Study on NH₃-SCR of Cerium-based Substances in Rare Earth Concentrates from Bayan Obo

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In this paper, CePO₄ and CeCO₃F were prepared by hydrothermal synthesis based on the ratio of bastnaesite to monazite in the process mineralogy of Baiyun Ebo rare earth concentrate. A comparison of the two treatments, ball milling and ball milling sulphation, revealed that the denitrification efficiency of the catalysts treated with ball milling sulphation increased by 20 percentage points, compared to those treated without sulphation, with denitrification efficiencies of up to 80%. The surface properties, redox properties and catalytic mechanism of the samples before and after the sulphation treatment were analyzed, by using XRD, NH₃-TPD, H₂-TPR, XPS and in situ IR characterization. The results showed that the CeF₃ diffraction peaks in the XRD patterns disappeared in the sulphated samples, NH₃-TPD showed that the adsorption capacity of NH₃ on the surface of the samples was enhanced, and the introduction of sulphuric acid provided a large number of acidic sites on the catalyst surface, among which the Lewis acidic sites might be more favorable for the promotion of SCR reaction. The acidification of sulphuric acid greatly increases the redox capacity of the catalyst, and the interconversion between Ceⁿ⁺ was enhanced. XPS showed a significant increase in the amount of adsorbed oxygen on the surface of the sample. The presence of -NO₂, an important intermediate in the L-H mechanism, was also detected by IR analysis. reactant species during the L-H mechanism reaction were monodentate nitrate, bridged nitrate and NH₄⁺ species produced by NH₃ adsorption on the Brønsted acidic site of the catalyst surface.

Keywords: Rare earth concentrate, Sulfation, Denitrification, Catalytic synergy.

INTRODUCTION

At present, coal-fired thermal power generation is still the main mode of power generation in China, and fossil fuels such as coal release large amounts of NO_x during the combustion process, and the environmental hazards caused by NO_x have become the focus of long-term national governance¹. The mainstream industrial flue gas denitrification technology is NH₃-SCR², a process whereby NH₃ reacts selectively with NO_x on the catalyst surface to form N₂ and H₂O without consuming excess O₂. Conventional denitrification catalysts V₂O₅-WO₃-MoO₃/TiO₂ were toxic and suffer from a narrow activity temperature window (320–400 °C), and a complex preparation process³. It was therefore urgent to develop new NH₃-SCR catalysts that were non-toxic, have a wide temperature window, and were simple to prepare.

The Cerium and other rare earth elements are the most widely studied catalysts for NH₃-SCR denitrification. The introduction of cerium can not only improve the catalytic performance of the catalyst^{4, 5}, but also the potassium resistance, sulfur resistance, water-resistance of Catalysts has a significant effect^{6–10}. It was well known, the Bayan Obo Mine was a super large rare earth deposit, and cerium was the main rare earth element. Cerium has a unique 4f electron structure which has good catalytic properties in catalytic reactions. Cerium has two oxidation valence states in its oxide CeO₂, namely Ce⁴⁺ and Ce³⁺, which can be converted to each other through the redox process, giving the oxide the ability to store and release oxygen, which was widely used in catalysis, and the redox activity of cerium-based catalysts can promote the rapid activation of NH₃ to reduce NO_x and complete the redox cycle, which plays a crucial role in the NH₃-SCR reaction process. In contrast, the number of acidic

sites on the surface of rare earth concentrates was low, and need to additional modification and treatment were required to enhance the adsorption capacity of NH₃ to improve the denitrification efficiency and N₂ selectivity of the NH₃-SCR reaction. Therefore, acid modification of rare earth concentrates was required. It was found that the sulphation of cerium-based catalysts resulted in improved catalytic performance, and enhanced resistance to alkali metal poisoning^{11, 12, 13}. Currently, many scholars have used sulphuric acid solution to modify the catalysts, which greatly promoted the denitrification performance of the catalysts and has good application prospects. Chen Wangsheng¹⁴ et al. obtained sulphuric acid-modified sinterite catalyst (SSOC) by using sulphuric acid solution to modify the sinterite catalyst (SOC). The results showed that the sintered ore was impregnated in a 5 mol/L sulphuric acid solution for 30 min, dried and calcined at 400 °C for 3 h, the SSOC catalysts were prepared to achieve 92% NO_x conversion at 300 °C. Zhang Qiuling¹⁵ et al. Acidification of CeO₂ to improve its denitrification performance, the results showed that, the SO₄²⁻/CeO₂ catalyst with 2.5 wt.% SO₄²⁻ content exhibited more than 90% of NO conversion at 229–485 °C.

Therefore, in this study, based on previous research by scholars, sulphuric acid acidification was used to treat rare earth concentrates. The denitrification performance of the rare earth concentrate catalysts increased after sulphation, probably because sulphuric acid facilitates the removal of some impurity components from the samples and can further enhance the catalytic performance of the catalysts. However, due to the complex mineral cascade relationship of its rare earth concentrates, the existing characterization tools were unable to explore its catalytic mechanism. To investigate the specific mechanism of

action of the mineral catalyst NH_3 -SCR denitrification, the role of the main mineral phases of the concentrate in the catalytic reaction needs to be investigated on a case-by-case basis, which in turn provides theoretical guidance for the high-value utilization of rare earth concentrates.

The two main mineral phases of Baiyun Ebo rare earth concentrate, bastnaesite and monazite, contain more than 95% of Ce. This paper was based on the two main minerals of Baiyun Ebo rare earth concentrate, bastnaesite and monazite. The CeCO_3F and CePO_4 were synthesized, and sulphated according to the ratio of Ce in bastnaesite and monazite. By comparing the denitrification performance and mechanism analysis before and after sulphation, the effect of sulphation on their catalytic performance was investigated to provide new ideas for the research of catalysts and to provide a reference value for the modification of concentrate catalysts and mechanism research.

EXPERIMENTAL PART

The basis of sample selection and its preparation method

The samples prepared in this paper were based on a cerium fluorocarbon rare earth concentrate (hereinafter referred to as “concentrate”) from Baiyun Ebo (see Table 1).

Table 1. Main rare earth minerals and content in Baiyun Ebo fluorocarbon-cerium rare earth concentrate

Mineral category	Mineral name	Formula	Content
Rare earths	Parisite	$\text{Ce}_2\text{Ca}[\text{CO}_3]_3\text{F}_2$	5.59
	Bastnaesite	$(\text{Ce, La})[\text{CO}_3]\text{F}$	6.00
	Bastnaesite	CeCO_3F	30.82
	Monazite	CePO_4	23.05
	Subtotal	—	65.46

From the composition of the main rare earth-like minerals in the concentrate, it appears that the ratio of bastnaesite to monazite was 13:7. Based on this, the synthesized CeCO_3F and CePO_4 were mixed in proportion to each other and the mixing was done, by grinding, ordinary ball milling and high energy ball milling. The process parameters of the ball mill were 400 r/min, 10 min forward and reverse rotation interval and 1 h ball milling time.

Using the wet impregnation method, a certain amount of cerium nitrate hexahydrate, sodium fluoride, sodium bicarbonate in aqueous solution, stirring impregnation 24 h, extraction, 80 °C drying oven, that is, CeCO_3F sample. Dissolve a certain amount of cerium nitrate hexahydrate in distilled water, add phosphoric acid aqueous solution drop by drop, put in a hydrothermal kettle at 120 °C constant temperature stirring 1 h, drying, 500 °C roasting 2 h, that is, CePO_4 sample. The CeCO_3F sample and CePO_4 sample were pretreated by ball milling and roasted to obtain sample 1, sample 2 and sample 3 (see Table 2 for specific treatments). The pretreated samples

Table 2. Sample label names of different pretreatment methods

Tag name	Sample 1	Sample 2	Sample 3
Pretreatment method	Grind	Ordinary ball mill	High energy ball mill

were sulphated by taking 5 g of the sample and adding 10mL of $x\text{mol/L}$ sulphuric acid solution ($x = 0, 0.4, 0.5, 0.6, 0.7, 1, 3$), placed in a magnetic stirrer and stirred for 1h, dried and roasted.

The calculation formula of NO_x conversion rate is as follows:

$$\eta = 1 - \frac{\text{NO}_{x(\text{out})}}{\text{NO}_{x(\text{in})}} \times 100\%$$

Where η is the conversion rate of NO_x under this working condition, $(\text{NO}_x)_{\text{in}}$ is the inlet concentration of NO under this working condition, in ppm, $(\text{NO}_x)_{\text{out}}$ is the outlet concentration of NO and NO_2 under this working condition, in ppm. Among them, NO_x contains NO and NO_2 .

Characterization of the catalyst

It is heated by a riser furnace with a rated temperature of 1600 °C produced by Nanjing Boyuntong Instrument Technology Co., Ltd., and the GASMET-DX4000 Fourier Infrared Spectroscopy (FTIR) flue gas analyzer produced in Finland is used in conjunction with a data acquisition system for online measurement the smoke composition. The temperature-programmed desorption test of the catalyst was carried out with the PCA-1200 temperature-programmed chemical adsorption instrument produced by Beijing Bood Electronics Co., Ltd. Use Chinese PERSEE XD-3 X-ray diffraction (XRD) to analyze crystal form and mineral phase. X-ray photoelectron spectroscopy (XPS) using EDX1800E ray fluorescence spectrometer (Tianrui Instrument Co., Ltd.). VERTEX70 infrared spectrometer (including MCT detector and high-temperature micro-infrared accessories) from German Bruker company for in-situ infrared adsorption experiment.

RESULTS AND DISCUSSION

Catalytic performance and surface properties

Figure 1 showed the activity test graph of the synthetic rare earth concentrate after ball milling. The results showed that the denitrification capacity of the ball-milled samples remained stable in the temperature range of 250–400 °C. The best denitrification capacity was found for the normal ball mill treated samples, with the de-

Figure 1. Denitrification performance of samples with different pretreatment methods

nitrification rate remaining above 60%. The activity of the catalyst was also increased after the high-energy ball milling process, but the effect was less than that of normal ball milling. This may be because the pore channels inside the catalyst collapse at too high an energy level, causing the pores to become blocked and preventing the gas from adsorbing onto its surface, thus causing a reduction in activity. Based on the future practical use of the samples, the samples selected for this paper were pre-treated with a normal ball mill.

Figure 2a showed a comparison of the denitrification capacity of samples that had undergone normal ball milling after acidification with 0 mol/L, 1 mol/L and 3 mol/L sulphuric acids. The trend between 0 mol/L and 1 mol/L in the graph reveals that the denitrification performance of both was similar, but there was an increase in the denitrification efficiency of the sample after 1 mol/L acidification. From the results shown in Figure 2a, it can be analyzed that the optimum acid quantity for sulphuric acid acidification should be in the range of 0–1 mol/L. Therefore, the treated sample with sulphuric acid concentration near 0.5 mol/L was selected for denitrification performance analysis. As shown in Figure 2b, the best results were found for the sulphuric acid-treated samples with a 0.6 mol/L sulphuric acid concentration. The best denitrification efficiency was 80.13% at 0.6 mol/L sulphuric acid concentration, an increase of 20 percentage points compared to the non-acidified sample. It was found that the activity of the 0.6 mol/L sulphuric acid-treated catalysts was less variable in the reaction temperature range of 300–400 °C,

Figure 2. Comparison of denitration performance of samples treated with different acids

which indicated that a wider temperature window and that the higher catalytic activity was concentrated in the high-temperature range, which may be due to the introduction of sulphuric acid providing more Lewis acidic sites on the catalyst surface, resulting in an increase in activity in the high-temperature range.

To investigate the changes in the crystalline phase of the surface material before and after the sulphuric acid treatment, XRD analysis of the catalyst was carried out and the results are shown in Figure 3. As can be seen from the graphs, the mineral composition and crystalline shape of the samples produced significant changes before and after the sulphate acidification treatment. The 2Theta angle of some of the diffraction peaks was shifted, which indicated that the sulphuric acid acidification may have caused lattice distortion in the synthetic rare earth concentrates, which required further calculation of the cell constants to prove. The minerals before sample acidification are dominated by CeO_2 , CePO_4 and CeF_3 . It is known that CeCO_3F was highly susceptible to decomposition to cerium oxides by high-temperature roasting. High-temperature decomposition was a key step in the use of rare earth concentrates for NH_3 -SCR denitrification, as the excellent oxygen storage and release of cerium oxides can improve the redox capacity during the catalytic reaction. The diffraction peak of CeF_3 was detected in XRD, which indicated that some of the cerium elements were pulled by fluorine elements to form CeF_3 during the decomposition of CeCO_3F . This suggested that CeF_3 could be a hindrance to the NH_3 -SCR process, due to the inhibitory effect of fluorine ions. After impregnation with 0.6 mol/L sulphuric acid, a variety of cerium sulphur oxide substances were generated. This substance was the product of the reaction of CeCO_3F or an intermediate product of CeCO_3F with sulphuric acid. Furthermore, the disappearance of the diffraction peak of CeF_3 was found, which indicated that sulphuric acid acidification can effectively inhibit the process of cerium traction by fluorine ions, and thus facilitate the reaction. The diffraction peaks of the CeO_2 species weakened in the presence of acid, which indicated that the homogeneous dispersion of the cerium oxide in the bulk phase, and facilitated the SCR reaction.

From the cell parameters in Table 3, it can be seen that the crystal plane spacing of the catalyst increased

Figure 3. XRD comparison of samples before and after acidification with sulfuric acid

Table 3. Change of intercrystalline area and grain size before and after acidification

Catalyst type	Crystal interplanar distance(nm)	Grain size(nm)
Before acidification	7.214	145
After acidification	7.244	33

after the sulphation treatment. This indicated that the introduction of sulphuric acid causes lattice expansion, but the grain size decreases compared to pre-acidification, which suggested that sulphuric acid inhibits grain growth, promotes activation of oxygen species and accelerates the SCR reaction. The increase in denitrification efficiency after acidification also provides evidence for the inhibitory effect of elemental fluorine.

Absorption and desorption performance and chemical state

To investigate the number of acid centers as well as the acidic strength of the catalyst before and after sulphation, the catalyst was subjected to an experimental study of NH_3 -TPD. The adsorption and desorption properties of the samples were key to characterizing the catalytic performance of the samples, and it was evident from Figure 4 that both the pre- and post-acidification samples produced a broad desorption peak around 200 °C. This desorption peak was attributed to the adsorption of NH_3 on the surface of the samples by physically adsorbed NH_3 , and NH_3 on the weak Brønsted acidic sites. From the peak intensity here, The acidified sample was significantly higher than the pre-acidified sample, which suggested that the acidified sample has a higher capacity to adsorb NH_3 on its surface. The possible reason for this was that the CeF_3 produced by the roasting of CeCO_3F , occupies part of the cerium element, resulting in a reduction of the cerium sites and hence a lack of NH_3 adsorption capacity of the sample. After sulphuric acid acidification, the catalyst showed two distinct desorption peaks around 300 °C and 570 °C. The peak around 300 °C can be attributed to the combination of NH_3 adsorbed on the catalyst surface with a moderately strong acidic site.

The peak around 570 °C was attributed to the binding of NH_3 to the Lewis acidic site on the catalyst surface.

Figure 4. NH_3 -TPD of samples before and after acidification with sulfuric acid

It can be seen that both Brønsted and Lewis acidic sites on the catalyst surface were elevated after sulphuric acidification, with the Brønsted acidic site being particularly elevated. Previous studies have shown that NH_4^+ species produced by adsorption on the Brønsted acidic site were less thermally stable than NH_3 species bonded to the Lewis acidic site. Based on the activity test results, the excellent NOx conversions of the catalysts were all above 300 °C. Therefore it is likely that the catalytic activity was promoted by the emerging Lewis acidic sites on the catalyst surface, and the active component providing the Lewis acidic sites was likely to be the emerging metal sulphide oxide species.

Stronger redox properties can increase the oxidation rate and reaction activity of NO to NO_2 conversion. To investigate the redox ability of the catalyst before and after acidification with sulphuric acid, the catalyst was characterized by H_2 -TPR. The results were shown in Figure 5, and the redox ability of the acidified samples was significantly increased. The reduction peaks of the samples before acidification appeared at 650 °C and 810 °C. The reduction peaks at 650 °C belonged to the reduction of the bulk phase CeO_2 on the catalyst surface, and the reduction peaks at 810 °C belonged to the reduction of the bulk phase Ce^{4+} to Ce^{3+} on the catalyst surface. It can be found that the catalyst before acidification has a poor redox ability, this was because the main component of monazite, CePO_4 , was very stable, and cerium cannot be easily oxidized or reduced, neither through the $\text{Ce}^{4+}/\text{Ce}^{3+}$ transformation to achieve the redox cycle. However, it still has some catalytic activity, which was attributed to the fact that Ce can act as a defect center and produce some adsorption of NO and NO_2 , which generate active nitrate intermediates on the catalyst surface to participate in the reaction¹⁶. Not only that, CeFCO_3 also undergoes roasting to produce Ce_7O_{12} species, which promotes redox. After acidification with sulphuric acid, the area of the reduction peak increases significantly, which was probably due to the reduction peak of the metal sulphate. Metal sulphates are very thermally stable and may only decompose above 600 °C. The resulting metal sulphides and metal sulphate species may have some influence on the interconversion between Ce^{n+} in the original catalyst. The increase in peak area can also indicate that the introduction of sulphuric acid can promote the conversion between metal ions, making the formation of stronger electronic interactions between the Ce-O-Ce species and the sulphate group, The redox capacity of the catalyst was increased, and facilitating the catalytic reaction. Furthermore, in addition to promoting the valence conversion between other metal ions and enhancing the redox capacity, sulphate also has a certain redox capacity of its own, which jointly participates in the oxidation cycle reaction in the NH_3 -SCR reaction.

To better analyze the XPS profile of Ce3d of the samples, we fitted the samples to split peaks. The fit of the sample before acidification can be divided into seven peaks (as in Fig. 6a), where u1v1 was the XPS peak of Ce^{3+} , and the rest were the XPS peaks of Ce^{4+} ^{17, 18}. In Figure 6(a) it can be found that the diffraction peak intensity of Ce^{4+} was significantly higher than that of Ce^{3+} , which indicates that Ce^{4+} was the major oxidation state of cerium in the sample, while Ce^{3+} in it mainly

Figure 5. H_2 -TPR of samples before and after acidification with sulfuric acid

Figure 6. XPS spectrum of Ce 3d before acidification (a) After acidification (b)

acted in the valence equilibrium, oxygen vacancy and unsaturated bond generation. The sample fit after acidification can be divided into 8 peaks (Fig. 6b), of which v_{1u1} was the XPS peak for Ce^{3+} , and the rest were the Ce^{4+} XPS peaks. It was evident that after acidification of the catalysts with sulphuric acid, the peak of Ce^{3+} was enhanced, which leads to an increase in chemisorbed oxygen or weakly bound oxygen species on the surface of the samples, and the increase in oxygen vacancies would

promote the adsorption of NH_3 and NO species on the catalyst surface, which would facilitate the conversion of NO to NO_2 . After acidification, the binding energy of Ce 3d was shifted to a higher level, which indicated a strong interaction between Ce and sulphate ions, which may promote the production of new species, as well as the valence conversion between ions, which was consistent with the results of the H_2 -TPR analysis. The introduction of sulphuric acid further promotes the SCR reaction process.

The spectra of the O1s fitted to the split peaks of the samples before and after acidification were shown in Figure 7. The samples before and after acidification both fitted two distinct peaks at binding energies of around 531 eV and 528 eV, attributed to adsorbed oxygen (O_{α}) and lattice oxygen (O_{β}) on the catalyst surface respectively¹⁹. It can be found that the ratio of adsorbed oxygen to lattice oxygen on the surface of the catalyst before sulphation was not very different, and the content of adsorbed oxygen on the surface of the sample increases significantly after the acidification treatment. It was well known that the formation of adsorbed oxygen on the catalyst surface was due to the presence of oxygen vacancies, and since the activation process of both NH_3 and NO adsorption was transferred to the adsorbed oxygen via oxygen vacancies, this suggested that the introduction of sulphuric acid can increase the number of oxygen vacancies on the catalyst surface thereby promoting the increase of adsorbed oxygen,

Figure 7. XPS spectrum of O 1s before acidification(a) After acidification(b)

and facilitating the conversion of NO to NO₂, and the binding energy of O 1s was shifted towards high, which may be due to the interaction of oxygen in the sulphate with intermediate products of CeCO₃F decomposition, which was consistent with the XRD results, producing species such as Ce₂O₂S₂ as sulphur oxides.

Catalytic mechanism analysis

In this experiment, the adsorption and activation of NH₃ on the catalyst surface were investigated by in situ infrared spectroscopy at different temperatures, and the presence of NH₃ species on the catalyst surface at different temperatures was studied. The results were shown in Figure 8a. In the range of 50 °C to 150 °C, infrared absorption peaks appear at 1622 cm⁻¹, 1482 cm⁻¹ and 1420 cm⁻¹ on the catalyst surface, where all three peaks were symmetrically deformed vibrational diffraction peaks of NH₄⁺ at the Brønsted acidic site²⁰, and the infrared absorption peak at 1190 cm⁻¹ was a diffraction peak of NH₃ absorption vibration at the Lewis acidic site. As the temperature increases, the diffraction peak of NH₄⁺ on the Brønsted acidic site disappears, while the diffraction peak of NH₃ on the L acidic site does not change significantly, which indicated that when the temperature was below 150 °C, the surface of the catalyst sample was dominated by adsorption on the Brønsted acidic site with a small amount of adsorption on the Lewis acidic site. The symmetrically deformed vibrational diffraction peaks of NH₄⁺ on the Brønsted acidic sites almost disappear when the temperature was in the range of 200 °C to 400 °C. The infrared absorption peaks attributed to the NH₄⁺ species on the Brønsted acidic site at 1420 cm⁻¹ were also present on the catalyst surface to a lesser extent, and participate in the reaction at different temperatures. In contrast, the infrared absorption peak at 1190 cm⁻¹ for the NH₃ absorption vibration on the Lewis acidic site was relatively stable, with the strongest peaks for the adsorbed species at 350 °C, which indicated that the Lewis acidic site was predominant in the medium to high-temperature section. The above results indicated that both Brønsted and Lewis acids were involved in the reaction from 50 °C to 400 °C, with Brønsted acid adsorption dominating in the low-temperature range and Lewis acid adsorption in the medium to the high-temperature range.

The adsorption and activation processes of NO+O₂ species on the catalyst surface under different temperature conditions were subsequently investigated by in situ infrared spectroscopy. The form and variation of the presence of NO_x species on the catalyst surface under different temperature conditions were discussed. From Figure 8b, it can be seen that in the range of 50–150 °C, an absorption peak appears on the catalyst surface at 1622 cm⁻¹, where the peak was attributed to the NO₂ species²¹, which can be found to be more strongly adsorbed in the low-temperature section. The absorption peak appearing at 1545 cm⁻¹ was attributed to the bridged nitrate species, and the absorption peak appearing at 1261 cm⁻¹ was attributed to the monodentate nitrate species. The NO adsorption products on the catalyst surface in the low-temperature section are dominated by NO₂ species and monodentate nitrate species. As the temperature increases, the NO₂ species

and monodentate nitrate species decompose rapidly at 200 °C, which indicated that both were more sensitive to temperature and prone to pyrolysis reactions. When the temperature range was 200–400 °C, the infrared absorption peak at 1400 cm⁻¹ belonged to the bidentate nitrate species. It can be found that as the temperature increases, the overall NO adsorption species was weaker in the high-temperature range, and only the bidentate nitrate species exists in a relatively stable state, which indicated that it occupies the main NO adsorption site. This also means that the adsorption products of NO in the low-temperature range of the SCR reaction were mainly NO₂ species and monodentate nitrate species, and in the medium to high-temperature range mainly dentate nitrate species were the main active species.

Figure 8. In-situ infrared spectra of NH₃ and NO+O₂ adsorbed species on the catalyst surface under different temperature conditions

Figure 9a showed the infrared profile of the sample over time when the sample was pre-sorbed with NH₃ and then passaged with NO+O₂. From the figure, it was found that when NH₃ was passed in for one hour, infrared absorption peaks appeared on the catalyst surface at 1480 cm⁻¹, 1416 cm⁻¹ and 1185 cm⁻¹, where the peaks at 1480 cm⁻¹ and 1416 cm⁻¹ were diffraction peaks of NH₄⁺ species on the Brønsted acidic site, and the peak at 1185 cm⁻¹ belonged to the diffraction peak of NH₃ on

the Lewis acidic site²². When the NH_3 adsorbed species were stably present on the catalyst surface, $\text{NO} + \text{O}_2$ gas was passed in. From Figure 9a, it can be found that the diffraction peaks of NH_4^+ at 1480 cm^{-1} and 1416 cm^{-1} belonged to the Brønsted acidic sites disappeared, after 2 min of $\text{NO} + \text{O}_2$ introduction. And the diffraction peaks of NH_3 at 1185 cm^{-1} belonged to the Lewis acidic sites weakened, which indicated that the NH_3 adsorbed species on the catalyst surface were mainly the NH_4^+ species adsorbed on the Brønsted acidic sites. With increasing $\text{NO} + \text{O}_2$ influx time, all the NH_3 adsorbed species on the catalyst surface disappeared and stable nitrate species resulting from NO adsorption appeared. Two diffraction peaks appeared at 1347 cm^{-1} and 1278 cm^{-1} on the catalyst surface, both of which were free nitrate species and monodentate nitrate species respectively²³, with peak intensities increasing with time. The depletion of ammonia species indicated their involvement in the catalytic reaction process and that the catalytic process was dominated by Brønsted acidic site adsorption.

Figure 9b showed the in situ IR spectra of the reaction between NH_3 and pre-adsorbed $\text{NO} + \text{O}_2$ species on the catalyst surface, at optimum denitrification temperature conditions. When $\text{NO} + \text{O}_2$ was introduced into the reaction cell system for 60 min, nitrate species from

NO adsorption were observed on the catalyst surface at 1519 cm^{-1} , 1420 cm^{-1} , 1126 cm^{-1} and 1322 cm^{-1} , and all species were stable on the catalyst surface, with the absorption peak at 1519 cm^{-1} being the $-\text{NO}_2$ species, which was an important intermediate product of the L-H mechanism. In addition, the absorption peaks at 1420 cm^{-1} and 1126 cm^{-1} belonged to the bridged nitrate species and 1322 cm^{-1} to the bidentate nitrate species. The diffraction peak of the bridged nitrate either disappeared or weakened after 2 min of NH_3 introduction, and at 5 min of NH_3 introduction, an absorption peak appeared on the catalyst surface at 1322 cm^{-1} attributed to the NH_4^+ species at the Brønsted acidic site and disappeared at 20 min. At 2 min, a diffraction peak belonging to the Lewis acidic site was produced at 1207 cm^{-1} , and diminished at 10 min. It indicated that the catalytic process was most active with monodentate nitrate and bridged nitrate, which could react with ammonia species. It indicated that the reaction process on the catalyst surface followed the L-H mechanism and that the reactant species were monodentate nitrate, bridged nitrate and NH_4^+ species produced by NH_3 adsorption on the Brønsted acidic sites on the catalyst surface.

The proposed catalytic reaction mechanism is shown in Figure 10:

(a) Pre-adsorbed NH_3

(b) Pre-adsorbed $\text{NO} + \text{O}_2$

Figure 9. In-situ infrared spectra of the reaction of NH_3 and $\text{NO} + \text{O}_2$ pre-adsorbed species on the catalyst surface under the optimal reaction temperature

Figure 10. Schematic diagram of the catalytic process

The sample prepared in this paper was consistent with the L-H mechanism in the catalytic mechanism, and the intermediate product- NO_2 absorption peak can be used as an important basis. As the better catalytic activity temperature interval was concentrated in the mid to high-temperature section. Combined with the IR analysis results, it was concluded that the catalytic activity in the low-temperature section of this sample was dominated by the Brønsted acidic sites, and the activity in the medium to high temperature was dominated by the Lewis acid. Another interesting finding was that, after the roasting of CePO_4 mixed with CeCO_3F , the F element forms an inclusions layer on the catalyst surface, which hinders the promotion of Ce element in the catalytic process, The sulphation treatment can dissolve some of the F elements and expose more effective elements such as Ce. This finding provides an important basis for the catalytic process of Baiyun Ebo rare earth concentrates.

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DATA AVAILABILITY STATEMENT

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

LITERATURE CITED

- Deng, L. & Zhang, Z. (2018). Assessing the features of extreme smog in China and the differentiated treatment strategy. *Proceedings of the Royal Society A: Mathemat. Phys. Engin. Sci.* 474(2209), 20170511. DOI: 10.1098/rspa.2017.0511.
- Li, X.H. (2017). Optimization and reconstruction technology of SCR flue gas denitrification ultra low emission in coal fired power plant. *IOP Conference Series: Mater. Sci. Engin.* 231, 012111. DOI: 10.1088/1757-899X/231/1/012111.
- Zhu, M., Lai, J.K., Tumuluri, U., Wu, Z. & Wachs, I.E. (2017). Nature of Active Sites and Surface Intermediates during SCR of NO with NH₃ by Supported V₂O₅-WO₃/TiO₂ Catalysts. *J. Am. Chem. Soc.* 139(44), 15624–15627. DOI: 10.1021/jacs.7b09646.
- Xie, S.Z., Li, L.L., Jin, L.L., Wu, Y., Lin, H., Qin, Q., Liu, J., Dong, L. & Li, B. (2020). Low temperature high activity of M(M=Ce, Fe, Co, Ni) doped M-Mn/TiO₂ catalysts for NH₃-SCR and in situ DRIFTS for investigating the reaction mechanism. *Appl. Surf. Sci.* 515, 146014. DOI: 10.1016/j.apsusc.2020.146014.
- You, X.C., Sheng, Z.Y., Yu, D.Q., Yang, L., Xiao, X. & Wang, S. (2017). Influence of Mn/Ce ratio on the physicochemical properties and catalytic performance of graphene supported MnOx-CeO₂ oxides for NH₃-SCR at low temperature. *Appl. Surf. Sci.* 423, 845–854. DOI: 10.1016/j.apsusc.2017.06.226
- Guo, D.Y., Guo, R.T., Duan, C.P., Liu, Y.Z., Wu, G.I., Qin, Y. & Pan, W.G. (2021). Enhanced K resistance of Cu-SSZ-13 catalyst for NH₃-SCR reaction by the modification with Ce. *Molec. Catal.* 502, 111392. DOI: 10.1016/j.mcat.2021.111392.
- Ma, Y.Y., Li, Z.F., Zhao, N. & Teng, Y.L. (2020). One-pot synthesis of Cu-Ce co-doped SAPO-5/34 hybrid crystal structure catalysts for NH₃-SCR reaction with SO₂ resistance. *J. Rare Earths.* 39(10), 1217–1223. DOI: 10.1016/j.jre.2020.07.028.
- Zhang, L., Qu, H.X., Du, T., Ma, W. & Zong, Q. (2016). H₂O and SO₂ tolerance, activity and reaction mechanism of sulfated Ni-Ce-La composite oxide nanocrystals in NH₃-SCR. *Chem. Engin. J.* 296, 122–131. DOI: 10.1016/j.cej.2016.03.109.
- Wang Y., Li, G.G., Zhang, S.Q., Zang, X.Y., Zhang, X. & Hao, Z.P. (2020). Promoting effect of Ce and Mn addition on Cu-SSZ-39 zeolites for NH₃-SCR reaction: Activity, hydrothermal stability, and mechanism study. *Chem. Engin. J.* 393, 124782. DOI: 10.1016/j.cej.2020.124782.
- Ma, S., Tan, H., Li, Y., Wang, P., Zhao, Ch., Niu, X. & Zhu, Y. (2020). Excellent low-temperature NH₃-SCR NO removal performance and enhanced H₂O resistance by Ce addition over the Cu_{0.02}Fe_{0.2}Ce_yTi_{1-y}O_x (y = 0.1, 0.2, 0.3) catalysts. *Chemosphere.* 243, 125309. DOI: 10.1016/j.chemosphere.2019.125309.
- Chang, H., Ma, L., Yang, S., Li, J., Chen, L., Wang, W. & Hao, J. (2013). Comparison of preparation methods for ceria catalyst and the effect of surface and bulk sulfates on its activity toward NH₃-SCR. *J. Hazard. Mater.* 262, 782–788. DOI: 10.1016/j.jhazmat.2013.09.043.
- Lei, M., Chang, Y.S., Mohit, N., Xiaoyin, CH., Junhua, L. & Szwank, J.W. (2018). Shape dependence and sulfate promotion of CeO₂ for selective catalytic reduction of NOx with NH₃. *Appl. Catal. B: Environ.* 232, 246–259. DOI: 10.1016/j.apcatb.2018.03.065.
- Zhou, Z.Z., Lan, J.M., Liu, L.J. & Liu, Z. (2021). Enhanced alkali resistance of sulfated CeO₂ catalyst for the reduction of NOx from biomass fired flue gas. *Catal. Commun.* 149, 106230. DOI: 10.1016/j.catcom.2020.106230.
- Chen, W.S., Zhang, C.G. & Hu, F.L., et al. (2019). Study on the denitrification performance of sulfuric acid modified sintered ore catalysts. *Sintered pellets.* 44(5), 6. DOI: 10.13403/j.sjqt.2019.05.079.
- Zhang, Q.L., Zhang, J.H., Song, Z.X., Ning, P., Li, H. & Liu, X. (2016). A novel and environmentally friendly SO₄²⁻/CeO₂ catalyst for the selective catalytic reduction of NO with NH₃. *J. Ind. Engin. Chem.* 34, 165–171. DOI: 10.1016/j.jiec.2015.11.006.
- Cong, Q.L., Chen, L., Wang, X., Ma, H., Zhao, J., Li, S., Hou, Y. & Li, W., (2020). Promotional effect of nitrogen-doping on a ceria unary oxide catalyst with rich oxygen vacancies for selective catalytic reduction of NO with NH₃-ScienceDirect. *Chem. Engin. J.* 379, 122302–122302. DOI: 10.1016/j.cej.2019.122302.
- Duan, C.P., Guo, R.T., Liu, Y.Z., Wu, G.L., Miao Y., Gu, J. & Pan, W., (2020). Enhancement of potassium resistance of Ce-Ti oxide catalyst for NH₃-SCR reaction by modification with holmium. *J. Rare Earths.* DOI: 10.1016/j.jre.2020.10.018.
- Zhang, Y., Qu, R.Y., Su, W.K. & Li, J.H. (2015). A novel Ce-Ta mixed oxide catalyst for the selective catalytic reduction of NOx with NH₃. *Appl. Catal. B: Environ.* 176, 338–346. DOI: 10.1016/j.apcatb.2015.04.023.
- Dong, W.K., Somin, L., Jongsik, K., Kwan Y.L., Young, L. & Heon P.H. (2021). Influence of support composition on enhancing the performance of Ce-V on TiO₂ comprised tungsten-silica for NH₃-SCR. *Catalysis Today.* 359, 112–123. DOI: 10.1016/j.cattod.2019.07.002.
- Zeng, Y.Q., Song, W., Wang, Y., Zhang, S., Wang, T. & Zhong Q. (2020). Novel Fe-doped CePO₄ catalyst for selective catalytic reduction of NO with NH₃: The role of Fe³⁺ ions. *J. Hazard. Mater.* 383, 121212. DOI: 10.1016/j.jhazmat.2019.121212.
- Qian, J.N., et al. (2017). Study on the Catalytic performance of CO reduction of NO over copper-based catalysts supported by hydrotalcite. *J. Guangxi Univ. (Natural Science edition).* 42(05), 1843–1850.
- Pena, D.A., Uphade B.S., Reddy, E.P. & Smirniotis, P.G. (2004). Identification of surface species on titania-supported manganese, chromium, and copper oxide low-temperature SCR catalysts. *J. Phys. Chem. B.* 108(28), 9927–9936. DOI: 10.1021/jp0313122.
- Zeng, Y.Q., Wang, Y., Zhang, S., Zhong, Q. & Rong, W., Li, X. (2018). One-pot synthesis of ceria and cerium phosphate (CeO₂-CePO₄) nanorod composites for selective catalytic reduction of NO with NH₃: Active sites and reaction mechanism. *J. Colloid Inter. Sci.* 524, 8–15. DOI: 10.1016/j.jcis.2018.04.003.