A Study on the Effect of Different Ball Milling Methods on the NH$_3$-SCR Activity of Aluminum-Laden Bayan Obo Tailings

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Abstract: Rich in Fe, Ce, Mn, Si and other elements which have good catalytic activity, Bayan Obo rare-earth tailings are naturally advantaged as the carrier of denitrification catalysts. In this paper, pseudo boehmte ($\gamma$-Al$_2$O$_3$) was mixed with Bayan Obo tailings using different ball milling methods for modification to prepare NH$_3$-SCR catalysts. The effect of different mixing methods on the SCR denitrification activity at a low temperature was investigated and the prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), temperature programed desorption (NH$_3$-TPD), temperature programed reduction (H$_2$-TPR) and other means. The conversion rate of NOx at 250–350 $^\circ$C was above 80% and the highest conversion rate of NOx of 90% was achieved at 300 $^\circ$C. SEM and XRD revealed that the tailings modified by pseudo boehmite ($\gamma$-Al$_2$O$_3$) using the ordinary ball milling method have loose structure and good dispersion of active substances, and specific surface area (BET) analysis shows that the tailings have the maximum specific surface area and pore volume. However, over grinding and secondary spheronization were observed in the tailings modified by pseudo boehmite ($\gamma$-Al$_2$O$_3$) using high energy ball milling method, leading to the decrease of specific surface area and pore volume, poor dispersion of active substances, and ultimately low denitrification rate.

Keywords: rare-earth tailings; carrier; pseudo boehmite; ball milling; NH$_3$-SCR activity

1. Introduction

The Bayan Obo mine, the largest polymetallic iron–niobium–REE (rare earth elements) deposit in the world, is characterized by a wide variety of elements, fine-grained dissemination and complex mineral compositions. After magnetic separation and REE flotation, the tailings still contain a large number of valuable minerals such as iron, niobium and rare earth elements which are not effectively utilized, causing serious waste of resources. The question of how to efficiently use Bayan Obo rare-earth tailings has always been the research focus of domestic scholars [1–3]. In view of today’s serious air pollution, using precious metals as the active ingredient to prepare catalysts is not only expensive, but also may cause sulfur poisoning. Hence, it is of particular importance to find a denitrification catalyst which is cheap and readily available, with large reserves of raw materials and good catalytic performance. Catalytic materials made of Fe–Ce complex oxides have received wide attention because of these characteristics [4,5]. Moreover, the average grade of rare earth oxides, which are minerals with good catalytic activity in Bayan Obo rare-earth tailings is still as high as 6%~8%. There are also a large number of minerals containing Al and Si in the tailings that can be doped into the catalyst to provide specific surface area and act as the rigid carrier. Transition metal elements such as Fe, Nd, Mn, Cu are the main active compositions of the catalyst and can act as the active carrier. For these reasons, preparing...
denitrification catalysts from tailings can not only achieve good catalytic effect at low temperature, but also can play a major role in improving the utilization rate of mineral resources in China [6–10]. Wang et al. improved the activity of iron through acid treatment and acid-base treatment of Bayan Obo tailings. At 900 °C, the denitrification rate of the catalyst was as high as 96.2% [11]. The $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ prepared by Caixia Liu using the coprecipitation method were highly selective to N$_2$ [12], and the addition of Fe gave the catalyst a wide operating temperature window and improved sulfur resistance [13–15]. MnO$_X$–CeO$_2$ prepared by Gongshin Qi exhibited high catalytic activity in the reduction process of NO with NH$_3$. In the lower temperature range of 80–150 °C, the selectivity of MnO$_X$–CeO$_2$ to N$_2$ was 100%, and complete conversion of NO could be realized when the temperature was below 120 °C. The addition of Ce not only increases the Mn valence, but also improves its oxidizing ability [16–18].

In this paper, different mixing methods (high energy ball milling and ordinary ball milling) are applied to improve the denitrification performance of rare-earth tailings. Due to the complex intergrowth in the Bayan Obo rare-earth tailings, active elements such as Fe and Ce in the active minerals feature large particle size and uneven dispersion, and there is a lack of critical acid sites of NH$_3$-SCR catalyst. For this cause, pseudo boehmite ($\gamma$-Al$_2$O$_3$) is added into the tailings to prepare the catalyst, which not only provides the acid site for reaction, but also increases the specific surface area of the catalyst. Milling intensity and milling time play a significantly role on the reaction process between minerals and $\gamma$-Al$_2$O$_3$. The strengthening effect of ball milling increases with the increase of milling intensity and milling time. A longer milling time may continuously increase the chemical reactivity of materials, and excessive milling will decrease the specific surface area of mineral materials due to agglomeration effect [19–21]. Moreover, the grain boundary area of mineral particles will increase as finer particles are generated by milling, resulting in the increase of free energy of the system. The internal stress of mineral particles will increase with the impact of ball milling, resulting in defects inside grains and promoting the dispersion of minerals [22]. In the process of ball milling, the powder is repeatedly broken and welded and a large number of fresh atomic level interfaces are generated, forming refined multilayered composite grains [23]. When $\gamma$-Al$_2$O$_3$ is added, ball milling will strengthen the bond between minerals and $\gamma$-Al$_2$O$_3$, and make $\gamma$-Al$_2$O$_3$ more evenly dispersed in minerals, so that metal oxides with denitrification activity can fully contact with each other to produce synergistic effect, thus improving the denitrification activity and improving the sulfur and water resistance of the catalyst at the same time. This experiment uses rare earth tailings to prepare denitrification catalysts, which has changed the traditional use of analytically pure preparation catalysts such as high cost and obvious unity. At the same time, the denitrification active components in rare earth tailings are fully utilized to achieve the purpose of waste treatment.

2. Results and Discussion
2.1. XRF Multi-Element Analysis Results

X-ray fluorescence spectrometry (XRF) multi-element analysis results of the tailings are shown in Table 1. The content of rare earth, iron, and calcium in the rare earth tailings is relatively high. Fe$_2$O$_3$, MnO, TiO$_2$, ZnO are transition metal oxides, which are the main elements that determine the performance of the catalyst, and them content in the rare earth tailings accounts for a large proportion, indicating that the rare earth tailings are suitable for the preparation of denitration catalyst. Gangue minerals are mainly fluorite, calcite, barite, feldspar, quartz and so on. Rare earths include bastnaesite and monazite. Iron is mainly found in hematite, magnetite, and silicate iron ore, while Si may be abundantly present in quartz or silicate minerals. Among them, Si and Al can be used as rigid carriers in tailings.
Table 1. Chemical composition of rare-earth tailings (wt %).

| Components   | Content |
|--------------|---------|
| Fe₂O₃        | 28.62   |
| CaO          | 21.97   |
| F            | 14.03   |
| SiO₂         | 11.48   |
| SO₃          | 4.88    |
| BaO          | 3.78    |
| MgO          | 3.67    |
| P₂O₅         | 2.80    |
| MnO          | 1.76    |
| La₂O₃        | 1.58    |
| Nd₂O₃        | 1.32    |
| Al₂O₃        | 1.12    |
| TiO₂         | 1.04    |
| Na₂O         | 0.75    |
| K₂O          | 0.50    |
| NbO          | 0.17    |
| Pr₆O₁₁       | 0.14    |
| ZnO          | 0.11    |
| SrO          | 0.10    |
| PbO          | 0.08    |
| Y₂O₃         | 0.03    |
| ThO₂         | 0.03    |
| CuO          | 0.007   |
| CO₂          | 0.01    |

2.2. SCR Catalyst Performance Testing

Selective catalytic reduction (SCR) denitrification technology has become one of the most popular options for reducing NOx emissions for its excellent NOx removal rate, high N₂ selectivity and good economic benefits [24]. In this experiment, the 150–450 °C temperature window was used to investigate the denitrification activity of catalysts prepared using high energy ball milling mixing and ordinary ball milling mixing methods and to compare with rare-earth tailings after microwave calcination. The curve is shown in Figure 1a under the same ratio of grinding media to material and milling time, the denitrification activity of catalysts prepared using different ball milling methods differ greatly. The denitrification efficiency curve of catalysts prepared using high energy ball milling and tailings is similar at 150–250 °C and rise steadily, while that of catalysts prepared using ordinary ball milling is high at 150 °C. For catalysts prepared using high energy ball milling, the maximum denitrification rate of 61.5% was achieved at 400 °C, while catalysts prepared using ordinary ball milling achieved a denitrification rate of around 80% at 250, 300 and 350 °C, and the denitrification temperature window is wide. The denitrification rate reached 90% at 300 °C, which was the optimal denitrification performance.

The activity data of γ-Al₂O₃ is shown in Figure 1b, the overall denitration effect of γ-Al₂O₃ is not good. The highest denitration activity is only 11.3, but the best denitration activity reaction temperature is 250 °C. Compared with tailings and tailings after different ball milling treatments, the reaction temperature is earlier. This is the richness of γ-Al₂O₃ Caused by the acidic sites.
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2.3. Analysis of Phase Composition

Figure 2 is the XRD imaging of tailings and catalysts prepared by calcinating the mixture of tailings and γ-Al₂O₃ mixed using two different ball milling mixing methods. It can be seen from the figure that in the original tailings, the diffraction peaks of fluorite, quartz and bastnaesite are sharp, and the mineral crystallinity is better, and its content is higher. The main peaks of hematite and barite are wider, the diffraction peaks are lower, and the crystallinity of the minerals is poor, indicating that the content of these minerals is lower, the crystal grains are finer, and the distribution is more uniform. There are characteristic peaks of Ce₇O₁₂ in the catalyst prepared by ordinary ball milling, while there are fewer characteristic peaks of bastnaesite. This is because ordinary ball milling improves the dissociation of bastnaesite, and most of them decompose and become amorphous after calcination. In contrast, the quantity of characteristic peaks of bastnaesite increases after high energy ball milling. This is because over grinding of minerals causes agglomeration of γ-Al₂O₃ and minerals, and minerals are not fully decomposed after calcination. As ordinary ball milling can improve the dispersion of active mineral components, most of
minerals are amorphous, and when used as the carrier, the specific surface area will slightly increase. Compared with tailings, the CaF$_2$ peak of catalysts prepared using two ball milling methods and calcination is significantly reduced. The reason is that the high content of CaF$_2$ in the tailings, which dissociates after ball milling, and other minerals wrapped by CaF$_2$ are exposed, other minerals wrapped by CaF$_2$ are exposed after ball milling, and the dispersion of CaF$_2$ is better after grinding. From the comparison of characteristic peaks in the figure, there are 23 main characteristic peaks in the tailings treated by ordinary ball milling, including 8 characteristic peaks containing Fe, 2 characteristic peaks containing Ce, 1 characteristic peak containing Al and 4 characteristic peaks containing Si. From the XRF results, because Bayan Obo tailings have the characteristics of multi-chemical composition, it is a natural mineral that is very suitable as a carrier.

Figure 2. XRD spectrum of the modified catalyst.

2.4. Particle Size and Morphology of Catalysts

It can be seen from Figure 3 that the particle size distribution of γ-Al$_2$O$_3$ used in the experiment is around 1–37 μm. The γ-Al$_2$O$_3$ is dominated by fine particles and the distribution is uniform. The original tailings have a wide particle size range. Most of the original tailings are distributed in the particle size range of 37–250 μm and are unevenly distributed, with the coarse grains accounting for a higher percentage. In the SEM images of the original tailings in Figure 4a,b, there are still a large number of incompletely dissociated minerals. Figure 4b shows the comparison of disseminated SE$_2$ (left) and AsB (right) of the original tailings. It can be seen that minerals with particle size of about 100 μm are disseminated with other minerals with a particle size of about 10 μm or finer. Fortunately, this is conducive to the generation of joint action during denitrification. The dominate particle size of the ordinary ball milling mixture is 2–37 μm, and the curve is basically in normal distribution. After mixing the raw ore and γ-Al$_2$O$_3$ for 5 h, γ-Al$_2$O$_3$ is fully dispersed into the raw ore, and most of the coarse-grained raw ore is reduced to the particle size close to that of γ-Al$_2$O$_3$. By comparing the SEM images of ordinary ball milling mixture in Figure 4c,d, it can be found that γ-Al$_2$O$_3$ is uniformly wrapped on the surface of mineral particles. The loose and porous γ-Al$_2$O$_3$ provides the acid site lacking in minerals and increases the specific surface area of the catalyst at the same time. After mixing for 5 h by high energy ball milling, three obvious peaks appear in the high energy ball milling mixture at 1, 15 and 90 μm, respectively. The 1 μm peak indicates that high energy ball milling has high speed and strong impact force, and compared with ordinary ball milling, the grinding effect is stronger and the tailings are ground to a finer particle size. As for the 15 μm peak, by comparing Figure 4c, we know that this peak is generated due to secondary spheroidization.
ball milling, the grinding effect is stronger and the tailings are ground to a finer particle size. As for the 15 μm peak, by comparing Figure 4e, we know that this peak is generated due to secondary spheroidization.

![Graph showing particle size analysis of minerals.](image)

**Figure 3.** Particle size analysis of minerals.

![SEM images](image)

**Figure 4.** SEM imaging of raw ore, ordinary ball milling mixture and high energy ball milling mixture; (a) SEM image of the original tailings; (b) comparison of SE$_2$ and AsB of original tailings; (c) the morphology of the catalyst of ordinary ball mill; (d) partially enlarged topography of the catalyst surface of ordinary ball milling; (e) SEM image of high-energy ball milling catalyst; (f) partially enlarged topography of the catalyst surface of high-energy ball milling.

2.5. Analysis of Specific Surface Area, Pore Volume and Pore Size of the Catalyst

Table 2 is the specific surface area, pore volume and pore size of the catalyst. As a porous medium, γ-Al$_2$O$_3$ has a larger specific surface area of 367.84 m$^2$/g and a smaller pore size of 6.68 nm. The specific surface area of tailings is small, which is 0.92 m$^2$/g, and the pore size is large, which is 11.73 nm. It can be seen from Table 2 that the addition of γ-Al$_2$O$_3$ provides the acid site lacked in the tailings and increases the specific surface area of the catalyst, which greatly improves the specific surface area, pore volume and pore size of γ-Al$_2$O$_3$-modified tailings. However, comparing the test results of γ-Al$_2$O$_3$-modified tailings prepared using two different ball milling methods, the specific surface area, pore volume and pore size of ordinary ball milling mixture are higher than those of high energy ball milling mixture, which is more conducive to the diffusion of NH$_3$ and NO. From the comparison of particle size analysis results, the rotational speed of high energy ball milling is higher than that of ordinary ball milling, for which cause the impact force of milling balls on the mineral is large. After 5 h of ball milling, minerals with catalytic activity are over grinded, and the space becomes smaller because of extrusion, which reduces the area that can react with gas, and finally lead to the decline of denitrification efficiency [25].
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Table 2. BET of the catalyst.

| Sample Name | Specific Surface Area (m²/g) | Pore Volume (ml/g) | Pore Size (nm) |
|-------------|------------------------------|--------------------|----------------|
| Sample 1    | 0.92                         | 0.0018             | 11.73          |
| Sample 2    | 200.93                       | 0.23               | 13.62          |
| Sample 3    | 195.26                       | 0.18               | 5.69           |
| γ-Al₂O₃     | 367.84                       | 0.42               | 6.68           |

2.6. NH₃-TPD, NO-TPD and H₂-TPR Analyses

2.6.1. NH₃-Temperature-Programed Desorption

The data shows that the NH₃-SCR reaction starts with the adsorption of NH₃, which is a key step of the reaction. The adsorption of NH₃ on the SCR catalyst largely depends on the acidity of the catalyst surface. To explore the adsorption capacity of the catalyst for NH₃-TPD, the adsorption and desorption experiments of NH₃-TPD on the γ-Al₂O₃-modified tailings were carried out, and compared with the original tailings. As can be observed in Figure 5 that Sample 1 has five desorption peaks, with the total desorption amount being 638.77 mmol/g, while Sample 2 has 6 desorption peaks, with the total desorption amount being 2789.97 mmol/g, and Sample 3 also has 6 desorption peaks, with the total desorption amount being 3085.90 mmol/g. The tailings treated by different ball milling methods all have desorption peaks below 200 °C, and those below 200 °C are usually weakly acidic sites. The desorption peaks generated are attributed to the desorption of NH₄⁺ at B acid site. Strong acid sites are above 200 °C, and the desorption peaks are generated because of the desorption of NH₃ at L acid site [26]. As can be observed in the figure that in the low temperature range of 100–200 °C, γ-Al₂O₃-modified tailings have desorption peaks, indicating that the tailings have been acid modified by adding γ-Al₂O₃. By increasing a large number of B acid sites, the NH₃ absorption capacity is enhanced, which gives rise to the significant increase of desorption peaks and desorption amount. Adsorption amount and sites also increase, and the desorption peaks move towards low temperature to facilitate desorption reaction. The reason that Sample 3 has the largest desorption peak area is because high energy ball milling ensures more uniform and tighter connection between tailings and γ-Al₂O₃. However, a prominent desorption peak at 500 °C appears because of over grinding of the tailings, due to which the surface of silicate, carbonate and phosphate are excessively exposed, causing strong adsorption of NH₃ and the adhesion of ammonia salt on the catalyst surface. Because of this, desorption reaction is difficult to occur at low temperatures. This is also the reason why the denitrification rate reaches the highest at 400 °C for catalysts prepared by high energy ball milling method.
2.6. NO-Temperature-Programed Desorption

Figure 6 is the NO-TPD spectrum of the original tailings and \(\gamma\)-\(\text{Al}_2\text{O}_3\)-modified tailings processed by different ball milling methods. It can be seen from Figure 6 that the original tailings have a smaller NO denitrification desorption amount, while that of \(\gamma\)-\(\text{Al}_2\text{O}_3\)-modified tailings is significantly higher. The NO desorption peak of ordinary ball milling mixture is stable at 350–700 °C and the temperature window is wide, which indicates that the reaction of NO adsorption and desorption is stable and is suitable for industrial production. There is a high NO desorption peak in the high energy ball milling mixture at 500 °C, which is caused by the same reason as that of desorption peak at 500 °C in the NH3-TPD spectrum.

2.6.3. \(\text{H}_2\)-Temperature-Programed Reduction

The strong redox property can improve the oxidation rate and oxidation activity of NO to \(\text{NO}_2\) conversion. Therefore, in order to study rare earth tailings and their redox ability after different ball milling and mixing \(\gamma\)-\(\text{Al}_2\text{O}_3\), the \(\text{H}_2\)-TPR characterization and analysis of each sample. As shown in Figure 7, the original tailings have three reduction peaks at 578, 621 and 712 °C, respectively. The ordinary ball milling mixture has four reduction...
peaks appeared at 421, 472, 548 and 668 °C, while high energy ball milling mixture has three reduction peaks at 435, 507 and 712 °C, respectively. The reduction temperature of the original tailings moves toward high temperature while that of γ-Al₂O₃-modified tailings moves toward the low temperature and has obvious reduction peaks. The positions of the reduction peaks of the three samples at high temperatures did not shift much, but the H₂ adsorption capacity was increased, indicating that the tailings mixed with γ-Al₂O₃ can improve the oxidation-reduction activity of the catalyst. Data show that reduction peaks in the temperature range of 400–600 °C are the reduction peak of adsorbed oxygen on the catalyst surface; those in the temperature range of 600–800 °C are the reduction peak of lattice oxygen on the catalyst surface [27]; the peak at 400–500 °C belongs to the overlapping peaks of Fe₂O₃ reduction to Fe₃O₄ and Ce⁴⁺ reduction to Ce³⁺ [28]. The peak at 500–600 °C is the reduction of Fe₃O₄ to FeO, and the peak above 700 °C is the reduction of FeO to elemental iron and the bulk CeO₂ structure [29]. By comparing the three samples, ordinary ball milling mixture has the most reduction peaks, the highest reducing capacity and the optimal denitrification activity.

![Figure 7. H₂-TPR of the catalyst before and after modification.](image)

3. Materials and Methods

3.1. Preparation of Catalyst Materials

Raw materials used in this experiment were taken from the tailings after magnetic separation and REE flotation in the Bayan Obo mining district in Inner Mongolia Autonomous Region of China [30]. The experimental samples were prepared by high energy ball milling and ordinary ball milling. The rotating speed was 1100 r/min and 600 r/min respectively; the mixing time was 5 h; 3 mm zircon balls were used; and the ratio of grinding media to material was 10:1. Ethanol (Damao manufacturer, Tianjin, China) of equivalent mass with the tailings was added as the process control agent (PCA) in the mixing process. The addition ratio of pseudo boehmite (γ-Al₂O₃, Jinghuo Technology Glass Co., Ltd., Dezhou, China) and tailings was 1:1. After mixing, the samples were put in the drying oven for drying at 50 °C for 10 min, and then taken out and granulated using a 20 mesh sieve. Finally, granulated samples were put into the microwave muffle furnace for calcination at 350 °C for 20 min. After cooling down to room temperature, the NH₃-SCR catalyst is obtained. The tailings calcinated in the microwave muffle furnace at 350 °C for 20 min is marked as Sample 1; the tailings added with γ-Al₂O₃ and processed by ordinary ball milling and calcinated in the microwave muffle furnace at 350 °C for 20 min is marked as Sample 2; and the tailings added with γ-Al₂O₃ and processed by high energy ball milling and calcinated in the microwave muffle furnace is marked at 350 °C for 20 min as Sample 3. The ball milling methods investigated in this paper are high energy ball milling and ordinary ball milling. The technology roadmap is shown in Figure 8.
3.2. Methods

3.2.1. Detection of Catalytic Activity

The catalytic activity detection system is composed of the gas distribution system, the reaction system and the on-line gas measuring system. The gas distribution system (gas mixing device) and the reaction system (vertical tube furnace) are manufactured by Nanjing Boyutong Instrument Technology Co., Ltd. (Nanjing, China) with models being GXD08-4E and VTL1600. The on-line gas measuring system uses Fourier Infrared Spectroscopy (FTIR) flue gas analyzer made in Finland for on-line measurement of flue gas composition and the model is GASMET-DX 4000 (Finland Gasmet Technologies Oy, Beijing, China). In this experiment, O\textsubscript{2} (pure O\textsubscript{2}, 99.5%), N\textsubscript{2} (equilibrium gas, 99.99%) and NO (standard gas, 10% NO) were used to simulate flue gas and the reducing agent was NH\textsubscript{3} (standard gas, 10% NH\textsubscript{3}). The gas flow of each component was controlled by a rotameter. The mixed gas was composed of 500 ppm NO and NH\textsubscript{3}, 6 vol% O\textsubscript{2} and N\textsubscript{2}, and the gas hourly space velocity was 8000 h\textsuperscript{-1}. In each experiment, 0.6 g of samples were weighed and placed in the heating section of the reactor, and then the reactor was heated from room temperature to the experimental reaction temperature of 150, 200, 250, 300, 350, 400 and 450 °C, with the heating rate of 10 °C/min. The FTIR flue gas analyzer and computer data acquisition system were used to measure the changes of NH\textsubscript{3} and NO on line. The reaction time of each sample was no less than 20 min. Finally, the conversion rate of NOx is calculated using the following formula:

\[ \eta = \frac{(NO)_{in} - (NO)_{out}}{(NO)_{in}} \times 100\% \]

\( \eta \)—conversion rate of NO under this working condition, %;
\( (NO)_{in} \)—inlet concentration of NO under this working condition, ppm;
\( (NO)_{out} \)—outlet concentration of NO under this working condition, ppm.

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**Figure 8.** Flow chart of catalyst preparation.
3.2.2. Characterization Method

X-ray diffractometer (D/MAX2500, PANalytical, Almelo, Netherlands) was used to analyze the crystal structure, with the range of diffraction angle 2θ being 10–90° and the scanning rate being 5°/min; X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Kyoto, Japan) was used for quantitative analysis of elements; and H2-temperature-programed reduction (H2-TPR) and ammonia temperature-programed desorption (NH3-TPD) experiments were carried out on the chemical adsorption instrument (PCA-1200, Biod Electronics, Beijing, China) to test the acid-base property and oxidation reducibility of the catalyst. Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area based on the N2 adsorption isotherm, and Barrett–Joyner–Halenda (BJH) equation was used to calculate the pore volume based on the N2 desorption isotherm. Particle size and particle size distribution were analyzed using the laser particle size analyzer (MALVERN 2000, Shanghai, China).

3.2.3. Experimental Equipment and Model

The experimental equipment and models are shown in Table 3.

| Equipment Name                              | Model                        | Factory                                      |
|---------------------------------------------|------------------------------|----------------------------------------------|
| Electronic balance                          | TE2101-L                     | Germany Sartourius (Guxhagen, Germany)       |
| Ordinary ball mill                          | BSA124S                      | Germany Sartourius                           |
| High energy ball mill                       | BM04                         | Nanjing Kangye Optical Technology Co., Ltd. (Nanjing, China) |
| Microwave roaster                           | PM0.4L                       | Changsha Deke Instrument Equipment Co., Ltd. (Changsha, China) |
| 20 mesh standard sieve                      | CY-R01000C-S                 | Hunan Changyi Microwave Technology Co., Ltd. (Changsha, China) |
| X-ray diffractometer                        | D/MAX2500                    | PANalytical (PANalytical, Almelo, Netherlands) |
| X-ray fluorescence                          | LABCENTER XRF-1800           | Shimadzu (Kyoto, Japan)                      |
| scanning electron microscope                | X-3400                       | Hitachi (Tokyo, Japan)                       |
| Energy spectrometer                         | INCA 3294                    | Oxford Instruments (Oxford, United Kingdom)  |
| Chemisorption Apparatus                     | PCA-1200                     | Biod Electronics (Beijing, China)            |
| Vertical tube furnace                       | VTL1600                      | Nanjing Boyuntong Instrument Technology Co., Ltd. (Nanjing, China) |
| Blast drying box                            | FCD-3000                     | Huitai Instruments (Dongwan, China)          |
| Specific surface area and pore size analyzer| 3H-2000PS1                   | Best Instrument Technology Co., Ltd. (Changsha, China) |

4. Conclusions

Bayan Obo rare-earth tailings are rich in Fe, Ti, Ce, Mn and other minerals that can be used as active carriers, and Al, Si and other minerals that can be used as rigid carriers, making Bayan Obo a natural advantage as a denitrification catalyst carrier.

By comparing the two different ball milling mixing methods, although the catalyst after the ordinary ball milling mixture does not have the high-energy ball milling catalyst γ-Al2O3 and the minerals are tightly combined, the minerals have not been over-milled, and the loose structure provides a larger specific surface area of 200.93 m²/g, the highest NOx conversion rate of 90% is achieved at 300 °C, H2-TPR has four reduction peaks at 421, 472, 548 and 668 °C. Although the combination of minerals and γ-Al2O3 is tighter for the catalyst after adopting high-energy ball milling mixture, due to the fierce collision between the high-energy ball milling particles, the mineral has over-milled phenomenon and its specific surface area is reduced to 195.26 m²/g, the maximum denitrification activity 61.5% is reached at 400 °C, H2-TPR only shows three reduction peaks at 435, 507 and 712 °C.

The XRD results show that the dispersion of active components in the catalyst prepared by ordinary ball milling is better than that of the catalyst prepared by high energy ball milling, and most of them decompose into amorphous state, which provides a higher denitrification activity.
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