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Prepare a catalyst consist of rare earth minerals to denitrate via NH_3 -SCR

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Abstract: To research the roles of rare earth minerals in denitrification via the NH_3 -SCR, a mixture was made by certain ratio of rare earth concentrates and rare earth tailings, then treated by microwave roasting, and acids and bases to form a denitrification catalyst. The mineral phase structure and surface morphology of the catalyst were characterized by XRD, BET, SEM and EDS. The surface properties of the catalyst were tested by TPD and XPS methods, and the denitrification activity of the catalyst was evaluated in a denitrification reactor. The results showed that the denitrification efficiency increased up to 82% with complete processing. XRD, BET, SEM, and EDS spectrum analysis stated that the treated minerals contained cerium oxides and Fe–Ce composite oxides. The surface of the modified minerals became rough and porous, the surface area increased, and the surface-active sites were exposed. The results of NH_3 -TPD and NO-TPD showed that the catalyst surface could gradually adsorb more NH_3 and NO after each step. XPS analysis indicated that there were more Ce^{3+} , Fe^{2+} , and lattice oxygen in rare earth minerals catalyst after each treatment step.

Keywords: denitrification; rare earth concentrates; rare earth tailings; microwave; catalysis

1 Introduction

NO_x is one of the major atmospheric pollutants and an important precursor to cause acid rain and photochemical

smog. Excessive emissions pollute the environment and damage human health. With the increasing awareness of environmental protection, the National Environmental Protection Department has set strict limitations for NO_x emission. How to reduce NO_x emissions has become a research hotspot around the world. At present, selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR) is the most developed technique to reduce NO_x emissions.

Many denitrification catalysts are used in NH_3 -SCR because of its importance. Ren et al. used Keggin-tungstophosphoric acid decorated Fe_2O_3 nanoring as a new catalyst for selective catalytic reduction of NO_x by ammonia. This catalyst has a wide denitrification reaction temperature range, and the NO_x conversion rate is higher than 92% in the range of 230–500°C. Additionally, the catalyst exhibited an excellent SO_2 -resistance capacity [1,2]. WO_3 -doped Fe_2O_3 catalyst was investigated by Liu et al. for NH_3 -SCR. It was found that the highly dispersed WO_3 acted as both “chemical” and “structural” promoters, which inhibited the crystallization of the Fe_2O_3 phase and increased the surface area. Synergistically denitrate of highly dispersed WO_3 and Fe_2O_3 enhanced NH_3 -SCR performance [3]. Fe–Ce–Ti catalyst made by Liu et al. via the hydrothermal method was found that it had a good denitrification activity and strong resistance against H_2O and SO_2 [4].

Wei et al. used transition metals (Co, Zr, Ti) modified iron-oxide as another efficient catalyst for NH_3 -SCR. Titanium was the most suitable assistant in the three transition metals which could improve the NH_3 -SCR activity, broaden the reaction temperature range and improve the N_2 selectivity. When the molar fraction of titanium was 0.15, the NH_3 -SCR reaction could reach its highest NO conversion rate up to 95% between 150°C and 300°C [5]. Adding LnPW increased the NH_3 -SCR activity of the iron oxide catalysts. The conversion rate of NO_x was highest when the doped content of NdPW was 25% [6].

Mn/TiO₂ and Mn–Fe/TiO₂ catalyst has been prepared by impregnation and deposition-precipitation techniques. The results indicated that the catalyst prepared by the deposition precipitation and impregnation technique has higher activity. The deposition precipitation method of preparation lowered the metal loading requirement to reach the optimum activity compared to the impregnation method [7].

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Most of the mentioned catalysts used in denitrification were prepared through artificial synthesis. However, they indeed have remarkable denitrification performances, but they cannot be applied widely and easily in industries because of expensive raw materials, complex preparation, and difficult treatment if failure happens. Natural Bayan Obo rare earth ore contains a large number of transition metals, rare earth metals, alkali metals and alkaline earth metals, and these metals are widely used in denitrification catalysts. The purpose of this article is to use natural Bayan Obo raw materials for microwave roasting and acid-base treatment. Based on the current denitrification technologies and previous research results, the feasibility of natural minerals as denitrification catalysts is preliminarily discussed.

2 Experimental

2.1 Catalysts preparation

The rare earth tailings and concentrates with a particle size of $48\ \mu\text{m}$ were 1:1 mixed. Different weights of Na_2CO_3 and $\text{Ca}(\text{OH})_2$ were added and ground for 2 h. Then the mixture was placed in a microwave roaster for 15 min. 0.1 mol of hydrochloric acid and 0.01 mol of citric acid were prepared separately, the calcined minerals and the acid solutions were mixed together and stirred at a mass ratio of 1:10 for 2 h, filtered the mixture solution, and then

air dried the sediment. The obtained solid was a prepared denitrification catalyst.

2.2 Activity test

Figure 1 shows a schematic diagram of experimental apparatus. The experimental devices were composed of a gas supply system, a fixed bed reaction system, and a flue gas analysis system. The simulated industrial flue gas was formed by mixing four channels of gas (NO , CO , N_2 and NH_3) through a mixing tank. The reactor was a vertical tube furnace, and the flue gas analyzer used was an FTIR gas analyzer, model number GASMET-DX4000.

Each experiment used a gas mixture of 500×10^{-6} NH_3 , 500×10^{-6} NO , 3% O_2 , and the remainder was N_2 as a balancing gas. The heating rate was $10^\circ\text{C}/\text{min}$, the reaction temperature range was $100\text{--}500^\circ\text{C}$, the measurement of the conversion rate of NO was performed every 50°C , the total gas flow rate was $100\ \text{mL}/\text{min}$, and the space velocity was $25000\ \text{h}^{-1}$. The conversion rate of NO , η_{NO} was calculated with the following equation:

$$\eta_{\text{NO}} = \frac{(C_{\text{NO},\text{inlet}} - C_{\text{NO},\text{outlet}})}{C_{\text{NO},\text{inlet}}} \times 100\% \quad (1)$$

where $C_{\text{NO},\text{inlet}}$ represents the NO concentration at the reactor inlet, and $C_{\text{NO},\text{outlet}}$ represents the NO concentration at the reactor outlet.

Figure 1: Reaction device schematic.

Table 1: Element analysis (wt%).

Element analysis of rare earth tailings (wt%)										
Fe	Ce	La	Nd	Pr	O	Ca	Mn	F	Si	Others
25.60	3.39	1.79	1.00	0.31	30.50	23.50	2.24	7.49	2.43	1.75
Element analysis of rare earth concentrates (wt%)										
Ce	La	Nd	Pr	Fe	O	Ca	P	F	Mn	Others
16.06	10.12	10.53	2.55	10.36	11.96	19.21	11.63	5.67	0.58	1.33

2.3 Catalyst characterization

The test equipment included an X-ray diffractometer (PANalytical B.V., Almelo, The Netherlands), a Sigma-500 field emission scanning electron microscope (Zeiss, Jena, Germany), a PCA-1200 temperature programmed chemical adsorption instrument (Builder, Beijing, China), and a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

3 Results and discussion

3.1 Analysis of rare earth minerals components

Some of materials major elements are listed in Table 1. The main elements in the rare earth tailings were Fe, O and Ca, which together were 79.6% of the tailings. There were smaller concentration of the rare earth elements La, Ce, Pr and Nd, with a combined content of 6.49%, and there was 2.24% Mn. The rare earth elements La, Ce, Pr, and Nd together were 39.26% of the rare earth concentrates. The Fe and Mn percentages were low at 10.36% and 0.58%, respectively, and the Ca content was 19.21%. Table 1 shows that transition metals, rare earth metals, alkali metals, and alkali earth metals are contained in both tailings and concentrates, suggesting that the combination of tailings and concentrates could be efficient catalysts. It can be seen from the XRF analysis that after the rare earth concentrates and the rare earth tailings are mixed, the content of transition elements and rare earth elements was uniform, which was beneficial to the combined denitrification.

The XRD analysis described in Figure 2 shows that the rare earth tailings mainly included bastnaesite, hematite, fluorite, and quartz. The tailings contained other mineral phases, such as iron-silicate minerals and carbonate minerals, but their content was too small to be detected by XRD. Fluorite had the highest peak

Figure 2: XRD of rare earth tailings.

intensity, indicating a stable crystal form and the highest percentage, which corresponds to the XRF elemental analysis in Table 1. The peak intensity of the hematite phase and the bastnaesite phase were relatively low, and the half peak width was wide, which indicates that the crystal form had low maturity and good dispersion. The reason was that the hematite and bastnaesite in the rare earth tailings are fine-grained minerals phases, and most of them are wrapped-type continuous bodies containing fluorite.

The XRD analysis results in Figure 3 show that the rare earth concentrates included various mineral phases, mainly bastnaesite, monazite, fluorite, and fluorapatite. Among them, bastnaesite and monazite had the highest peak intensity, indicating stable crystal forms and the highest percentages, which was consistent with XRF elemental analysis. The peak intensity of fluorite and fluorapatite was lower, and the half peak width was wide, which means that the crystal form had lower maturity and greater dispersion. The reason was that the fluorite and fluorapatite in rare earth concentrates have mostly fine-grained minerals phases, and most of them have wrapped-type continuous bodies containing bastnaesite and monazite.

Figure 3: XRD of rare earth concentrates.

3.2 Denitrification activity

3.2.1 Effects of different ratios of tailings and concentrates on the denitrification activity

When a large number of fluorite additives are added during the mixing of the rare earth minerals [8], a composite oxidation catalyst composed of hematite, iron-bearing carbonate minerals, and silicate minerals from tailings, and bastnaesite and monazites from concentrates form.

In the first step, the tailings and concentrates were mixed and ground in various proportions. The mixing ratios were selected as 0:1, 1:2, 1:1, 2:1, and 1:0. Figure 4 showed changes in the NO conversion rates with increasing temperature.

In the reaction temperature range from 100°C to 500°C, the average denitrification rate of the mixing minerals catalyst was only 15%. In the reaction temperature range from 300°C to 400°C, the denitrification rate of 1:1 mixing ratio was the higher than other ratios, and the highest denitrification rate was 25% at 350°C. It can be seen that the active components in tailings and concentrates are both promoted and restricted. The mixing ratio was chosen as 1:1 for next steps because it is the optimum mixing ratio.

3.2.2 Effects of microwave roasting temperature on denitrification activity

Microwave roasting was chosen to prepare rare earth minerals catalyst to increase heating rate and shorten roasting time. From chemical and mineral composition analysis, rare earth tailings had a higher iron element content that mostly existed in iron oxide and various iron-containing salt mineral phases. The tailings are ideal absorption materials,

Figure 4: Comparison the denitrification rate for different tailings and concentrates mixing ratios.

the monazite is weak absorption material and the fluorite and quartz are non-absorption materials.

The thermal effect principles for microwave absorption materials in microwave roasting determine the characteristics of the overall heating mode. While being heated, strong microwave absorption materials raise temperature rapidly, but weak absorption and non-absorption materials cannot. This phenomenon causes a large temperature gradient in materials. Because of the different thermal stresses among the mineral phases, the internal mineral structure collapses, changing the mineral pore structure and increasing the surface area. General mineral absorption microwave performance is weak, but after microwave roasting, the crystal particles interact with each other and form different types of magnetic media and dielectrics. In the microwave electromagnetic field, the magnetic and dielectric losses are enhanced, thus improve the absorption characteristics. On the one hand, due to the thermal effect of microwave, cracks and pores generate and increase the surface area and active sites of the catalyst. This corresponds to the results shown in Table 3. On the other hand, the microwave thermal and non-thermal effects with a large number of fluorite mineral additives promote the decomposition of bastnaesite in concentrates and iron-bearing minerals in the tailings. Non-melted substances such as iron, manganese, and rare earth metals migrate and diffuse to increase the chaos and dispersion of the active materials. This converts the stable crystalline phase to an amorphous composite oxide, which improves denitrification.

The second step of the preparation was to test the effects of different microwave roasting temperatures on the catalyst's denitrification performance. The mixing minerals were roasted at 200°C, 250°C, 300°C, 350°C, 400°C, 450°C, and 500°C. The temperature of the roasted

Figure 5: Comparison the denitrification rate for different microwave roasting temperatures.

minerals increased from 100°C to 500°C while measuring the NO conversion rate. The results were shown in Figure 5 that the denitrification efficiency of the sample initially increased with temperature rising, reached the highest conversion rate at 350°C, and then gradually went down. When the roasting temperature was over 500°C, it cannot boost the efficiency any more. At the roasting temperature of 350°C, the sample showed the best denitrification activity with a 40% denitrification rate because the bastnaesite and the monazite were directly decomposed by heat and exposed the active components. After the roasting temperature was higher than 400°C, the mineral surface had different degrees of sintering that inhibited the denitrification rate. The maximum denitrification rate of the sample roasted at 500°C was only 31%. Therefore, the research determined that the optimum microwave roasting temperature was 350°C.

3.2.3 Effects of different roasting methods on denitrification activity

This part studied whether there was a difference between an ordinary muffle furnace and the microwave roaster in denitrification rate for mixed minerals. Muffle furnace heating temperatures were selected as 300°C, 400°C and 500°C. The results were shown in Figure 6. Compared with microwave roasting, for the reaction temperature range from 250°C to 500°C, the denitrification efficiency after roasting in the muffle furnace was lower at 350°C. When the roasting temperature was 500°C, the peak denitrification rate was only 32%, compared to 40% for the microwave roasting technique at 350°C. When the mixed minerals were calcined in a muffle furnace, the surface

Figure 6: Comparison the denitrification rate for the microwave roasting and the muffle roasting at different temperatures.

of the mineral particles was easily sintered, reducing the surface area and surface-active sites.

As mentioned above, for microwave roasting, the relationship between the microwave absorption substances and the weak or non-absorption substances in the mixed tailings and concentrates causes the differences between ordinary muffle furnace roasting and microwave roasting. The various mineral phases containing rare earth elements and iron elements were separated from the other mineral phases along the dissociation surface. This process, as well as the micromigration diffusion of a variety of active components, resulted in an increase in the dispersion of the active components and the number of active sites. Therefore, the research concluded that the preparation of mineral catalytic materials by microwave heating has great application prospects.

3.2.4 Effect of bases addition amount on denitrification activity

This section was to study the effect of adding different amounts of bases in the mixing minerals on the denitrification performance after microwave roasting. Original sample added 1.5 g Na_2CO_3 powder and 2.3 g $\text{Ca}(\text{OH})_2$ powder into 6.2 g mixed minerals to make the $\text{Ca}(\text{OH})_2$ 23% of the mixture and the Na_2CO_3 15% for a total bases mass percentage 38%. The amounts of bases added in other four trials were 1/2, 1/4, 1/8, and 1/10 compared to the original amount. The experimental results were shown in Figure 7. With the amount of bases added decreasing, the denitrification rate increased. The bases content of 1/10 of the original amount (or 3.8% by mass) corresponded to the maximum denitrification rate of

Figure 7: Comparison the denitrification rate for the different addition of bases amounts.

the sample. In the reaction temperature range of 100°C to 500°C, the denitrification rate increased gradually, reached a maximum of 70% at 400°C, and then decreased.

Bases roasting could make pores on the surface of particles, increase the surface area and expose more active components. The results corresponded to the results in Table 3. During the microwave roasting of mixture with bases, the bases further increased the decomposition of the bastnaesite and monazite in the concentrates and accelerated the microscopic migration and diffusion of various active components. The bases promoted the formation of Ce-Fe-Mn-other metals symbiotic oxide-type mineral catalysts containing active components, such as rare earth elements, iron, manganese, and other transition elements. The 3.8% by mass bases had the best effects on the decomposition of bastnaesite.

3.2.5 Effects of acids concentration on denitrification activity

Next step explored whether adding different concentrations of hydrochloric acid and citric acid into mixed minerals after microwave roasting would cause differences on the denitrification performance. Two combinations of acids were selected. (1) 1 mol/L hydrochloric acid and 0.5 mol/L citric acid and (2) 0.1 mol/L hydrochloric acid and 0.01 mol/L citric acid. Figure 8 showed that the low-concentration mixture of acids led to higher denitrification activity, and the maximum denitrification rate of the sample reached 82% at the reaction temperature of 350°C.

The higher concentrations of acids corroded the surface-active sites of the mineral crystal phase,

Figure 8: Comparison the denitrification rate for different acid concentrations.

dissolved the active components and reduced the number of active sites on the surface of sample, resulting in a decrease of denitrification efficiency. The addition of the lower concentration acids changed the surface morphology of the mineral, increased the number of active sites, and enhanced the adsorption of NH_3 . It also reacted with quartz and fluorite to further accelerate the non-determination of the more active components in the mineral phase. This result was consistent with the decrease in peak intensity and the broadening of the half-peak width of the XRD analysis of bastnaesite as described below in Figure 10. The better acid concentration was 0.1 mol/L hydrochloric acid and 0.01 mol/L citric acid.

3.2.6 Denitrification activity of progressive processing

The research prepared four samples (Table 2) to test a process for obtaining the most efficient catalyst. The rare earth tailings and the rare earth concentrates were mixed and ground in a 1:1 mixture ratio to obtain Sample 1. Sample 1 was microwave roasting at 350°C for 15 min to obtain Sample 2. Sample 1 was mixed and ground with 0.15 g of Na_2CO_3 and 0.23 g of $\text{Ca}(\text{OH})_2$, and then roasting at 350°C for 15 min to obtain Sample 3. To obtain Sample 4, Sample 3 was acids-treated by adding 0.1 mol/L hydrochloric acid and 0.01 mol/L citric acid. The denitrification rates were measured for each sample. Figure 9 shows that the maximum denitrification rate was 25% for Sample 1, 40% for Sample 2, 70% for Sample 3, and 82% for Sample 4, showing that the steps were used for the preparation of these samples was an efficient way to prepared catalyst.

Table 2: Preparation procedure and test plan of mineral denitrification catalyst.

Sample serial number	Raw material	Sample preparation					Sample	Test items
		Grinding	Mixing	Roasting				
				Mode	Temperature	Time		
Sample 1	tailings + concentrates	2 h	—	microwave	150°C	15 min	Mixed mineral	DR XRD BET SEM NH ₃ -TPD NO-TPD
Sample 2	tailings + concentrates	2 h	—	microwave	150°C	15 min	Microwave roasting mixed mineral	DR XRD BET SEM NH ₃ -TPD NO-TPD XPS
Sample 3	tailings + concentrates + Na ₂ CO ₃ + Ca(OH) ₂	2 h	—	microwave	150°C	15 min	Adding alkali to microwave roasting mixed mineral	DR XRD BET SEM NH ₃ -TPD NO-TPD XPS
Sample 4	tailings + concentrates + Na ₂ CO ₃ + Ca(OH) ₂ + HCl + C ₆ H ₉ O ₇	2 h	2 h	microwave	150°C	15 min	Adding alkali to microwave roasting mixed minerals and pickling	DR XRD BET SEM XPS NH ₃ -TPD NO-TPD EDS

where: DR – denitrification rate; XRD – X-ray diffraction; BET – Brunauer-Emmett-Teller; SEM – scanning electron microscope; TPD – temperature programmed desorption; EDS – energy dispersive spectrometer; XPS – X-ray photoelectron spectroscopy

Figure 9: Comparison the denitrification rate for progressive treatment process.

3.3 Catalyst characterization

3.3.1 XRD characterization of catalysts

The formation of cerium oxides in the mixed minerals was important for improving its catalytic action. It has been reported that the formation of cerium oxides from CeCO₃F could be divided into three stages [9,10]. First, when CeCO₃F was calcined in air, it would become CeOF. Second, the CeOF decomposed to form Ce₂O₃. Third, most of Ce₂O₃ were converted to Ce₇O₁₂. As shown in Figure 10, peaks for CeCO₃F and Ce₇O₁₂ in the XRD plot were found when a sample was heated to 350°C, indicating that some

Figure 10: XRD of the different samples roasting at 350°C.

CeCO₃F was not converted at this temperature. Because the amounts of CeOF and Ce₂O₃ in the minerals were small, and the characteristic peak of Ce₂O₃ was very close to the characteristic peak position of Ce₇O₁₂, the characteristic peaks of CeOF and Ce₂O₃ were not observed. Because Ce³⁺ was contained in CeOF, Ce₂O₃, and Ce₇O₁₂, the content of Ce³⁺ would increase.

When processing the Sample 3, the effect of adding Ca(OH)₂ was to accelerate the decomposition rate of CeCO₃F [11], and adding Na₂CO₃ was to promote the conversion of CeOF to CeOF–CeO-like mixing crystals, which increased the amount of CeOF and cerium oxides [12]. Figure 11 showed the XRD plot for the roasting of Sample 4 at 500°C. There was a peak for Ce₇O₁₂ showing that the CeOF and Ce₂O₃ were converted to Ce₇O₁₂. The peak for bastnaesite

has disappeared, indicating that the decomposition of bastnaesite was complete at this temperature. This limits the amount of Ce^{3+} . The peak intensity was related to the absolute content, and the peak intensity was lowered, indicating that the substance was consumed. Figure 10 showed that the peak intensity of Fe_2O_3 also had a downward trend. This indicated that microwave roasting [13] and the addition of bases cause Fe_2O_3 and some other iron salts to react with the decomposition products of CeCO_3F to form Fe–Ce composite oxides.

3.3.2 BET characterization of catalysts

Table 3 showed the surface areas (m^2/g), pore volumes (cm^3/g), and average pore diameters (nm) of the four samples. The table showed that the surface area of the untreated mixed minerals was only $2.5895 \text{ m}^2/\text{g}$, but it

increased to $5.3946 \text{ m}^2/\text{g}$ after microwave roasting. Then the bases was added, the surface area of the sample increased to $7.8211 \text{ m}^2/\text{g}$.

3.3.3 SEM characterization of catalysts

Figure 12 showed SEM images of four samples. Figure 12a showed that Sample 1 had relatively smooth surfaces with no obvious pore structure or cracks, and some small particles were clustered together. Figure 12b (Sample 2) showed that after microwave roasting at 350°C , some large particles broke into small particles, increasing surface area. The particle distribution was relatively uniform, and there was no obvious clustered. Internal heating of the microwaves eliminated the cold center of the material, and due to the different microwave absorbing properties of each mineral phase in the samples, the internal particles produce a force from the inside to the outside [14–18], causing large particles to break into small particles, increasing the surface area.

Figure 12c (Sample 3) showed that after adding the bases, there were obvious deep cracks on the larger particles. In summary, the combination of microwave roasting and the addition of bases could make smaller particle sizes, larger pores, and more cracks, all of which

Figure 11: XRD of Sample 2/4 roasting at 500°C .

Table 3: Physical properties of different samples.

Samples	Sample 1	Sample 2	Sample 3	Sample 4
Surface area (m^2/g)	2.5895	5.3946	7.8211	7.6745
Pore volume (cm^3/g)	0.0368	0.0476	0.0431	0.0403
Average pore diameter (nm)	13.99	16.49	17.63	17.44

Figure 12: SEM diagram of different samples: (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4.

lead to a more surface area, which was one of the important reasons that improved efficiency of denitrification.

Finally, Figure 12d (Sample 4) showed that after the acids-treatment, the surface of cracks was wavy. Although the acids concentration was very low, there was still a significant corrosive effect on the surface of the particles to increase the surface roughness. The surface area of the acids-treatment minerals was not significantly different from that after the addition of the bases. This showed that although the acids could corrode the surface of the particles, it did not have a great influence on the surface area of the materials. Therefore, the main effect of adding acids on the samples was to increase the surface acid sites, making it easier for NH_3 and NO to be adsorbed.

3.3.4 NH_3 -TPD characterization of catalysts

Figure 13 showed a comparison of NH_3 -TPD signals between different processing steps. This figure showed that there was almost no occurrence of desorption of NH_3 in the mixed minerals before any treatment. After microwave roasting, a slightly higher desorption peak appeared, and the peak temperature of the sample advanced by about 30°C . The desorption peak was enhanced after microwave roasting with bases. After acids washing, the desorption peak was significantly enhanced. Acids washing caused the particle surface to become rougher and more porous, and it increased the acid sites, making it easier for NH_3 to be adsorbed.

3.3.5 NO-TPD characterization of catalysts

Figure 14 showed the comparison of the NO-TPD signals between each of the four treatment samples. As with NH_3

adsorption, the desorption peaks after each step had a corresponding increase, and the ability of Sample 4 to adsorb NO was significantly enhanced. As with the NH_3 -TPD results, acids treatment after microwave roasting with bases could increase the active sites on the surface of the sample and make it easier to adsorb NO. From the results of NH_3 -TPD and NO-TPD tests, it can be found that the adsorption capacity of NH_3 and NO significantly increased by acids treatment after microwave roasting with bases. The increase in adsorption capacity facilitated the denitrification reaction.

3.3.6 EDS characterization of catalysts

Figure 15 showed the EDS images for Sample 4 after the complete treatment. The EDS images showed that the main elements were Fe, O, F, Ca, and rare earth elements. The samples contained a large amount of CaF_2 , and the positions of fluorine and calcium in the EDS images were far apart, so it excluded the possibility that all of the fluorine was in the form of CaF_2 . From the XRD results, cerium oxides such as CeOF and Ce_2O_3 were found in mixture. Figure 13 showed that the distribution of F, O, and the rare earth elements were concentrated. Therefore, CeOF and other cerium oxides were present where F, O and rare earth elements were aggregated. After conversing CeOF to cerium oxides, the fluorine remained in the crystal lattice. Therefore, the addition of bases had an effect on fixing the fluorine. Therefore, during the process, the fluorine remained in the crystal lattice. The XRD results showed that the distributions of Fe, Ce, and O partially overlap, suggesting that a Fe–Ce composite oxide formed which improved the denitrification activity.

Figure 13: NH_3 -TPD diagram for the different samples.

Figure 14: NO-TPD diagram for the different samples.

Figure 15: EDS spectra diagram for Sample 4.

Figure 16: XPS diagram of Sample 2: (a) Ce 3d, (b) Fe 2p, and (c) O 1s.

3.3.7 XPS characterization of catalysts

The changes in the element valence played an important role for denitrification catalysts. For example, the changes of the oxidation states of cerium and iron ions greatly contributed to the increase in denitrification activity. The change in the oxidation state of cerium ions ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$) was often accompanied by the appearance of oxygen vacancies [19-24]. The conversion between adsorbed oxygen and lattice oxygen could increase the amount of active oxygen and improve the denitrification efficiency. In experiment, Ce, Fe, and O were detected by the XPS in Samples 2, 3, and 4. The oxidation state changes of these three elements were determined, and the concentration of Ce^{3+} and Fe^{2+} [2,25] could be used to explain why the denitrification activity increased.

Figure 16 showed the XPS results for Sample 2. The sample had 29% Ce^{3+} and 32% Fe^{2+} in the mineral itself, and the rest formed the amorphous composite oxide crystal phase after microwave roasting and the ions migrate and diffuse. All of the oxygen was adsorbed.

Figure 17 showed the XPS results for Sample 3. After adding bases, the percentage of Ce^{3+} increased from 29% to 37%, indicating that adding bases promoted the decomposition of bastnaesite and monazite into CeOF and Ce_2O_3 . This result corresponds to the XRD pattern in Figure 10. The sample also had 49% Fe^{2+} , 73% adsorbed oxygen, and 27% lattice oxygen, showing that the addition of bases led to an increase of Fe^{2+} and helped the adsorbed oxygen convert to the more active lattice oxygen. The reason was that after microwave roasting, an unstable composite oxide in the mixing minerals was formed due to Fe doping from the hematite and iron-bearing carbonate of the tailings, and the Ce in the bastnaesite from the concentrates.

Figure 18 showed the XPS result for Sample 4. The sample contained 43% Ce^{3+} , 55% Fe^{2+} , 70% adsorbed oxygen, and 30% lattice oxygen. Compared with the acid-free minerals, the content of Ce^{3+} and Fe^{2+} increased by 6%. The reason was that after the roasting, the amorphous Ce-Fe composite oxide in Sample 3 was more fully exposed on the outer surface of the mineral. Relevant data proved that the increase in the Fe^{2+} content had a great

Figure 17: XPS diagram of Sample 3: (a) Ce 3d, (b) Fe 2p, and (c) O 1s.

Figure 18: XPS diagram of Sample 4: (a) Ce 3d (b) Fe 2p (c) O 1s.

effect on improving the denitrification efficiency [26,27]. At the same time, a large amount of adsorbed oxygen was converted to lattice oxygen, which benefited the denitrification reaction.

4 Conclusions

In this study, rare earth tailings and rare earth concentrates were mixed in different ratios, then the mixture was processed by certain steps to prepare catalysts with a denitrification rate up to 82%, showing that it was feasible to prepare denitrification catalysts using rare earth minerals as raw materials. Denitrification activity tests and sample characterization were conducted to determine that the best conditions for the preparation of the catalyst is that minerals were mixed with the bases, then subjected to microwave roasting, and finally pickled. Microwave roasting was selected in this article because it could lower the roasting temperature and shorten the roasting time. Microwave roasting made cracks on the surface of the mineral after roasting, which increased the surface area of the mineral. Adding bases increased the decomposition rate of bastnaesite, and created pores on the surface of mineral particles, allowing more active components to be exposed. Low-concentration acids treatment modified the mineral surface to increase the

mineral surface acid sites, making it easier for NH_3 and NO to be adsorbed. After each step, the contents of Ce^{3+} and Fe^{2+} increased, which promoted the conversion of adsorbed oxygen to lattice oxygen. This also had the effect on promoting the denitrification reaction. In summary, efficient denitrification catalysts could be prepared by microwave roasting of mixture of minerals and bases, followed by treatment with acids.

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