Study on the Calcination Time of V2O5-WO3-MoO3/TiO2 Catalysts for SCR DeNOx

Tuo Ye *, Donglin Chen and Xi Zeng

School of Energy and Power Engineering, Changsha University of Science and Technology, Changsha 410114, China.

*Corresponding author e-mail: Ye_Tuo@sina.com

Abstract. In order to improve the activation effect of deactivation catalysts, calcination of V2O5-WO3-MoO3/TiO2 catalysts were investigated. The experimental results demonstrate that calcination time have an effect for recovering the activity of V2O5-WO3-MoO3/TiO2 catalyst. Calcination not only ensures the better mechanical strength and integrity of the catalyst, but also plays an important role in the denigration activity of the catalyst. However, the particles of the catalyst surface enlarged with the increase of the calcination temperature. The suitable calcination time can improve the denigration efficiency and increase the mechanical strength of the catalyst. In addition, the calcination time mainly affects the formation of MoO3. These findings can provide reference for the activation of SCR-Den Ox catalyst.

Keywords. Calcination; V2O5-WO3-MoO3/TiO2 Catalysts; Den Ox Activity; SCR.

1. Introduction

Nowadays, the issue for reducing NOx of the large majority of the current industrial is accomplished by means of the Selective catalytic reduction (SCR) method [1] which is efficient and reliability as well as stability of the catalytic reaction [2]. Obviously, the catalyst is the key of SCR-Den Ox technology, but it can be easily clogged [3], covered [4], poisoned [5] in operation by the flue gas and thereby the reactivity of the catalyst is significantly decreased and the Den Ox efficiency is decreased accordingly. The performance of catalysts has become the focus of attention. Therefore, it is very necessary to study the calcination time of the V2O5-WO3-MoO3/TiO2 catalysts.

Research of V2O5-WO3-MoO3/TiO2 catalyst is focused on improving the design of the catalyst to improve the NOx reduction performance and reducing the oxidation activity of SO2 [6, 7]. The calcination process has an important influence on the microstructure, specific surface area and surface active site distribution of the catalysts [8]. Zhang et al. [9] studied the influence of calcination temperature on the activity of catalytic DE nitrification. The results show that the calcination temperature has a significant influence on the catalytic activity of the catalyst. Adrian Mar Berger et al. [10] Studied the calcination and aging of catalysts cause a change of the surface area that is directly linked to the surface density of vanadium species and as a consequence also the catalytic performance. The calcination time is likely to impact on the surfactant catalyst load and pore structure in the process of catalyst activation. Thereby affecting the activation effect of deactivated catalysts. However, the
soaring price of SCR catalyst has limited its application, especially in small factories. Thus, it is important to lower the cost of the catalyst while keeping its catalytic activity.

Although the research on vanadium titanium catalysts has been carried out for several years, few studies have been conducted on the differences in the performance of catalysts due to the different calcination conditions. In order to study the mechanism of the calcination of the catalyst, the fresh, deactivated and regenerated catalysts were characterized by scanning electron microscope (SEM), Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD) and Energy Dispersive Spectrometer (EDS). We expect that these results can pave the way for the application of the above catalysts to enhance DE nitrification.

2. Experiment

2.1. Material preparations
Deactivation commercial honeycomb catalysts were obtained from a coal-fired power plant. Type of prepared catalyst samples was ZERONOX1831K. The activating solution composition was calculated according to the mass percentages of active precursors. The main components of the prepared activating solution are listed in Table 1.

| Component                      | Percentage content (wt%) |
|--------------------------------|--------------------------|
| Ammonium vanadate              | 1.0                      |
| Ammonium tungstate             | 9                        |
| ammonium molydate              | 6                        |
| Oxalic acid                    | 7.6                      |
| JFC                            | 0.5                      |
| OP-10                          | 0.5                      |
| Deionized water                | Allowance                |

2.2. Catalyst activation
To improve the efficiency of the deactivated catalyst, the activation of the deactivated catalyst was carried out by the activation device. The frequency of the draft fan and the blower was adjusted to 45 Hz, the calcination time (5, 10 and 30 minutes) was experimental. During the calcination process, a chemical reaction occurs of the active component, such as 1) ~ 3):

\[
2\text{NH}_4\text{VO}_3 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{V}_2\text{O}_5
\]

\[
(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6\text{H}_2\text{O} \rightarrow 10\text{NH}_3 + 7\text{H}_2\text{O} + 12\text{WO}_3
\]

\[
(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24})_6 \cdot 4\text{H}_2\text{O} \rightarrow 6\text{NH}_3 + 7\text{H}_2\text{O} + 7\text{MoO}_3
\]

The main active ingredient (V₂O₅) will evenly precipitate and attached to the surface of the catalyst to supplement the active ingredient lost by the deactivation catalyst, which is lost or poisoned or abraded at high temperature. At the same time, a chemical reaction also occurs on the surface of the catalyst to produce WO₃ and MoO₃, and evenly distributed on the surface of the catalyst.

3. Methodology

3.1. Activity measurements and evaluations
The inlet gas streams consisted of NH₃ (1000 ppm), NO (1000 ppm), SO₂ (1200ppm), CO₂ (13%) ,O₂ (5%), H₂O (5%) in N₂. The NOx concentration before and after the reaction was measured by a flue gas analyzer (T-350, Testo Company). The NO removal rate is calculated according to the formula 4).

\[
\eta_{\text{NOx}} = \frac{C_{\text{NOx},\text{in}} - C_{\text{NOx},\text{out}}}{C_{\text{NOx},\text{in}}} \times 100\%
\]
The coefficient κ is usually used to characterize the activity of the catalyst, which is calculated by the formula 5).

$$\kappa = \frac{V_{fg}}{V_{cat}} \ln(1 - \frac{\eta_{NOx}}{M}) = -S_V \ln(1 - \frac{\eta_{NOx}}{M})$$

(5)

Where κ is the catalyst activity coefficient, Vfg is the flue gas flow (m$^3$/h), Vcat is the catalyst volume (m$^3$), ηNOx is the nitrogen oxide removal rate, M is the NH3/NO molar ratio, and SV is the space velocity. Based on the experimental conditions, M is always 1.0, and SV is always 6000 h$^{-1}$.

3.2. Catalyst characterization

The morphology of the samples was analyzed by the SEM (Sirion200, FEI). Which yielded important information about the structural features. Crystal structures of the samples were established by using an X-ray diffract meter (XRD, D/MAX-2200). The XRD patterns of all samples were recorded on a Phillips X-pert (50KV, 40 mA, and 10° min$^{-1}$ from 10 to 80°).

4. Results and discussion

4.1. Removal rate of NO

The NO removal rate of activated catalysts under the calcination time (5, 10, 30 minutes) is displayed in the Figure 1. Increasing the calcination time from 5 to 10 minutes resulted in an increase of NO removal rate. However, the NO removal rate of activated catalysts was decreased when increase the calcination time from 10 to 15 minutes. It is reasonable to suppose that the calcination time is too long that cause partial sintering of the catalyst and the volatile loss of the active component was prolonged when the catalyst was exposed to high temperature for a long time. It is worthwhile mention that the removal rate of NO increased with the increase of the reaction temperature, and reaches the highest when the reaction temperature reaches 370°C.

![Figure 1. Effect of calcination time on NO removal rate of activated catalyst](image-url)
4.2. **SEM**
Morphology and microstructure evolution analysis of claimed products by different calcination times are collected in the Figure 2. A high magnification SEM image of the sample reveals that the pores on the surface of the activated catalyst is larger. The particles of the activated catalyst which calculated for 10 minutes without agglomeration. However, the agglomeration could be observed on the deactivation catalyst. The agglomeration also appeared over the activated catalyst when calculated for 30 minutes. Due to the particles agglomeration, the gap between particles on the catalyst surface decreases, making it difficult for the flue gas and the active ingredient to come into contact, the quantity of the reachable active sites over the catalyst decreased which results in a reduction of the catalyst denigration efficiency [11-13]. Essentially, the results demonstrate the great influence of the catalyst preparation method on the catalyst pore and surface characteristics due to the difference in calcination.

![SEM photos of catalysts activated under different calcination time](image)

**Figure 2.** SEM photos of catalysts activated under different calcination time Activation conditions:
drying temperature--105°C; drying time--30min; calcination temperature --500°C/

4.3. **XRD**
X-ray diffraction results of the samples under different calcination time are shown in the Figure 3. The deactivated sample only shows the diffraction peaks of that are typical of anatase TiO₂. No characteristic diffraction peaks of active ingredient are observed because of its lower loading content and weak crystallization. Compared with calcination temperature, the influence of calcination time on the crystalline morphology of the catalyst is relatively small, and the effect of calcination time on the catalyst denigration efficiency is weaker than that of calcination temperature. There are numerous possible reasons for this observation. One is that the active ingredient (V₂O₅) has been depleted. Another one is that the vanadium oxide has been disseminated on the surface of the catalyst support in an amorphous or highly dispersed form. The extension of calcination time mainly increased the MoO₃ content of the catalyst surface. It is also known that the effect of MoO₃ on the activity of the catalyst is less than other active components. The increase in calcination time facilitates the loading of active material.
5. Conclusion

In this work, the effects of calcination time for activating catalysts were investigated. The following conclusions can be drawn from the results of this study:

(1) Calcination not only ensures the better mechanical strength and integrity of the catalyst, but also plays an important role in the denigration activity of the catalyst. As the calcination time increases, the mechanical strength of the catalyst increases gradually, and the mechanical strength can be further enhanced by the removal of crystalline water and the oxidation of the re impregnated material into an active state. However, the effect of calcination time on the catalyst denigration efficiency is weaker than that of calcination temperature.

(2) The calcination time mainly affects the formation of MoO$_3$. The effect of MoO$_3$ on the activity of the catalyst is lower than that of other active substances. When the calcination time is 10 minutes, the recovery degree of the catalyst activity and the activity of the catalyst is the highest. The calcination time of catalyst activation was studied, which promotes the application and extension of the catalyst in the furnace activation technology. Our findings suggest that the calcination is very important for improving the activation effect of deactivated catalysts.
References

[1] Mejri I, Ayari F, Mhamdi M. Microporous & Mesoporous Materials, 2016, 220:239-246.
[2] Z. Liang, X. Ma, H. Lin, Appl. Energ. 88 (2011) 1120–1129.
[3] Peng Y, Li J, Si W, Applied Catalysis B Environmental, 2015, 168:195-202.
[4] Wilburn R T, Wright T L. Powerplant Chemistry, 2004.
[5] Guo B, Xiaoyu. Poisoning and Sulfation on Vanadia SCR Catalyst Poisoning and Sulfation on Vanadium SCR Catalyst. 2006.
[6] Pio Forzatti. Applied Catalysis.A, 2001, 222(1/2):221-236
[7] Dirk Bosteels, obert A, earles. Platinum Metals Review, 2002, 46(1):27-36
[8] Lina Gan , Feng Guo, Jian Yu, Guangwen Xu, Catalysts, 2016, 6, 25
[9] Zhang P, Chen T H, Zhu C Z, Chinese Journal of Catalysis, 2014, 35: 99-107.
[10] A Marberger, M Elsener, D Ferri, Catalysts, 2015, 5, 1704-1720
[11] J Yu, F Guo, Y Wang, Appl. Catal.B 95: 160-168.
[12] BX Shen. Acta Physico-Chimica Sinica, 2010, 26(11):3009-3016.
[13] H Qiang, Q Liu. Materials Review, 2008, 22(Special XII): 285-287(in Chinese).