the catalyst completely. Some damaged catalyst can be refreshed. Under high operation temperature, H₂O exhibits no harm influence on DeNO_x efficiency.

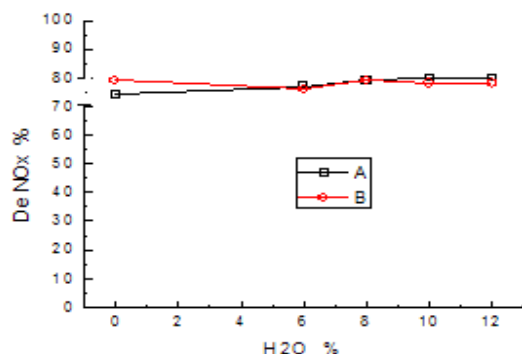


Fig. 8 H₂O concentration on DeNO_x efficiency

2.8 Toxic Study of Alkali Metal

Alkali metals (K, Na) can react directly with activate point of catalyst's surface due to their strong water-solubility and penetrability. So in the alkali solution Catalysts will be poisoned. The loss activity was studied at this experiment and the result is shown in Fig. 9. It is clear to see that the DeNO_x efficiency of the after-treatment catalyst is lower than 50%. H⁺ on the catalyst surface probably is replaced by the alkali metal and thus induce lower absorption of NH₃. Catalyst A has a better activity because of a shorter impregnated time. Both catalysts' activity increased gradually and perhaps SO₂ in the smoke increased the acid points on the catalysts' surface. This is in a good agreement with the phenomenon reported that the loaded SO₄²⁻ on SCR catalyst's surface can increase the amount of NH₃ absorption.

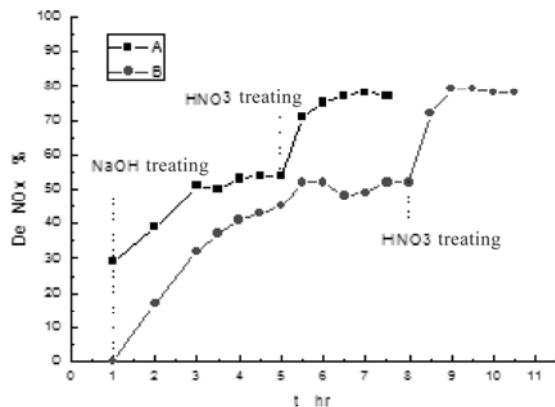


Fig. 9 Toxic Study of Alkali Metal

2.9 High CaO on DeNO_x Efficiency

Domestic coals usual contain high SO₂ and high CaO ash. CaO in the ash reacts with SO₃ absorbed in catalysts' surface. The product CaSO₄ then coats the catalyst's surface. Thus NO_x and NH₃ can not diffuse into the inner of catalyst. In this experiment, CaO latex was coated both in and out of catalyst's surface. Firstly the catalysts were dried in room temperature, then heated in 75 °C for 3 hours. The loaded situation is shown as table 3. Both catalysts' DeNO_x performance were examined and the result is shown in Fig. 9.

Table 3 CaO Loaded Amount of Catalysts

Catalysts' type	Pre-treatment mass (g)	After-treatment mass (g)	Ratio of CaO
Catalyst A	37	71	48
Catalyst B	71	102	30

But the efficiency is still lower than the new catalyst and the coated layer shades the activity area of the catalyst's surface. The long time poisoned effect of the catalyst is to be investigated. After experiment, the surface of catalysts presented uniform cracks. It is deduced that the cracks are formed because of high reaction temperature, and the gas follows through the surface of the catalyst and digs into the cracks and then takes part in chemical reaction.

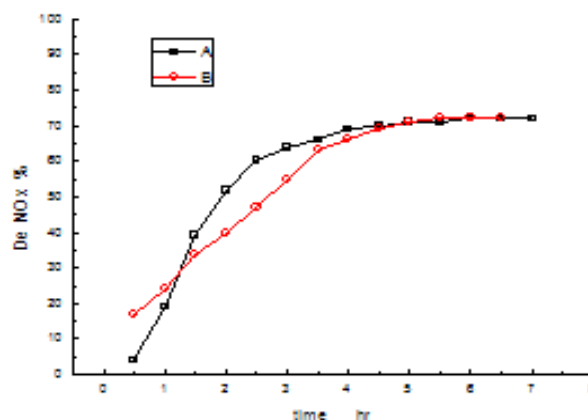


Fig. 10 High CaO on DeNO_x Efficiency

2.10 Deteriorate Life time of Catalysts

Restrained by the experiment condition, it is hard to take thousands of hours to test catalysts' life time. So it only investigates the DeNO_x efficiency when the catalyst is deteriorated. The deteriorate condition is realized by the enhancing concentration of NO_x and SO₂. At the experiment, NO_x concentration was 800 ppm, and SO₂ concentration 3000ppm. The result is shown as Fig. 11. After 1000 hours operating, the catalysts still presented a high DeNO_x efficiency. It shows that both catalysts have a good adaptability but it needs further experiment to investigate their life at a longer time.

From the DeNO_x curves, after 4 hours test, both catalysts basically achieved about 70% efficiency. It demonstrates that

coated CaO latex has little influence of the catalyst's activity.

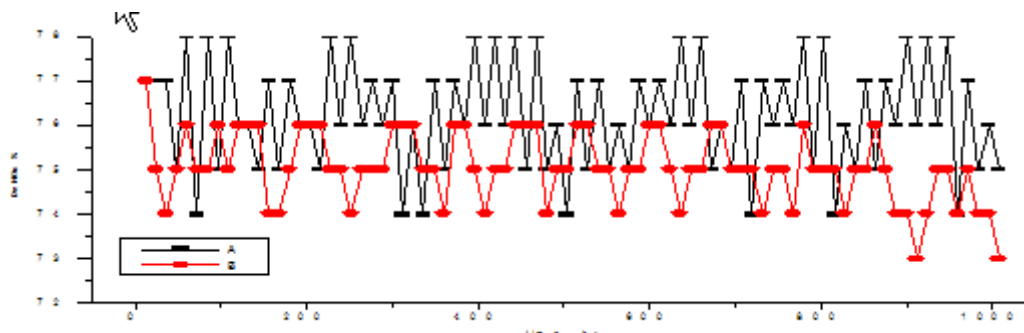


Fig. 11 Deteriorate Life time of Catalyst

3 CONCLUSIONS

The result shows the vanadium-titanium middling temperature SCR catalyst has a high DeNO_x efficiency. Different catalysts may have single or multiple temperature windows for the best chemical reaction; DeNO_x efficiency has a linear relationship with ratio of NH₃/NO_x; catalysts are sensitive to the toxicity of alkali metal, after poisoned, the activity decreases drastically; However, coating CaO on the surface of catalysts has little influence on the DeNO_x efficiency, which shows that the vanadium-titanium catalyst is available for high CaO ash condition. At mid-temperature, catalysts exhibit a good resistance against SO₂. Constrained by the experiment conditions, the conclusion deduced above is only for reference. It needs further research to investigate the influence of DeSO₂ and DeNO_x gas on downriver equipments. And the influence of longer period operating on catalysts is also to be studied.

REFERENCES

1. Gorge Baltin, Heinz Koser, Klaus-Peter Wendlandt, Sulfuric acid formation over NH₃ sulfate loaded V₂O₅-WO₃/TiO₂ catalysts by DeNO_x reaction with NO_x, Catalysis Today 2002 (75): 339-345.
2. Scot Pritchard Chris DiFranco Optimizing SCR Catalyst Design and Performance for Coal-Fired Boilers, EPA/EPRI 1995 Joint Symposium Stationary Combustion NO_x Control, May 16-19, 1995.
3. Hulgaard T, Iphansen K D.Nitrous oxide sampling, analysis, and emission measurements from various combustion systems [J]. Environ Prog, 1992, 11(4): 302-309.
4. J.Muniz, G. Marban, A. B. Fuertes. Appl. Catal. B. 2000 (27): 27.
5. G. Marban, Teresa Valdes-Sols, A. B. Fuertes, J. Catal. 2004 (226):138.
6. R. Long, R.T. Yang, J. Catal. 1999 (188): 332.
7. Zhang Huang, Zhenping Zhu, Zhengyu Liu, Influence of Water on V₂O₅/AC catalyst performance, Chinese Journal Catalysis, vol.22, No.6: 532-536.
8. Seng Moon Jung, Paul Grange, Characterization and reactivity of V₂O₅-WO₃ supported on TiO₂-SO₄²⁻ catalyst for the SCR reaction, Applied Catalysis B: Environmental. 2001 (32): 123.