

Comparative Study on NH₃-SCR of High Entropy Mineral Catalytic Materials for Different Ratios of Rare Earth Concentrate/Rare Earth Tailing

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A series of high-entropy mineral catalytic materials were obtained by mixing rare earth tailings containing Fe oxide and rare earth concentrate rich in Ce in Baiyun Obo in different proportions, and by acid-base leaching and microwave roasting. The effects of different proportions of mixed rare earth minerals on the denitrification activity of the samples were analyzed by various techniques, including XRD, EDS and SEM. The mineral phase structure and surface morphology of the catalysts were analyzed. The surface properties of the samples were tested by TPD and XPS methods. The denitrification activity of the sample was simultaneously evaluated and compared in the microreactor. The results show that the denitration efficiency of the active powder is the best when the mixing ratio of rare earth tailings/rare earth concentrate is 1:1, the denitration rate can reach 82%. In summary, different proportions of optimization are extremely effective methods to improve catalyst performance.

Keywords: rare earth concentrate; rare earth tailings; catalytic denitrification; modification; mineral catalysis.

INTRODUCTION

NO_x is a major air pollutant, which seriously endangers human health and plant growth, leading to acid rain, global warming, and ozone depletion. Effective removal of NO_x has always been a concern¹⁻². Ammonia selective catalytic reduction (NH₃-SCR) technology is one of the most effective means of flue gas denitration technology. The core of this technology lies in the development of catalysts to eliminate NO_x pollutants³⁻⁴.

At present, the most widely used commercial catalyst is a vanadium catalyst. Unfortunately, it has the following disadvantages: strict temperature window limitation, poor low-temperature activity, easy sublimation at high temperature, and biotoxicity⁵. In recent years, a large number of scholars have systematically studied the catalysts with high denitrification activity. Wang Xiaobo et al.⁶ prepared a series of Fe-Mn/AL₂O₃ catalysts and investigated the low-temperature selectivity of NH₃ on a fixed bed. The performance of the catalytic reduction of NO firstly investigated the denitrification performance of catalysts prepared with different Fe loadings and optimized the Fe loading. The results show that Fe is mainly in the form of Fe³⁺ on the surface of the catalyst, and the optimal load of both Fe and Mn is 8 wt%. Ma Jiewen et al.⁷ prepared a series of Fe₂O₃/SAPO-34 catalysts by urea precipitation method and investigated the catalyst calcination temperature (200, 300, 400 and 500°C) for low-temperature NH₃. The effect of selective catalytic reduction (NH₃-SCR) on NO performance indicates that the highly dispersed Fe₂O₃ exposes the catalyst to more strong acid sites and active sites, which is beneficial to the catalyst. NH₃ adsorption and activation ability and redox performance. Xiong Zhibo et al.⁸ prepared iron-based catalysts with high denitrification activity by the co-precipitation method. The effects of doping and other additives on the denitrification performance of iron-based catalysts were studied by the microwave hydrothermal method. The results show that the doping of cerium oxide

leads to an increase in the denitrification performance of iron oxide in medium and low-temperature SCR. Zhang Xinli et al.⁹ prepared a series of Mn-modified γ-Fe₂O₃ catalysts (Fe_{0.7}Mn_{0.3}O_z) by coprecipitation at different calcination temperatures. The influence of calcination temperature on Fe_{0.7}Mn_{0.3}O_z catalyst was studied. Moreover, the effect of low-temperature SCR denitrification activity has been revealed. The results show that the Fe_{0.7}Mn_{0.3}O_z catalyst obtained at 350°C has the best low-temperature SCR activity, and the catalysis has the largest specific surface area and specific pore volume, developed pore structure and proper crystallinity of γ-Fe₂O₃. Zhou Fei et al.¹⁰ constructed a novel magnetic iron-titanium complex oxide catalyst by coprecipitation microwave method and studied the effect of calcination temperature on its physical structure and NH₃-SCR denitrification performance. The results show that when the calcination temperature is raised from 300 to 500°C, the specific surface area and pore volume of magnetic iron oxide increase first and then decrease. The suitable calcining temperature is 400°C.

According to the current research situation, most of the raw material for denitration catalysts are pure materials, and many scholars use metallurgical waste as catalysts and good denitration effects¹¹⁻¹⁴, but rare earth minerals are used as raw materials to prepare catalysts. There are few studies on the purpose of denitrification. The rare earth oxide and iron-based oxides in the tailings of rare earth ore are the common raw materials for the preparation of catalysts¹⁵⁻¹⁶. The rare earth elements in the rare earth minerals interact with the transition metal elements to form solid solution¹⁷, which is the natural material for preparing the catalyst¹⁸. Baotou Bayan Obo Mine is a symbiotic ore of 71 kinds of elements such as iron, REE, strontium, barium, fluorine, phosphorus and potassium. More than 170 kinds of minerals and 15 kinds of REM¹⁹⁻²⁰. The synergistic joint mechanism of different proportions of RET/REC on the structure

and properties of materials and the efficient, clean and comprehensive utilization of the associated multi-metal oxide mineral materials can make the resources of Baiyun Obo mine scientifically utilized. Therefore, the research and development of co-concomitant mixed rare earth functional materials can achieve a balanced utilization of rare earth resources. Therefore, the research method of co-extraction of multi-target components of rare earth ore in secondary resources of Baiyun Obo is very important. It is an important research direction of green and high-value utilization.

MATERIALS AND METHODS

Selection of raw materials

In this paper, the catalyst raw material is selected from Baiyun Obo rare earth concentrate and rare earth tailings. The tailings particle size without any treatment is about 140–200 mesh (109–75 μm), the concentrate is about 200–300 mesh (75–48 μm) and the grinding size can reduce the particle size to 325 mesh (45 μm). The mixed ore is characterized by XRF chemical analysis and XRD mineral phase analysis.

Elements of rare earth tailings (XRF) and mineral phase analysis (XRD)

It can be seen from the XRF elemental analysis (Table 1) that the main elements contained in the rare earth tailings are Fe, O, Ca and also a small amount of rare earth elements. XRD results (Fig. 1) show that the dispersion of Fe_2O_3 is better because the Fe element ratio is 25.6 wt%, but there is no obvious and very high peak, and the CeCO_3F peak is low, which is due to low content.

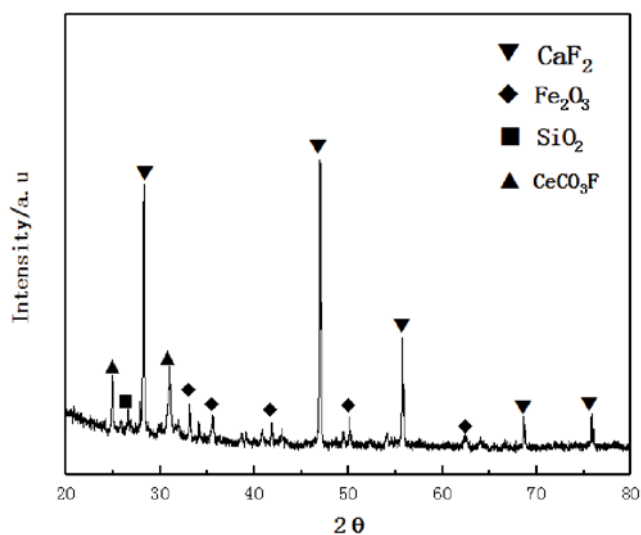


Figure 1. XRD pattern of rare earth tailings

Table 1. Element Analysis of Rare Earth Tailings (wt%)

Fe	Ce	La	Nd	Pr	O	Ca	Mn	F	Si	Others
25.6	3.39	1.79	1.00	0.31	30.5	23.5	2.24	7.49	2.43	1.75

Table 2. Element Analysis of Rare Earth Concentrates (wt%)

Ce	La	Nd	Pr	Fe	O	Ca	P	F	Mn	Othes
16.06	10.12	10.53	2.55	10.36	11.96	19.21	11.63	5.67	0.58	1.33

Elements of rare earth concentrates (XRF) and mineral phase analysis (XRD)

As can be seen from Table 2 and Figure 2 the main elements contained in the rare earth tailings are Fe, O, Ca, and small amount of REE. The REC contains a large amount of REE (above 50 wt%) and a small amount of Fe. The content of Fe and rare earth elements is uniform after the doping of rare-earth tailings and concentrates, which is beneficial to the joint action.

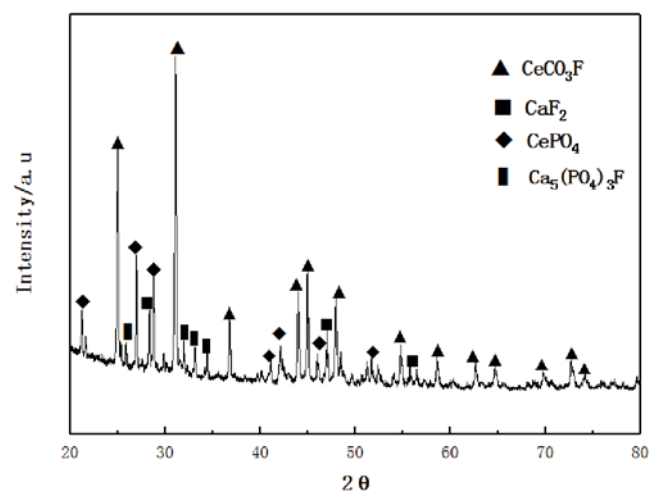


Figure 2. XRD pattern of rare earth concentrate

Selection of modifiers

In this experiment, the modifier was selected from two bases and two acids. The bases were solid $\text{Na}(\text{CO})_3$ and solid $\text{Ca}(\text{OH})_2$, and the pure solid powder was analyzed. The acids were hydrochloric acid (HCL) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (analytically pure solution).

Preparation of the catalyst

The rare earth tailings and rare earth concentrates are mixed in five ratios of 0:1, 1:2, 1:1, 2:1 and 1:0 because the tailings and concentrates obtained directly are not necessarily about 325 mesh (45 μm). The tailings are 140–200 mesh (109–75 μm) and the concentrate is 200–300 mesh (75–48 μm). Therefore, the tailings and concentrates are ground by a ball mill, sieved and used for about 325 mesh minerals. The particle dissociation degree under this mesh is very high. The total amount of the two minerals is 6.2 g, and then 0.15 g of NaCO_3 and 0.23 g of $\text{Ca}(\text{OH})_2$ are added for further grinding for 1 hour, and then calcined in a microwave baking furnace at 350°C for 15 minutes, and then taken out to prepare 0.1 mol. Hydrochloric acid and 0.01 mol of citric acid solution, the calcined sample and the prepared acid solution were mixed and stirred at a mass ratio of 1:10, and after two hours, the mixture was filtered and air-dried, and the solid matter was the prepared catalyst.

Catalyst characterization and equipment selection

X-ray diffraction analysis (XRD): X-ray diffraction analysis was performed on a PANalytical Axios diffractometer. The maximum output power is 300–600 w, the tube pressure is 40 kV, the tube flow is 30 mA, the scanning range is $2\theta = 20\text{--}80^\circ$, and the scanning speed is $3^\circ/\text{min}$.

Scanning electron microscope (SEM): Sigma-500 field-scanning scanning electron microscope, backscattered electron image resolution 2.0 nm, secondary electron image resolution 1.0 nm, acceleration voltage 0.02–30 kv, magnification 10-10000000x.

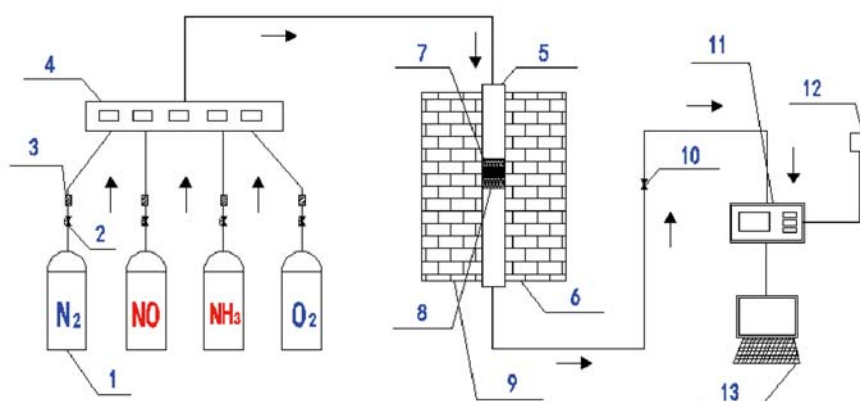
Chemical adsorption instrument: PCA-1200 temperature-programmed desorption analyzer, analysis pressure: atmospheric pressure – 8 MPa; accuracy: $\pm 0.3\%$ of reading.

XRF element analysis: Agilent Varian 700 Series ICP-OES Inductively Coupled Plasma Atomic Emission Spectrometer. Wavelength range: 175–785 nm continuous coverage, no breakpoints at all. The focal length is 0.4 meters, and the middle step grating is 97.4 lines/mm. Signal stability: $\leq 1.0\%$ RSD (4 hours). RF generator frequency: 40.68 MHz. Plasma output power 700~1700 watts. Plasma cooling gas is adjustable from 0~22.5 L/min.

XPS ion valence analysis: A high-performance imaging X-ray photoelectron spectrometer manufactured by Thermo Fisher Scientific, USA, model ESCALAB250XI. Identify the elemental species, chemical valence, and relative content of the sample surface. Double-anode XPS is more suitable for the study of different special transition metal elements, micro-area XPS analysis (monochrome XPS), for sample micro-area ($>20\mu\text{m}$) surface composition analysis, high-energy-resolved chemical state analysis.

Catalytic performance test

As shown in Figure 3, the mass of the catalyst was weighed to about 0.3 g, and the catalyst was placed in a quartz glass tube in a microreactor, and quartz fiber was placed at the lower end of the catalyst bed to fix the catalyst position. It was purged with NH_3 5×10^{-4} , NO 5×10^{-4} , O_2 3% and N_2 . The heating rate was $10^\circ\text{C}/\text{min}$, the temperature was examined at $100\text{--}500^\circ\text{C}$, and the detection was performed every 50°C , the gas flow rate was 100 ml/min, and the space velocity was 25000 h^{-1} .



1. Standard gas cylinder 2. Pressure reducing valve 3. Flowmeter 4. Mixing tank 5. Quartz tube 6. Tube furnace 7. Catalyst 8. Quartz cotton 9. Protective layer and furnace wall 10. Sampler 11. Leaf infrared spectrum (FTIR) flue gas analyzer 12. Exhaust gas treatment device 13. Computer data processing system

Figure 3. The schematic of the test apparatus

Activity evaluation indicators are calculated according to Equation 1:

$$\text{NO}_x \text{ conversion (\%)} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \quad (1)$$

where, $[\text{NO}_x]_{\text{in}}$ is the concentration of NO_x detected after the catalyst is not added to the reactor, and $[\text{NO}_x]_{\text{out}}$ is the concentration of NO_x detected after the catalyst is stabilized by the reactor (NO_x concentration is NO).

RESULTS AND DISCUSSION

Morphological representation

Scanning electron microscope x-ray micro-area analysis (SEM)

Figure 4 compares the surface morphology of the mixed minerals (1:2, 1:1 and 2:1) in the whole process of the experiment. The surface of the first 1:2 mixed ore is

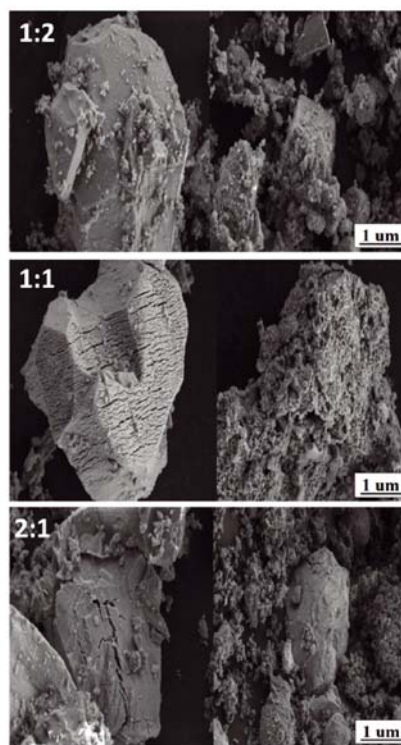


Figure 4. SEM images of intact care samples at 1:2, 1:1 and 2:1

completely treated smooth, no obvious pore structure and cracks, and some small particles are gathered together. After the complete treatment of 2:1 mixed ore some obvious cracks appear on the surface. The particles are evenly distributed without obvious agglomeration. For 1:1 mixing after the complete treatment of the ore, it can be seen that there are obvious and deep cracks on the large particles. The surface cracks on the particles are wavy and the surface becomes rough.

Scanning electron microscope x-ray micro-area analysis (EDS)

As shown in Figure 5, the EDS spectrum was measured after 1:1 complete treatment. The main objects were Fe, O, F, Ca and REE. Because the mineral contains a large amount of CaF_2 , it is also necessary to consider F. Whether it is similar to the position of Ca, but the positions of F and Ca are far apart. Figure 5 revealed that the distribution of F, O and REE is relatively concentrated, which can be considered intuitively. There is CeOF formation, and it is believed that there are Ce oxides in places where F, O and REE are aggregated. The F element after CeOF is converted into Ce oxide remains in the crystal lattice, and the addition of alkali has a solid F effect, so the reaction in the process, the F element does not go out of the lattice. It is considered that the FeCe composite oxide is formed at the end, and the distribution of the Fe, Ce and O elements is

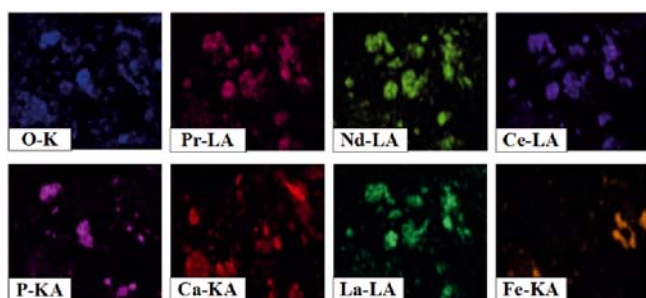


Figure 5. EDS Spectra of Completely Treated Samples at 1:1

partially overlapped so that the FeCe composite oxide can be formed.

Structural characterization

X-ray diffraction analysis (XRD)

It can be seen from Figure 6 that the samples of the three ratios are only subjected to microwave roasting, and the peak position of the characteristic peaks of each ore phase does not change. No new phase fractal peaks appear, but the peak of fluorocarbonite is strong. There have been significant changes, and the peak intensities of monazite, hematite and fluorite have changed slightly. The peak value of fluorocarbon cerium at a ratio of 1:1 is lower than the peak of the other two ratios. This indicates that the fluorocarbon strontium ore is more thermally decomposed after the microwave is calcined at the 1:1 ratio. The content of bastnasite is relatively small, and most of it exists in a dispersed form; the peak of monazite at a ratio of 1:1 will be slightly lower than the peak of the other two ratios, which may indi-

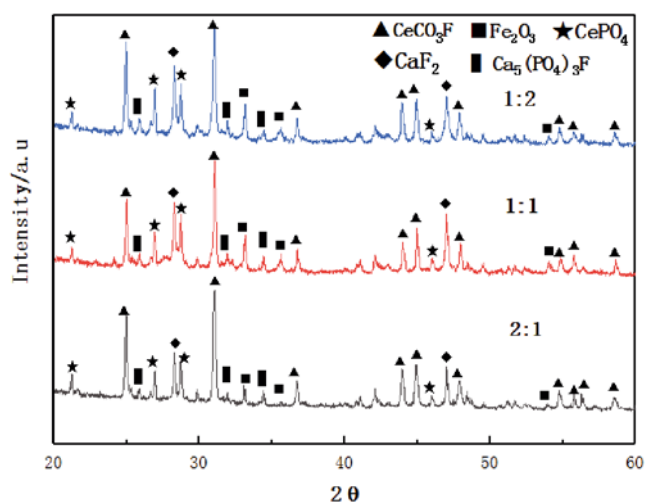


Figure 6. XRD patterns of microwave-fired samples at different ratios

cate that the monazite is slightly heated after heating. Decomposition, the peak of hematite and fluorite mines increased slightly. A good dispersion can be achieved when the mixing ratio is 1:1, and the high dispersion active material on the surface of the catalyst leads to the maximum denitration rate in this working condition. The tailings and concentrates mixed in different proportions lead to changes in the content of iron-containing oxide ore, carbonate and silicate minerals and iron-containing bastnasite. The content of these minerals directly affects magnetic loss and dielectric properties. Loss, the absorbing performance can be changed under the action of microwave. A reasonable proportion of mixed minerals promotes the migration and diffusion of rare earth metal ions and transition metal ions during the decomposition reaction.

XRD patterns of three samples with different proportions after complete treatment with weak acid by microwave oven at 350°C are presented in Figure 7. There is no change in the peak position of each mineral phase peak when the proportion of tailings and concentrates is 1:2 and 2:1, but the peak of bastnasite is higher at a ratio of 1:2. The relative content of concentrates increases and the content of bastnasite increases. The peak of hematite is higher at a ratio of 2:1, which is

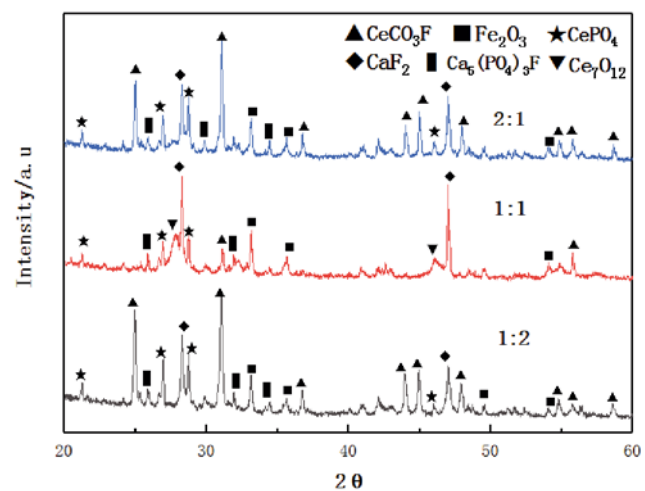


Figure 7. XRD pattern of intact care samples at different ratios

due to the increase in the relative content of tailings and the increase in the content of hematite. However, the characteristic peak of the sample at a ratio of 1:1 showed a significant change. Firstly, the peak of bastnasite with higher peak intensity decreases, and the weaker diffraction peaks disappear, indicating that most of the bastnasite meets with calcium hydroxide to accelerate fluorocarbon. The decomposition of bismuth ore and the formation of calcium fluoride, the peak intensity of calcium fluoride also indicates the existence of the decomposition reaction. Secondly, the new characteristic peak of Ce_7O_{12} appears, indicating the decomposition of fluorocarbonite during the process (Ce_2O_3 is converted to Ce_7O_{12}). Finally, the intensity of hematite and monazite ore peak is also reduced, indicating that the two minerals are relatively uniform in dispersion.

Ability to adsorb NH_3 on the catalyst surface (NH_3 -TPD)

Figure 8 exhibits a comparison of NH_3 -TPD in different proportions. It can be observed from the desorption peak that NH_3 desorption peak of the ore after the 1:1 complete treatment of the mixed mineral is the highest, which is higher than the desorption peak of other ratios. Additionally, only one main peak, indicating that a lot of substances work together to make a large amount of NH_3 adsorbed on the surface of the catalyst. The reason is that the mixed mineral 1:1 complete treatment not only modifies the mineral surface but also increases the surface active site of the mineral particles. Point, rough and porous morphology, and increase the mineral acid sites, it is easier to adsorb the basic gas NH_3 .

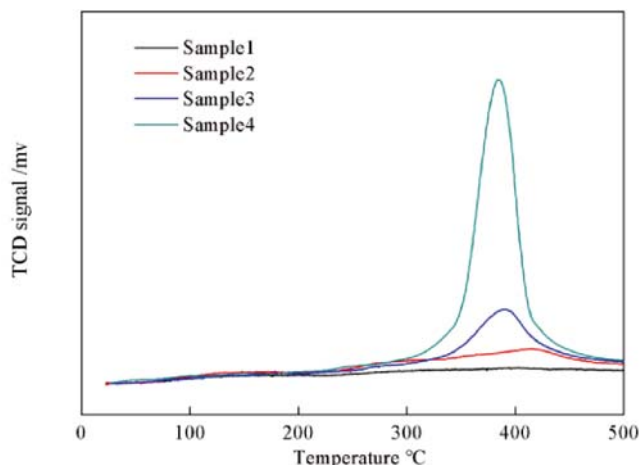


Figure 8. NH_3 -TPD analysis: 1:2 the completion of ore treatment (sample 1), 2:1 the completion of ore treatment (sample 2), (3) 1:1 microwave roasting of ore (sample 3) and 1:1 the completion of ore treatment (sample 4)

Ability to adsorb NO on the catalyst surface (NO-TPD)

A comparison of NO-TPD curves at different proportions are presented in Figure 9. The ability of minerals to adsorb NO in the 1:1 complete treatment of mixed minerals is enhanced, and the peak value is the highest. Other proportions also respond to NO, but there is a big gap compared with the treatment. The results of NH_3 -TPD are the same. From the results of NH_3 -TPD and NO-TPD, it can be seen that the minerals after mixed 1:1 complete treatment have a significant increase in the adsorption capacity of NH_3 and NO. The increase in adsorption capacity facilitates the denitration reaction.

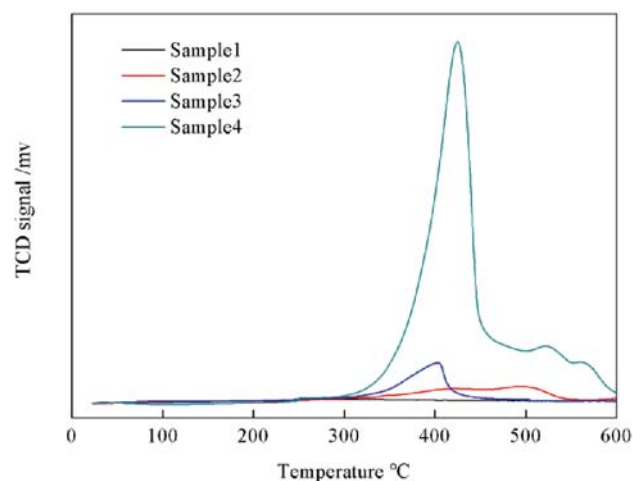


Figure 9. NO-TPD analysis: 1:2 the completion of ore treatment (sample 1), 2:1 the completion of ore treatment (sample 2), (3) 1:1 microwave roasting of ore (sample 3) and 1:1 the completion of ore treatment (sample 4)

X-ray photoelectron spectroscopy (XPS) Analysis

According to the literature, for the denitration catalyst, the change of ion valence state plays a big role. The change of Ce ion and Fe ion greatly contributes to the increase of denitration activity²⁴⁻²⁵, and the change of Ce ion valence state ($Ce^{4+} \rightarrow Ce^{3+}$) is often accompanied by the appearance of oxygen vacancies²⁶⁻³¹. The conversion between adsorbed oxygen and lattice oxygen can increase the amount of active oxygen and effectively improve the denitration efficiency. The ratio of mixed minerals was tested by XPS of Ce and Fe. The valence changes of these three elements were preliminarily judged. The contents of Ce^{3+} and Fe^{2+} ³²⁻³⁵ were used to explain the increase of denitration activity.

Figure 10 shows the results of XPS after microwave roasting of mixed ore at a ratio of tailings to concentrate of 2:1. The calculated content of Ce^{3+} and Fe^{2+} is 39 and is 43 %, respectively. Compared with the results of 1:1 ratio, the content of Ce^{3+} and Fe^{2+} increased due to the exposure of bastnasite and iron.

Figure 11 shows the XPS results after the complete treatment of tailings and concentrates at 2:1. The content of Ce^{3+} is 29 % and the content of Fe^{2+} is 31% after treatment with the first two steps. Compared with the sample, the content of the two ions decreased sharply, and the content of the sample differed greatly from the sample at the 1:1 ratio. The content of Ce^{3+} decreased from 38% at the highest level of 1:1 to 29%. The content of Fe^{2+} decreased from 55% at 1:1 to 31%.

As shown in Figure 12, the calculated Ce^{3+} accounted for 19%; Fe^{2+} accounted for 32%; O was all adsorbed oxygen, 19% of Ce^{3+} was due to the decomposition of fluorocarbon, $CeOF$ and Ce_2 Ce^{3+} is contained in O_3 , and it can be explained that the microwave treatment alone has no direct influence on the conversion of Ce ions and Fe ions.

As shown in Figure 13, the calculated ratio of Ce^{3+} is 33%; the ratio of Fe^{2+} is 55%; the content of Ce^{3+} is 6% higher than that without acid washing, and the active substance is not necessarily on the surface. Acid washing will expose the Ce oxide well, which is equivalent

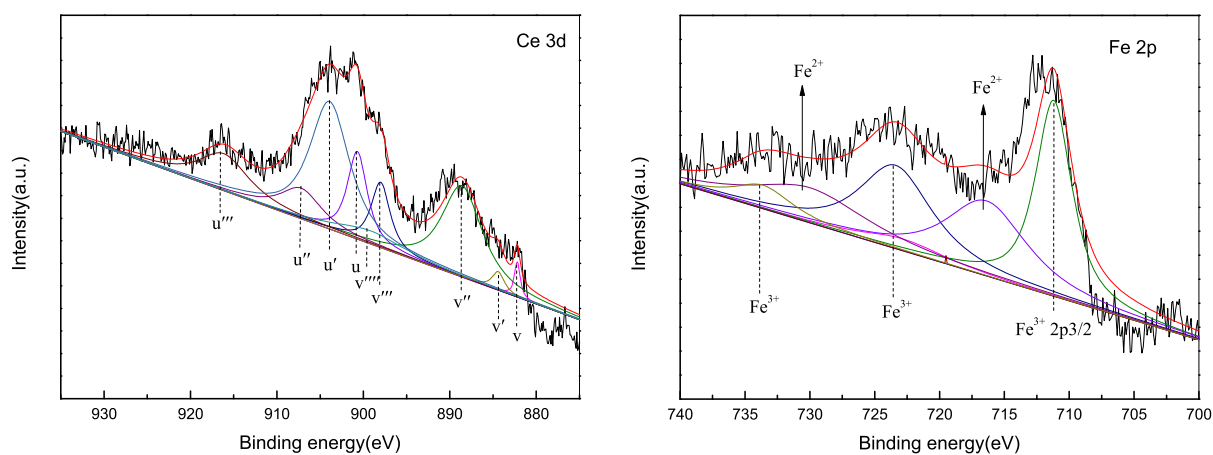


Figure 10. XPS spectrum of 2:1 ratio mixed ore only after microwave roasting (a) Ce3d (b)Fe2p

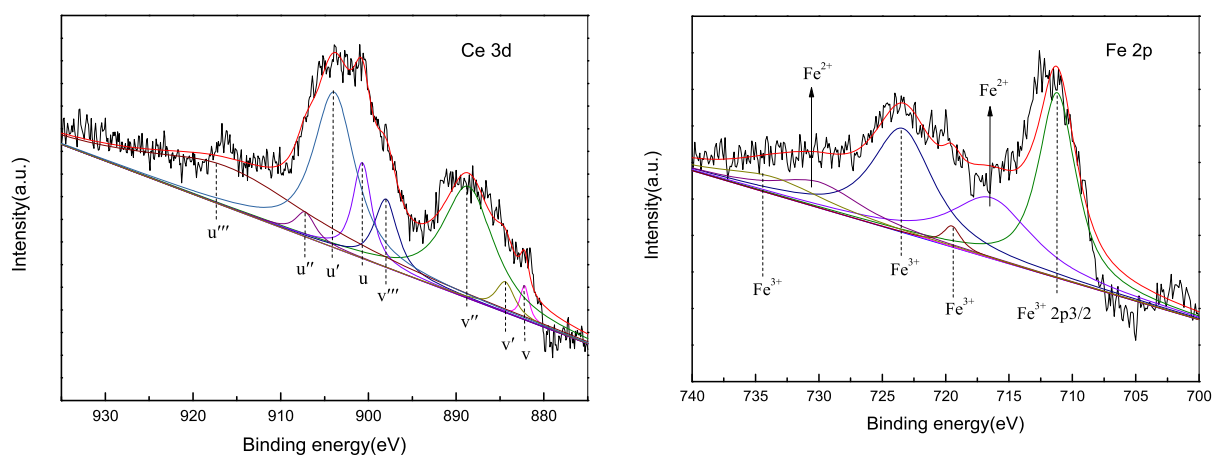


Figure 11. XPS pattern of intact care samples at 2:1: (a) Ce3d (b) Fe2p

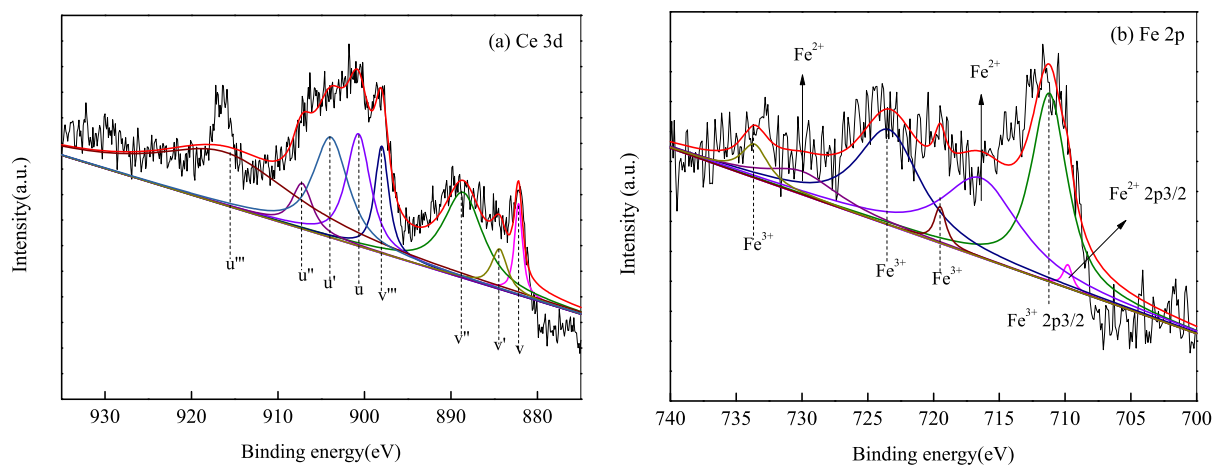


Figure 12. XPS spectrum of 1:1 ratio mixed ore only after microwave roasting (a) Ce3d (b)Fe2p

to increasing the active site of the surface and increasing the adsorption strength. The Fe^{2+} ion content of this sample is relatively high, reaching 55%. The Fe oxide contained in the iron concentrate is mainly Fe_2O_3 , and after treatment, Fe^{3+} is converted into Fe^{2+} , indicating that the electron transfer can be promoted after the complete treatment so that the Fe-based substances exist in different forms. A large number of documents prove that²¹⁻²³, Fe oxide has a great effect on improving the denitration efficiency, and at the same time, there is more adsorption oxygen. Conversion to lattice oxygen indicates an increase in oxygen vacancies, that is, an increase in active oxygen. The reason for the highest denitration activity incomplete treatment because of

the increase in the amount of ions that can increase the denitration activity.

Figure 14 shows the results of XPS after the microwave roasting of the mixed ore with a ratio of tailings to concentrate of 1:2. The calculated content of Ce^{3+} is 48% and the content of Fe^{2+} is 40%. Compared with the results of 1:1 ratio, the increase of Ce^{3+} content is due to the increase of concentrate ratio, and the increase of Fe^{2+} content is due to the exposure of iron species.

Figure 15 shows the XPS results after complete treatment at a ratio of tailings to concentrates of 1:2. The calculated content of Ce^{3+} is 29%, and the content of Fe^{2+} is 33% when compared with the ratio of 2:1. Compared with the sample results at a ratio of 1:1, the

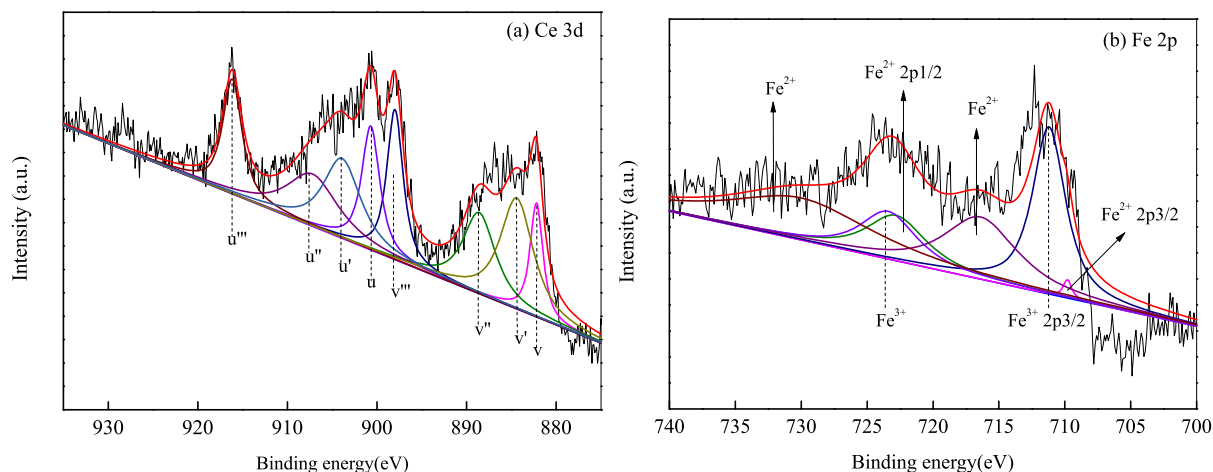


Figure 13. XPS pattern of intact care samples at 1:1 (a) Ce3d(b)Fe2p

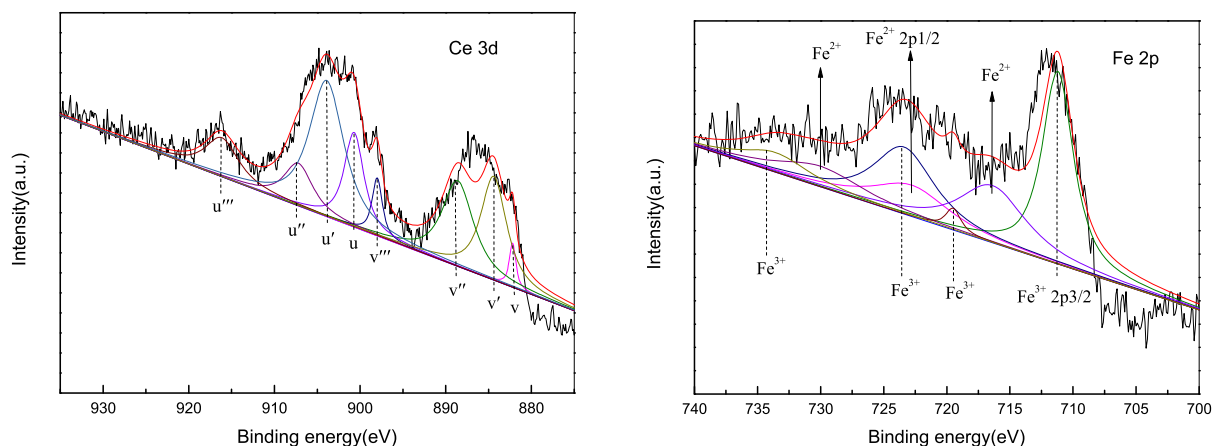


Figure 14. XPS spectrum of 1:2 ratio mixed ore only after microwave roasting (a) Ce3d (b)Fe2p

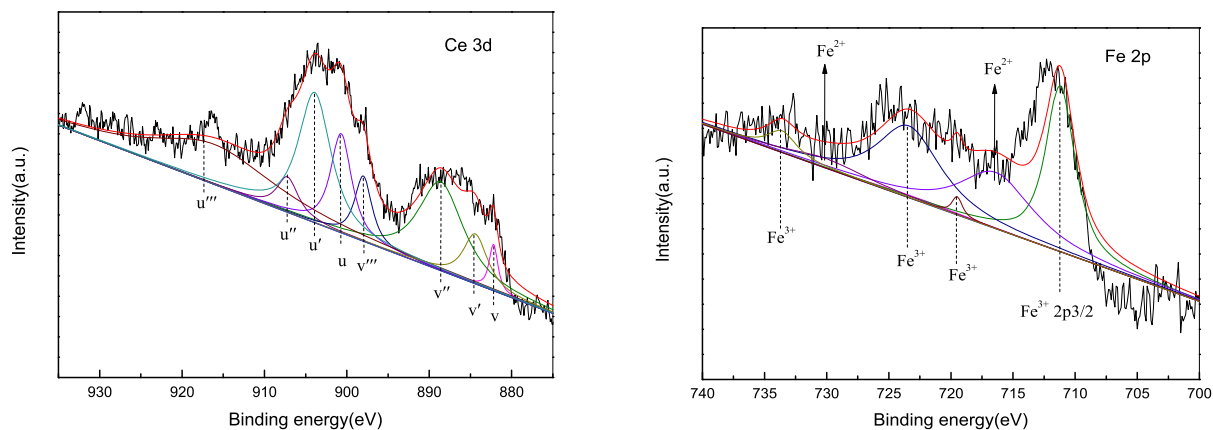


Figure 15. XPS pattern of intact care samples at 1:2 (a) Ce3d(b)Fe2p

difference is very large. Therefore, it is considered that the activity when the tailings and concentrate ratio is 1:2 is not as active as the 1:1 ratio. The content of these reactive ions is drastically reduced.

Catalyst denitration performance experiment

Because the ratio of tailings and concentrate is the first variable in the preparation of the catalyst in this experiment, it is necessary to carry out the activity detection on the first mixed salt in different proportions. However, it is considered that there is no mixing of the mine with no other treatment. Very good denitrification effect and there are many other variables in the experiment process. Therefore, it is necessary to prepare catalysts

with different proportions of complete treatment and to carry out activity detection. The results of these two experiments can determine the best of the rare earth tailing and rare earth concentrate. The other variables in the experiment are the determined values and no changes are made.

In the first step, the tailings and concentrates are mixed and ground in proportion, and there is no other treatment. The selected ratios are 0:1, 1:2, 1:1, 2:1, 1:0, and the results are shown in Figure 16. Although the denitration rate of the mixed ore samples at each ratio is lower, the 1:1 ratio of the samples is significantly higher than the other four ratios. The ratio of tailings and concentrates is 1:1, and the conversion rate is

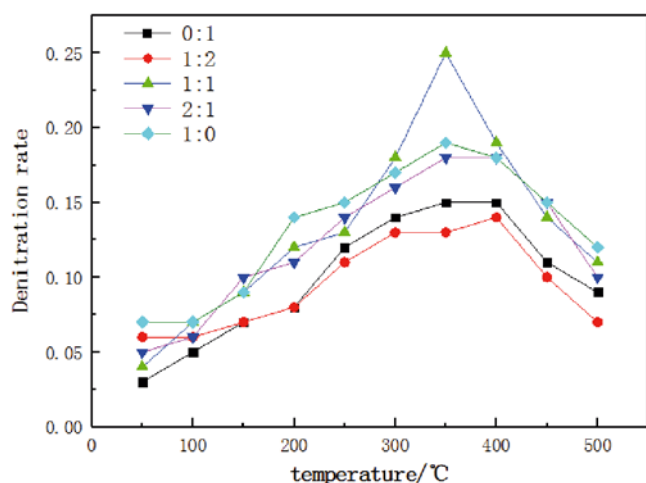


Figure 16. Denitration rate of mixed ore without other treatment

the highest. The addition of concentrate to the concentrate will cause a decrease in denitrification activity. It is worth noting that the denitration rate of the sample with tailings concentrate ratio of 1:0 is higher than that of the other three samples, and the highest activity at 1:1 is combined. The substances that play a role in denitrification activity in tailings and concentrates have a relationship of promotion and restriction. They are not as good as possible, nor can they be used to determine the most tailings and concentrates in this experiment. The good ratio is 1:1.

As shown in Figure 17, different proportions of the intact sample are prepared and tested for denitration performance. Compared with the results in Figure 16, to explore whether mixed ore 1:1 is the best ratio. The results are the 1:1 ratio of the sample showed the best denitrification activity, reaching 82% at 350°C, while the other four ratios of the sample were more highly denitrified than the samples with no other treatment, but there is no big change, the highest is only 41%, and the 1:1 ratio of the sample shows the best denitrification in these 5 ratios, whether it is only mixed or after the complete treatment. Activity, so combined with the results of these two experiments, the ratio of tailings to concentrate can be finally determined to be 1:1. The progress of the denitration rate of the sample after complete treatment is the same as that of the sample only when mixed, indicating that the active component

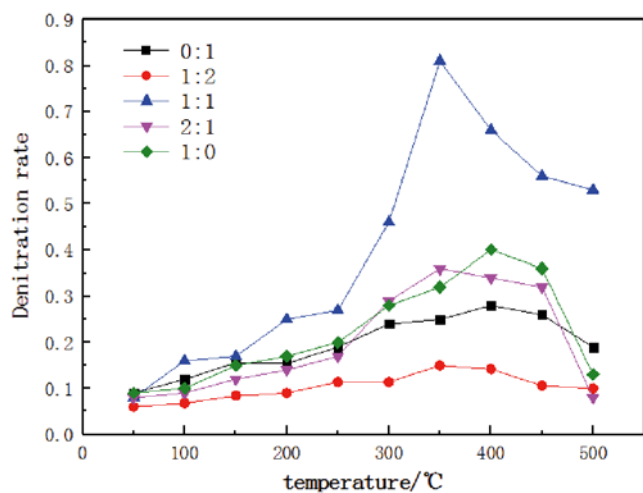


Figure 17. Denitration rate after complete treatment of mixed minerals in different proportions

in the sample after the complete treatment also has both combined and mutually constrained effects, and the denitration rate at the ratio of 1:0. In the second place, it is considered that the role of tailings in mixed mines is relatively large, and the concentrates are not as good as possible. It is necessary to reach a state of balance, such as Fe in tailings and Ce in concentrates. The substance exerts the greatest combined denitrification.

CONCLUSIONS

The Fe oxide rare-earth tailings and Ce rich oxide rare earth concentrate are mixed in different proportions in this paper, and a series of experiments and characterization of mineral catalytic materials are obtained by acid-base leaching and microwave roasting. The results are as follows:

(1) After mixed treatment of different proportions of rare earth tailings and rare earth concentrate, the best working conditions were obtained by the detection and comparison of each experimental variable during the preparation process: the denitrification efficiency of mineral catalytic materials at 1:1 was the best, which could reach 82%.

(2) The mixing of rare earth tailings and rare earth concentrates in different proportions can cause a large number of cracks on the surface of mineral particles, increase the specific surface area, shorten the time than traditional roasting methods, increase the surface active sites, rough and porous morphology characteristics of mineral particles by pickling, and increase the acidic sites of mixed minerals between rare-earth tailings and rare earth concentrate, which makes it easier to adsorb alkaline gas NH_3 .

(3) Increased Ce of rare earth tailings and rare earth concentrates during the complete 1:1 mixing process Ce^{3+} and Fe^{2+} concomitant, active components Ce to Ce^{3+} and Ce^{4+} ; Fe to Fe^{2+} and Fe^{3+} coexistence of forms. the conversion of adsorbed oxygen to lattice oxygen increases, and there are more oxygen vacancies for oxygen transfer. the change of valence state of Fe and Ce ions can also be shown that there is a joint synergistic effect with Ce when the 1:1 ratio is mixed. To sum up, it is considered that the mixture of rare earth tailings and rare earth concentrate to prepare high entropy mineral catalytic materials, and the optimization of different proportions is an extremely effective method to improve the performance of mineral catalysts.

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