Study on The Effect of ‘Ash Core’ on the Performance of Catalysts in the Preparation of SCR Honeycomb Denitration Catalyst

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Abstract. The SCR honeycomb denitration catalyst will have a “grey core” during the preparation process. In this paper, the same batch of fresh catalyst is used to prepare the “grey core” and the normal “yellow core” catalysts for comparison. Through the catalyst denitration performance evaluation test, when the denitration efficiency is 88.3%, the calculated activities of the two catalysts of "yellow core" and "grey core" are 24.9Nm/h and 25.3Nm/h, respectively; when the denitration efficiency is 85.5%, the calculated activity of the catalysts are both 24.5Nm/h. Through analysis of the physical and chemical properties of the catalyst, it is found that the alkali metal content and the alkaline earth metal content of the two catalysts are basically the same. The specific surface areas of the "yellow core" and "grey core" catalysts are 58.65m²/g and 58.24m²/g, respectively. By infrared spectroscopy, the "grey core" catalyst was produced due to the deposition of carbon, and then through the wear performance test, it is found that the "grey core" catalyst has better wear performance, but the "grey core" catalyst is more brittle, when there is external force. At the time, cracks are easily generated in both the axial direction and the radial direction, which is detrimental to the integrity of the catalyst, and also poses a safety hazard to the use of the regenerated catalyst.

1. Introduction
China is a big energy country, and coal accounts for more than 75% of China's energy. SO₂, dust and NOₓ emitted by coal accounts for 66%, 59% and 86% of the total national emissions, respectively [1,2]. At present, there are many methods for the removal of NOₓ, but the most mature and widely used is Selective Catalytic Reduction (SCR) denitration technology. The desulfurization effect of SCR highly depends on the performance of the catalyst. At present, the main SCR denitration catalysts used in China are honeycomb, flat and corrugated [3,4]. The honeycomb catalyst will produce a "grey core" during the calcination. In this paper, it will take the same batch of catalyst, preparing a pure "grey core" and a conventional "yellow core" type catalyst which can compare with each other. The contents of the comparison mainly include denitration efficiency, ammonia slip, activity and other process characteristics and physical and chemical properties such as specific surface, XRF, ICP, wear and compression.
2. Production process of SCR catalyst

2.1 Honeycomb Catalyst
Honeycomb catalysts belong to homogeneous catalysts. The bulk of honeycomb catalysts are all catalyst materials. When its surface is damaged by dust, it can still maintain the original catalytic performance [5,6]. The catalyst with the highest market share is the honeycomb catalyst, and its global market share reaches 70%-75%. It is made of Ti-W-V as the main active material, and is fully mixed with materials such as TiO₂ and other materials, and is calcined after extrusion molding. The honeycomb catalyst is characterized by high activity in per unit volume of catalyst, and the catalyst used for achieving the same denitration efficiency is small in volume, and is suitable for a flue gas environment with low ash content and low ash viscosity. The main processes of the production of honeycomb catalyst are as follows: (1) selecting suitable titanium dioxide, auxiliary materials, etc., mixing in a certain ratio, and uniformly stirring the raw materials at a high speed; (2) extruding the raw materials using a specific vacuum extruder; (3) The extruded body is cut into modules of different sizes according to the requirements of the finished product; (4) the packaged module is properly packaged to ensure that the product is not deformed; (5) drying, calcination; (6) extrusion module, cutting and shaping to a fixed size[7].

2.2 Plate Catalyst
The plate catalyst is a heterogeneous catalyst, which is suitable for denitration catalysts with ash content and ash viscosity and strong flue gas environment, and has strong corrosion resistance and anti-blocking characteristics. The plate catalyst uses Ti-Mo-V as the active component of the metal, and the metal mesh forms the skeleton of the catalyst. The combination of the metal mesh and the active components in the catalyst molding process is mainly achieved by means of extrusion on both sides.

2.3 Corrugated catalyst
The corrugated catalyst is coated with soft fiber as the carrier and coated with active substances such as V₂O₅ and WO₃. The market share of corrugated catalyst is low, and it is mostly used in gas units [8].

3. Reaction mechanism of SCR denitrification catalyst
The mechanism of Langmuir-Hinshelwood [9] suggests that NH₃ is adsorbed on V₂O₅ in the form of NH₄⁺(ads). When O₂ is present, NO is adsorbed on the surface of V₂O₅ in the form of NO₂(ads), and then NH₄⁺(ads) and NO₂(ads) react to form N₂ and H₂O. When there is no O₂, NO is not adsorbed on the surface of V₂O₅.

The Eley-Rideal mechanism [10] believes that ammonia rapidly adsorbs on the Bronsted acid site to form NH₄⁺(ads), and then reacts with NO in meteorology to form an activated complex. After the complex is decomposed to form nitrogen and water, oxygen can regenerate the active site. Topsoe et al. [11] considered that the Langmuir-Hinshelwood mechanism and the Eley-Rideal mechanism occur during the NH₃-SCR reaction, and NO is more likely to participate in the NH₃-SCR reaction in the form of weakly adsorbed species.

4. Characterization of catalysts
In this study, the reference comparison test method was adopted. The sample was taken from the fresh catalyst of the initial layer of 1000WM unit. As shown in figure 1, the catalyst with “grey core” inside was used as sample catalyst.
For the denitration performance evaluation, the cross section is 5 holes*5 holes (about 45mm*45mm), the length of the catalyst is consistent with the original height, one is the "grey core" part of the sample catalyst; the other is the "yellow core" part of the sample catalyst. And preparing the sample for testing physical and chemical properties of the denitration catalyst.

4.1 Catalyst denitrification performance evaluation

The prepared catalyst was charged into a laboratory denitration reactor, and the experimental apparatus is shown in figure 2. The device is mainly composed of a denitration reactor, a temperature control system, an infrared flue gas analyzer, a water inlet system, an air intake system, and an exhaust gas treatment system. In the experiment, the special gas is mixed and then introduced into the denitration reactor, and water vapor is sprayed into the reactor. After the inlet and outlet of the system are stabilized, ammonia gas reacts with nitric oxide. The analyzer measures the gas concentration in the flue gas at the inlet and outlet of the reactor [12].

![Figure 2. Catalyst process characteristics of the test system map](image)

Test flue gas working conditions: the total gas flow rate is 246L/min, wherein the volume fraction of O₂ is 2.79%, the volume fraction of water vapor is 8.46%, and the inlet NOₓ concentration was 302.8 mg/m³, and N₂ was used as the carrier gas, and the space velocity was 3037h⁻¹. In the catalyst technology agreement, there is a post-installation performance test efficiency and a guaranteed efficiency during the catalyst life. Therefore, this test will also correspond to a high efficiency and a low efficiency value, the denitrification efficiency is 88.3%, and the export NOₓ concentration control at 36mg/m³; the denitrification efficiency was 85.5%, and the outlet NOₓ concentration was controlled to be 44mg/m³. The two catalysts were tested and compared under the same initial conditions, and the ammonia nitrogen molar ratio and activity of the respective catalysts were calculated corresponding to the two denitrification efficiencies.

The denitrification efficiency of catalyst unit should be calculated according to formula (1):

\[
\eta = \frac{C_1 - C_2}{C_1} \times 100\%
\]  \hspace{1cm} (1)
$\eta$ is the denitrification efficiency of the catalyst unit, $C_1$ is the NO$_X$ concentration at the inlet standard dry base, in mg/m$^3$, $C_2$ is the NO$_X$ concentration at the outlet of the reactor.

The molar ratio of ammonia to nitrogen is calculated according to formula (2):

$$M_R = \eta + \frac{C_{NH_3}}{C_{NO}}$$  \hspace{1cm} (2)$$

$M_R$ is the molar ratio of ammonia to nitrogen, $\eta$ is the denitrification efficiency of catalyst unit, $C_{NH_3}$ is the measured ammonia escape concentration at reactor outlet and $C_{NO}$ is the measured NO$_X$ concentration at reactor inlet.

The activity of catalyst unit should be calculated according to formula (3):

$$K = 0.5 \times v_A \times \ln \frac{M_R}{(M_R - \eta) \times (1 - \eta)}$$  \hspace{1cm} (3)$$

$K$ is the activity of catalyst unit in m/h and $v_A$ is the surface velocity in m/h.

4.2 Evaluation of Physical and Chemical Properties of Catalysts

In this study, the NOVA 4000e automatic surface area analyzer was used to measure the specific surface size of the two samples. The main chemical components such as titanium dioxide, molybdenum trioxide, tungsten trioxide and vanadium pentoxide were measured by ZSX Primus IIX fully automatic sequential scanning X-ray fluorescence spectrometer; Optima 8000 inductively coupled plasma atomic emission spectrometer is used to measure trace elements such as arsenic, sodium, potassium, calcium and phosphorus. The wear performance of the honeycomb catalyst was tested by PFI100 continuous loss-in-weight feeder. The compressive performance of the honeycomb catalyst was tested by CDT1105 microcomputer controlled electronic pressure tester.

5. Results and discussion

5.1 Performance Analysis of Catalyst for Denitrification

Both catalysts were tested under the same initial operating conditions. In the case of working condition 1, the same denitration efficiency of 88.3% is ensured, and a stepwise stable ammonia injection is performed. In the case of ensuring that the outlet NO$_X$ concentration is 36mg/m$^3$, it is stable for 1 hour, and then the extraction and measurement of the exit ammonia escape is performed, and the measurement is performed every one hour for a total of four times; in the case of the second condition, the same denitration efficiency is ensured. 85.5%, the outlet NO$_X$ concentration was 44mg/m$^3$, and the measurement was repeated four times in the same manner. Each measurement uses a certain concentration of dilute sulfuric acid as an absorbent to absorb the escaping ammonia and then measure it using liquid phase ion chromatography.

![Figure 3. Ammonia escape concentration when denitrification efficiency is 88.3%](image1)

![Figure 4. Ammonia escape concentration when denitrification efficiency is 85.5%](image2)

As shown in figure 3, the blue box point represents the "yellow core" catalyst. When the denitrification efficiency is 88.3%, the ammonia slip concentration is measured four times in succession. The red
triangle point represents the concentration of the ammonia escape concentration which was measured four times in succession at the denitration efficiency of 88.3%. Similarly, figure 4 shows the results of measuring the ammonia slip concentration for the denitration efficiency of 85.5%. We can see from the figure that the deviation of the four results is extremely small, indicating that the concentration of gas in the reactor tends to be in equilibrium and stable. The average of four consecutive measurements is taken as the ammonia slip concentration, and the activity of the catalyst under the corresponding working conditions is calculated by means of formulas (1) (2) and (3), as shown in tables 1 and 2.

Table 1. Ammonia escape and activity when the denitration efficiency is 88.3%

| Catalyst     | Ammonia escape concentration (6% oxygen) mg/L | Active Nm/h |
|--------------|-----------------------------------------------|-------------|
| "Yellow core" | 1.03                                           | 24.9        |
| "Grey core"  | 0.93                                           | 25.3        |

Table 2. Ammonia escape and activity when the denitration efficiency is 85.5%

| Catalyst     | Ammonia escape concentration (6% oxygen) mg/L | Active Nm/h |
|--------------|-----------------------------------------------|-------------|
| "Yellow core" | 0.91                                           | 24.5        |
| "Grey core"  | 0.92                                           | 24.5        |

According to the analysis of Table 1 and Table 2, it can be concluded that in the case of two different denitration efficiencies, the difference between the ammonia slip and the calculated catalyst activity value measured at the outlet of the two catalysts is very small, so the denitrification performance of the two catalysts is small. The difference is not big.

5.2 Physical and Chemical Properties of Catalysts

5.2.1 Catalyst main chemical composition, trace elements and specific surface area. The two catalyst trace elements were measured using an inductively coupled plasma atomic emission spectrometer. The results are shown in table 3 below.

Table 3. Trace element content of two catalysts

| Catalyst     | As mg/Kg | P mg/Kg | Fe mg/Kg | Ca mg/Kg | Na mg/Kg | K mg/Kg |
|--------------|----------|---------|----------|----------|----------|---------|
| "Yellow core" | -        | 716     | 315      | 9788     | 835      | 102     |
| "Grey core"  | -        | 818     | 359      | 9778     | 724      | 106     |

According to research, alkali metal is one of the strongest poisons causing poisoning of SCR catalyst. The poisoning effect of alkali metal on the catalyst is to reduce the amount of effective active sites on the catalyst by combining with the acidic sites of V$_2$O$_5$, so that the ammonia adsorption amount on the catalyst surface is reduced, which leads to a decrease in catalyst denitration activity. Arsenic act as a gaseous As$_2$O$_3$ or a dimer As$_4$O$_6$, which diffuses into the catalyst surface and accumulates in the catalyst pores, and forms a V-As complex with the active component V, thereby reducing the activity of the catalyst. According to the data in Table 3, the composition of the two catalyst alkaline earth metals is basically the same, because there is a fresh catalyst, there is no As element.

The main chemical compositions of the two catalysts were measured using an X-ray fluorescence spectrometer, and the results are shown in table 4 below.
Table 4. Contents of main chemical components in the two catalysts

| Catalyst      | TiO₂  | WO₃  | V₂O₅ | SiO₂  | Al₂O₃ | BaO  | CaO  |
|---------------|-------|------|------|-------|-------|------|------|
| "Yellow core" | 89.34 | 3.74 | 0.34 | 2.82  | 0.83  | -    | 1.45 |
| "Grey core"   | 89.47 | 3.75 | 0.42 | 3.02  | 0.88  | -    | 1.43 |

Alkaline earth metal also reduces the activity of the catalyst. The mechanism of poisoning indicates that the alkaline earth can be attached to the acid sites on the surface of the catalyst, and it can also block the catalyst pores with the CaSO₄ formed by SO₂ in the flue gas, causing the catalyst to be deactivated. It can be seen from the data in Table 4 that the active component systems of V-Ti-W of the two catalysts are the same, and the composition of the alkaline earth metals have no large differences. From the data in Tables 3 and 4, the two catalysts fired from the same batch of raw materials, so the contain has almost no difference in the active ingredients, alkali metal and alkaline earth metal. This also proves the activity of the two catalysts are the same.

The specific surface area of the two samples was measured using a fully automatic surface analyzer. The results are shown in Table 5.

Table 5. Two catalyst specific surface sizes

| Catalyst     | Specific surface size m²/g |
|--------------|----------------------------|
| "Yellow core"| 58.65                      |
| "Grey core"  | 58.24                      |

The specific surface area of the catalyst reflects the size of the contact surface between the active material and the flue gas in the catalyst. According to the data obtained in Table 5, the specific surface areas of the two catalysts are also substantially the same, indicating that the area of the flue gas contacting the two catalyst surfaces is the same.

Two catalyst samples were analyzed using an infrared spectrometer, and the results are shown in Figure 5 below.

Figure 5. Infrared spectra of two catalysts

As shown in figure 5, blue is the background peak, purple is the curve of the "yellow core" catalyst, and red is the curve of the "grey core" catalyst. From the graph, the peak between 2500 and 200cm⁻¹ is obtained. The "grey core" catalyst is higher than the "yellow core" catalyst. The peaks in this interval represent the functional group such as -C≡C-, -C≡N, >C=C=C<, -N=C=O, -N=C=S. That is because during the production of the catalyst, some organic substances such as binders are added. During the calcination process, due to the unsmooth internal ventilation of the catalyst, the organic matter does not change to carbon dioxide breaking away from the catalyst at a high temperature, but deposits on the surface of the catalyst to form a "grey core".

5.2.2 Catalyst wear, compression, cutting mechanical properties. The wear performance of the honeycomb catalyst was measured using a continuous loss-in-weight feeder. The wear results for the "grey core" and "yellow core" catalysts are shown in the following table.
Table 6. Two catalyst wear properties

| Catalyst      | Hardened end %/kg | Non-hardened end %/kg |
|---------------|-------------------|-----------------------|
| "Yellow core"| 0.015             | 0.059                 |
| "Grey core"  | 0.012             | 0.044                 |

From table 6, the wear performance of the "grey core" catalyst is superior to the "yellow core catalyst" to some extent, whether it is a hardened end or a non-hardened end. The analysis is due to the fact that the "grey core" is produced to slightly improve the wear performance of the catalyst to some extent. This carbon deposition just increases the wear performance of the catalyst to some extent.

However, the production of "grey core" catalyst makes the strength between the "grey core" portion and the normal "yellow core" portion not very good. Moreover, the toughness of the "grey core" portion itself is inferior to the "yellow core" portion, as shown in the following figure.

![Figure 6. Catalyst after compression test](image6.png)

![Figure 7. cross-section of the end face of the catalyst](image7.png)

Figure 6 shows the cracking of the "grey core" and "yellow core" parts after the whole catalyst has been crushed after the compression test. Figure 7 shows the end face produced by cutting the cross section of the catalyst using an electric cutter. It can also be seen that the "yellow core" portion has significantly less cracks and breakage than the "grey core" portion. When the catalyst is manually cut, it is more obvious that the "grey core" portion is hard and brittle, and a slight external force causes cracks in the "ash core" catalyst. The figure below shows the case of a honeycomb catalyst in actual operation.

![Figure 8. Internal crack of the catalyst in operation](image8.png)

![Figure 9. "Gray core" partial crack in operation](image9.png)

Figure 8 and figure 9 show the internal conditions of a catalyst in an in-service unit. Before cutting the catalyst, the whole catalyst is intact in appearance, only some wear on the end face, but it is found that there is a disconnect inside after cutting. For cracks, there are also many cracks when viewed in the axial direction. According to the analysis, the flue gas flows inside the catalyst pores, and the gas flow causes jitter to the catalyst, and cracks are generated in the process, and the continuous shaking causes the cracks to continuously deepen. Such cracks are not visible on the surface of the catalyst, but
the inherent safety hazard of the catalyst in the SCR region which may cause collapse of the catalyst. Further, there is a demand for regeneration of a catalyst, and there is no problem in appearance of the catalyst, but mechanical properties after regeneration cannot be ensured, which is disadvantageous for using after regeneration.

6 Conclusion
1) Under the same operating conditions, when the denitrification efficiency is 88.3%, the “yellow core” and “grey core” catalysts have calculated activity values of 24.9Nm/h and 25.3Nm; when the denitrification efficiency is 85.5%, the calculated activity values were both 24.5 Nm/h. It is seen from the activity values that there is substantially no difference in the denitrification performance of the two catalysts.

2) For the V-Ti-W system of the two catalysts, the main chemical components are similar by XRF measurement, and the alkaline earth metal content is not greatly different. The alkali metal content measured by ICP is also substantially the same, and the degree of inhibition of the catalytic reaction by the alkali metal is also the same.

3) For the wear performance test of the two catalysts, it is shown that the "grey core" catalyst has better wear performance, and the wear resistance of the "ash core" catalyst itself is improved due to carbon deposition. However, the brittleness of the "grey core" catalyst is prominent. In the case of external force, radial and axial cracks may occur, and in severe cases, the collapse of the catalyst in the SCR region may occur. For the safety hazard of insufficient mechanical properties of the in-service catalyst, similarly, there is a problem of insufficient mechanical properties for the regenerated catalyst, which is disadvantageous for the use of the regenerated catalyst.

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