Study on Mid-temperature SCR DeNO\textsubscript{x} Catalyst under High SO\textsubscript{2} and CaO

DAI Yongyang, CUI Ying
(Zhejiang FEIDA Environment Science and Technology Co. Ltd., Zhu Ji 311800, PR China)

Abstract: This article introduce the performance of vanadium-titanium Middling temperature SCR DeNO\textsubscript{x} catalyst, considering the factor NH\textsubscript{3}/NO\textsubscript{x}, SO\textsubscript{2} concentration, GHSV, O\textsubscript{2} concentration, H\textsubscript{2}O concentration changes in high SO\textsubscript{2} and high CaO.

Keywords: Mid-temperature, DeNO\textsubscript{x}, Catalyst; High SO\textsubscript{2}, High CaO

1 INTRODUCTION

Chinese main energy resource is coal and fire power plant is the primary producer of NO\textsubscript{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 SO\textsubscript{2} and NO\textsubscript{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\textsubscript{x} industry and the DeNO\textsubscript{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\textsubscript{x}, which has been widely used in coal-fired plants of developed countries. However, in domestic, the commercial application of DeNO\textsubscript{x} has just stepped out. The constitutes of coals in China vary drastically, and many coals contain high SO\textsubscript{2}, high CaO, high ash, and contains of arsenic changes greatly. It is greatly different from the east area coal of America.\cite{1}

So far, our country SCR DeNO\textsubscript{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 (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and CaSO\textsubscript{4} in smoke poisoned catalysts of SCR and reduced the efficiency of DeNO\textsubscript{x}. Aiming at high SO\textsubscript{2} and high CaO ash in coals of China, this paper develops the DeNO\textsubscript{x} experiments of Mid-temperature SCR catalyst in high SO\textsubscript{2} and high CaO condition. The research is a great help for the pattern selection of catalyst in domestic DeNO\textsubscript{x} industry of coal fired plants.

2 EXPERIMENT

2.1 Experiment Set

It is used fixed tubular reactor to simulate the industry DeNO\textsubscript{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. SO\textsubscript{2}, NO\textsubscript{x}, liquid NH\textsubscript{3} and O\textsubscript{2} 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 SO\textsubscript{2}, NO\textsubscript{x} concentration is analyzed by the KM900 handle gas analyzer (made by KANE inc, British).

![Figure 1](image.png)
2.2 SCR Catalyst

This experiment uses commercial catalysts to study their adaptability under high SO\textsubscript{2} 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 include GHSV, temperature (T), NO\textsubscript{x}, ratio of NH\textsubscript{3}/NO\textsubscript{x}, O\textsubscript{2}, SO\textsubscript{2}, H\textsubscript{2}O, etc. All parameters’ references and study scope are shown in Table 1.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>Reference test condition</th>
<th>Study scope</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHSV</td>
<td>h\textsuperscript{-1}</td>
<td>3000</td>
<td>2000-9000</td>
</tr>
<tr>
<td>T</td>
<td>°C</td>
<td>380</td>
<td>310-400</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>ppm</td>
<td>400</td>
<td>200-800</td>
</tr>
<tr>
<td>NH\textsubscript{3}/NO\textsubscript{x}</td>
<td>1</td>
<td>0.8</td>
<td>0.6-1.0</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>%</td>
<td>6</td>
<td>2-8</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>ppm</td>
<td>1500</td>
<td>0-2000</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>%</td>
<td>8</td>
<td>0-12</td>
</tr>
</tbody>
</table>

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\textsubscript{x} process undergone a special temperature scope and a certain catalyst infection, and NO\textsubscript{x} was deoxidized into N\textsubscript{2} and H\textsubscript{2}O, the reaction process could be described as follows:

\[
4\text{NH}_3+4\text{NO}+\text{O}_2 \rightarrow 4\text{N}_2+6\text{H}_2\text{O}
\]
\[
2\text{NH}_3+\text{NO}+\text{NO}_2 \rightarrow 2\text{N}_2+3\text{H}_2\text{O}
\]
\[
8\text{NH}_3+6\text{NO}_2 \rightarrow 7\text{N}_2+12\text{H}_2\text{O}
\]

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\textsubscript{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\textsubscript{x} efficiency at a relative stable temperature scope (360 °C–380 °C). But catalyst A keeps a high DeNO\textsubscript{x} efficiency at interval temperature scopes (300 °C–320 °C, 380 °C–410 °C).

Experiment results show both catalysts have a high DeNO\textsubscript{x} efficiency at a wide temperature window(310 °C–400 °C).

3.2 Ratio of NH\textsubscript{3}/NO\textsubscript{x} Influence on DeNO\textsubscript{x}

Ratio of NH\textsubscript{3}/NO\textsubscript{x} on DeNO\textsubscript{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 NH\textsubscript{3}/NO\textsubscript{x} increases, the DeNO\textsubscript{x} efficiency accordingly increases. From catalytic chemical reaction equation, NO\textsubscript{x} reacts with NH\textsubscript{3} 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 NH\textsubscript{3} is the most important chemical impetus in the chemical reaction. And because the smoke exists SO\textsubscript{2} etc acid substance, they would react with NH\textsubscript{3} at the same time. So the actual NH\textsubscript{3} consumption is appreciably more than calculated.

![Fig. 2 Temperature Influence on DeNO\textsubscript{x}](image)

![Fig. 3 Ratio of NH\textsubscript{3}/NO\textsubscript{x} on DeNO\textsubscript{x} Efficiency](image)
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 NH3/NO$_x$ and the DeNO$_x$ efficiency**

<table>
<thead>
<tr>
<th>Catalytic type</th>
<th>Line equation</th>
<th>Analysis of covariance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$y=132.5x-33.667$</td>
<td>$R^2=0.997$</td>
</tr>
<tr>
<td>B</td>
<td>$y=85x+7$</td>
<td>$R^2=1$</td>
</tr>
</tbody>
</table>

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

**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.

**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.

**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 (NH$_4$)$_2$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. 4** GHSV on DeNO$_x$ Efficiency

**Fig. 5** NO$_x$ Concentration on DeNO$_x$ Efficiency

**Fig. 6** O$_2$ Concentration on DeNO$_x$ Efficiency

**Fig. 7** SO$_2$ Concentration on DeNO$_x$ Efficiency
2.7 \( \text{H}_2\text{O} \) concentration on \( \text{DeNO}_x \) efficiency

\( \text{H}_2\text{O} \) concentration on \( \text{DeNO}_x \) efficiency has been studied and the result is shown in Fig. 8. A bit increase of smoke humidity has no poisoned effect on the catalyst’s performance. It reported that liquid \( \text{H}_2\text{O} \) (condensed or unvaporized), had a negative effect on \( \text{DeNO}_x \) efficiency.[7] Perhaps \( \text{H}_2\text{O} \) has a competitive adsorption with reaction substance (\( \text{NH}_3 \) and \( \text{NO} \)) and thus but not poisons the catalyst completely. Some damaged catalyst can be refreshed. Under high operation temperature, \( \text{H}_2\text{O} \) exhibits no harm influence on \( \text{DeNO}_x \) efficiency.

![Fig. 8 H\(_2\text{O}\) concentration on DeNO\(_x\) efficiency](image)

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 \( \text{DeNO}_x \) efficiency of the after-treatment catalyst is lower than 50 \%. \( \text{H}^+ \) on the catalyst surface probably is replaced by the alkali metal and thus induce lower absorption of \( \text{NH}_3 \). Catalyst A has a better activity because of a shorter impregnated time. Both catalysts’ activity increased gradually and perhaps \( \text{SO}_2 \) in the smoke increased the acid points on the catalysts’ surface. This is in a good agreement with the phenomenon reported that the loaded \( \text{SO}_4^{2-} \) on SCR catalyst’s surface can increase the amount of \( \text{NH}_3 \) absorption.

![Fig. 9 Toxic Study of Alkali Metal](image)

2.9 High CaO on \( \text{DeNO}_x \) Efficiency

Domestic coals usual contain high \( \text{SO}_2 \) and high \( \text{CaO} \) ash. \( \text{CaO} \) in the ash reacts with \( \text{SO}_3 \) absorbed in catalysts’ surface. The product \( \text{CaSO}_4 \) then coats the catalyst’s surface. Thus \( \text{NO}_x \) and \( \text{NH}_3 \) can not diffuse into the inner of catalyst. In this experiment, \( \text{CaO} \) 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’ \( \text{DeNO}_x \) performance were examined and the result is shown in Fig. 9.

<table>
<thead>
<tr>
<th>Catalysts’ type</th>
<th>Pre-treatment mass (g)</th>
<th>After-treatment mass (g)</th>
<th>Ratio of CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst A</td>
<td>37</td>
<td>71</td>
<td>48</td>
</tr>
<tr>
<td>Catalyst B</td>
<td>71</td>
<td>102</td>
<td>30</td>
</tr>
</tbody>
</table>

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](image)

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 \( \text{DeNO}_x \) efficiency when the catalyst is deteriorated. The deteriorate condition is realized by the enhancing concentration of \( \text{NO}_x \) and \( \text{SO}_2 \). At the experiment, \( \text{NO}_x \) concentration was 800 ppm, and \( \text{SO}_2 \) concentration 3000ppm. The result is shown as Fig. 11. After 1000 hours operating, the catalysts still presented a high \( \text{DeNO}_x \) efficiency. It shows that both catalysts have a good adaptability but it needs further experiment to investigate their life at a longer time.

![Fig. 11 Deteriorate Life time of Catalysts](image)
From the DeNO\textsubscript{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.

![Graph showing DeNO\textsubscript{x} curves]

**Fig. 11** Deteriorate Life time of Catalyst

## 3 CONCLUSIONS

The result shows the vanadium-titanium middling temperature SCR catalyst has a high DeNO\textsubscript{x} efficiency. Different catalysts may have single or multiple temperature windows for the best chemical reaction; DeNO\textsubscript{x} efficiency has a linear relationship with ratio of NH\textsubscript{3}/NO\textsubscript{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\textsubscript{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 SO\textsubscript{2}. Constrained by the experiment conditions, the conclusion deduced above is only for reference. It needs further research to investigate the influence of DeSO\textsubscript{2} and DeNO\textsubscript{x} gas on downriver equipments. And the influence of longer period operating on catalysts is also to be studied.

## REFERENCES

1. Görge Baltin, Heinz Köser, Klaus-Peter Wendlandt, Sulfuric acid formation over NH\textsubscript{3} sulfate loaded V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} catalysts by DeNO\textsubscript{x} reaction with NO\textsubscript{x}, Catalysis Today 2002 (75): 339-345.
8. Seng Moon Jung, Paul Grange, Characterization and reactivity of V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3} supported on TiO\textsubscript{2}-SO\textsubscript{2}- catalyst for the SCR reaction, Applied Catalysis B: Environmental. 2001 (32): 123.