Research Article

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Effect of calcination temperature on rare earth tailing catalysts for catalytic methane combustion

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Abstract: Bayan Obo tailings are rich in rare earth elements (REEs), iron, and other catalytic active substances. In this study, mine tailings were characterized at different temperatures and tested for the catalytic combustion of low-concentration methane. Upon calcination at 600°C, high catalytic activity was revealed, with 50% CH₄ conversion at 587°C (space velocity of 12,000 mL/g h). The physicochemical properties of catalysts were characterized using thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, hydrogen temperature-programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy (XPS). Compared to the raw ore sample, the diffraction peak calcined at 600°C increased post calcination, whereas that of CeCO₃ decreased. A porous structure appeared after the catalyst was calcined at 600°C. Additionally, Fe, Ce, Ti, and other metal elements were more highly dispersed on the catalyst surface. H₂-TPR results revealed a broadening of the reduction temperature range for the catalyst calcined at 600°C and an increase in the reduction peak. XPS analysis indicated the presence of Ce in the form of Ce³⁺ and Ce⁴⁺ oxidation states and the coexistence of Fe in the form of Fe⁵⁺ and Fe⁴⁺. Moreover, XPS revealed a higher surface O_ads/O_latt ratio. This study provides evidence for the green reuse of Bayan Obo mine tailings in secondary resources.

Keywords: rare earth tailings, low-concentration methane, catalytic combustion, calcination

1 Introduction

Coal mine gas is an associated gas in coal seams. The main component of coal mine gas is methane (CH₄), which is often released into the atmosphere during mining through ventilation pipes. The greenhouse contribution of CH₄ to global warming is the emission of harmful NOₓ, CO, and other hydrocarbons. However, the synthesis of a reasonably designed catalyst with good low-temperature ignition performance and high-temperature thermal stability remains a challenge [6, 7]. Although noble metal catalysts, particularly, palladium-based catalysts exhibit high activity in the catalytic, 21 times higher than the greenhouse effect of carbon dioxide (CO₂) [1–5]. Therefore, effectively eliminating low-concentration CH₄ is highly significant for environmental protection. The catalytic combustion of CH₄ has many advantages over thermal combustion: reduction in ignition temperature, complete combustion, and reduction in combustion of CH₄; their price and easy sintering at high temperatures limit their industrial application [8–10]. Therefore, searching for a nonnoble metal catalyst to completely oxidize methane at low temperature is important.

The different metal components in a mixed metal oxide can interact with each other, e.g., through electron coordination or for structural stability, which increases their catalytic activity compared to the corresponding single-component catalyst. Currently, catalysts containing Cu and Mn exhibit high catalytic activity in the...
combustion of CH₄. Fe and Co catalysts modified by the addition of rare earth elements (REEs) as additives have attracted research attention [11–13]. Zhang et al. prepared a Mn–Ni catalyst using a coprecipitation method and investigated its role in the catalytic combustion of low-concentration CH₄ [14]. Li et al. showed that a Ce₁₋ₓFeₓO₂₋ₓ catalyst exhibits not only improved reducibility but also increased lattice oxygen, thereby increasing the catalytic oxidation capacity of the catalyst [15]. Zhang et al. showed that the addition of CeO₂, ZrO₂, La₂O₃, and CeO₂−ZrO₂ as additives can significantly improve the specific surface area of the catalyst, promote the dispersion of each active component, and increase the surface oxygen concentration; thus, the activity of the Cu–Mn–O/Al₂O₃/COR catalyst is significantly improved [16].

The Bayan Obo deposit in China is the largest REE resource worldwide [17]. The mine tailings in Bayan Obo are generated via separation and flotation. Till date, 160 million tons of mine tailings have been stockpiled in the Bayan Obo tailings dams. Using or recycling these resources is difficult owing to many complex factors, such as low grade, fine grain size, and a complex mineral composition [18,19]. However, the mine tailings still contain REEs and transition metal elements, of which REEs and iron oxides are a common raw material for catalyst preparation. Elements, such as Fe, Ce, and Mn, present in the mine trailing may display synergistic effects with other components to increase the catalytic activity in methane combustion. Therefore, this study uses mine tailings as a raw material to prepare a catalyst for the catalytic combustion of low-concentration CH₄. This reduces greenhouse gas emission and realizes the reuse of mine tailing resources.

2 Experiment

2.1 Catalyst preparation

The raw materials used in this experiment were mine tailings containing REEs (henceforth referred to as “mine tailings”) from the Bayan Obo area [20]. Tables 1 and 2 display the main elements present in the mine tailings. The composition of the mine tailings is complex; they contain numerous metal elements, including RE oxides (REE) (5.88%) and Fe₂O₃ (27.7%). Table 3 displays the major mineral species in the mine tailings, including iron ore, fluorite, bastnaesite, monazite, barite, and ankerite.

The following steps were performed for catalyst preparation: a certain amount of tailings containing REEs were crushed, ground, sieved, and dried and were then divided into 100–200, 200–300, 300–400, and 400–500 meshes. The particle size with the best catalytic activity was calcined at 400°C, 500°C, 600°C, and 700°C for 4 h, and the resulting samples were labeled as 2, 3, 4, and 5, respectively. The original RE-containing mine tailing sample of dolomite was labeled as 1.

2.2 Catalytic activity tests

Figure 1 shows the setup for measuring the activity for catalytic oxidation of methane. The catalysts’ activity was evaluated using a continuous-flow fixed-bed quartz tube microreactor (diameter 10 mm). The reaction conditions were as follows: 2% CH₄, 18% O₂, and N₂ as the balance gas, ordinary atmospheric pressure, a volumetric space velocity (SV) of 20,000 mL/g h, and 500 mg of catalyst. The reaction temperature was increased from 300°C to 750°C at a heating rate of 5°C/min, and data were recorded at each temperature point that is stabilized for 30 min. Finally, the methane content was monitored online via gas chromatography (Agilent 8890B) using a thermal conductivity detector (TCD). The catalytic efficiency of methane was calculated as follows:

$$\eta = \frac{w_0 - w_1}{w_0} \times 100\%$$

where \(\eta\) is the conversion rate of CH₄, \(w_0\) is the methane content before the reaction, and \(w_1\) is the methane content after the reaction.

| Components | REO | CeO₂ | Pr₂O₃ | Nd₂O₃ | La₂O₃ |
|-------------|-----|------|-------|-------|-------|
| Amount (wt%)| 5.88| 3.01 | 0.33  | 1.10  | 1.44  |

Table 3: Content of RE oxides in Bayan Obo mine tailings

Table 1: Chemical composition of Bayan Obo mine tailings

| Components | SiO₂ | Fe₂O₃ | CaO | TiO₂ | Na₂O | MnO₂ | MgO | Al₂O₃ | BaO | F | REO | Others |
|------------|------|-------|-----|------|------|------|-----|-------|-----|----|------|---------|
| Amount (wt%)| 11.9 | 27.7  | 27.2 | 1.00 | 1.28 | 1.96 | 3.31 | 1.26  | 2.70 | 8.92| 5.88 | 6.89    |

Table 2: Content of RE oxides in Bayan Obo mine tailings

| Components | REO | CeO₂ | Pr₂O₃ | Nd₂O₃ | La₂O₃ |
|-------------|-----|------|-------|-------|-------|
| Amount (wt%)| 5.88| 3.01 | 0.33  | 1.10  | 1.44  |
content after stabilization. The activity of the methane combustion catalyst was preliminarily evaluated using three performance indicators: the temperature at which methane conversion is 10%, 50%, and 100%, referred to as $T_{10}$, $T_{50}$, and $T_{90}$, respectively.

The kinetic parameters for CH$_4$ combustion were measured at a conversion rate below 20%. The reaction rate of CH$_4$ ($r$, mol/g$_{cat}$ s) conversion was calculated as follows:

$$r = \frac{V_{CH_4} \cdot \eta}{W_{cat}}$$  

(2)

where $V_{CH_4}$, $\eta$, and $W_{cat}$ are the CH$_4$ flow rate (mol/s) and the CH$_4$ conversion catalyst weight, respectively. According to the Arrhenius formula, the activation energy ($E_a$) of the catalyst for CH$_4$ combustion can be obtained from the slope of a linear plot of $\ln r$ versus $1/T$, according to the following equation:

$$\ln r = -\frac{E_a}{RT} + C$$  

(3)

2.3 Characterization of catalyst

To elucidate the relation between structure and catalytic activity, the catalysts were characterized. Herein, several techniques were applied. The thermogravimetric (TG) analysis curve was measured using STA449C, NETZSCH (Germany). The online mass spectrometer (MS) (HPR20) used in this study was manufactured by HIDEN (UK). X-ray fluorescence (XRF) was obtained using a Rigaku ZSX primus (Japan). XRF samples were prepared on glass disk melts in lithium tetraborate using automatic fusion apparatus with a mass ratio of 1:15. The operating voltage and current were 60 kV and 60 mA, respectively. XRF spectrometry was performed under vacuum. X-ray diffraction (XRD) results were recorded on a Bruker D8 Advance X-ray diffractometer, wherein the radiation source was Cu-K$\alpha$, the scanning angle range was $20^\circ$–$80^\circ$ with a scanning speed of $3^\circ$/min, and the voltage and current were 40 kV and 40 mA, respectively. Hydrogen temperature-programmed reduction (H$_2$-TPR) measurement was performed on a temperature rise chemical adsorption instrument (PCA-1200) with a TCD. Scanning electron microscopy (SEM) was performed using a Zeiss Sigma-500 field scanning electron microscope with a voltage of 30.0 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI Quantera II instrument. Calcination was mainly performed in a VTL1600 vertical tube furnace under an air atmosphere; therein, the inner diameter of the corundum tube is 80 mm, its length is 130 mm, and the heating element is a silicon and molybdenum rod.

3 Results and discussion

3.1 Thermogravimetric-mass spectrum analysis of catalyst

Figure 2a shows the TG curves of the REE-containing mine tailings. Between 200°C and 400°C, the TG curve shows a small weight loss phenomenon caused by the preliminary decomposition of cerium fluorocarbon or carbonate during calcination. Between 400°C and 700°C, the TG curve shows continuous and rapid weight loss caused by the further decomposition of fluorocarbon-
cerium ore into the oxides of the REEs by heating [18–20]. When the mine tailings are heated, they enter an endothermic state. Between 650°C and 930°C, weight loss continues to occur and an endothermic peak is present, which is caused by the sintering or melting of the REE-rich tailings.

During the calcination process, the RECO₃F completely decomposed to REOF, as the rare earth fluoride oxide generates phase separation to produce rare earth oxide and rare earth fluoride as the calcination temperature increases. Rare earth oxides include CeO₂ and other substances that are effective for catalysis. The presence of CeO₂ is important as it promotes the catalytic combustion of methane [20]. In summary, the catalyst’s calcination changes the mineral phase of the mine tailings. TG provides support for determining the optimal calcination temperature, with the disappearance of the fluorocarbon cerium ore peak representing the complete decomposition of the fluorocarbon cerium ore.

Figure 2b shows the mass spectrum of the REE-rich tailings. The first peak at 520°C is attributed to the decomposition of cerium fluoride. The following equation shows the decomposition of the fluorocarbon cerium ore [20]:

\[
\text{RECO}_3 \text{F} + \text{O}_2 \rightarrow \text{REOF} + \text{CO}_2 \quad (4)
\]

\[
\text{REOF} \rightarrow \text{Ce}_{0.75}\text{Nd}_{0.25}\text{O}_{1,875} + \text{(Ce,Pr)}\text{La}_2\text{O}_3\text{F}_7 \quad (5)
\]

The second peak at 680°C is attributed to the decomposition of MgCO₃ in iron dolomite. The decomposition of dolomite is divided into two steps: CaMg (CO₃)₂ decomposes in the dolomite sample to CaCO₃ and MgO at approximately 630–680°C, followed by [22]:

\[
\text{CaMg(CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2 \quad (6)
\]

### 3.2 Catalytic performance of methane combustion

The particle size of the mineral significantly influences the catalytic combustion of methane. As shown in Figure 3, the catalytic activity of the mine tailings with particle size above 300 mesh is significantly higher than that with particle size below 300 mesh. Typically, the catalytic performance of methane combustion increases with decreasing particle size of the original ore due to the increase in the relative dispersion with decreasing particle size, which produces a large contact area between the active components and CH₄. The catalytic activity of the mine tailings with the particle size of 300–400 mesh and 400–500 mesh was similar. However, the catalytic activity of tailings containing particles of 300–400 mesh size was slightly higher, and thus, these tailings were used further in the experiment.

As shown in Figure 4, the effects of the calcination temperature of the catalysts and the reaction temperature on the catalytic combustion of methane were studied herein. The activity of the catalytic combustion of methane increases as the transformation temperature decreases. Table 4 summarizes the corresponding
results. The catalytic activity increases with the calcination temperature. At a calcination temperature of 600°C, the catalyst is optimized. Compared to the original mine tailings, $T_{10}$ and $T_{90}$ are decreased by 56°C and 85°C, respectively. The catalytic activity of the catalyst decreases at a calcination temperature of 700°C. In summary, the catalytic activity decreases as follows: sample 4 > sample 3 > sample 2 > sample 1 > sample 5.

Cerium oxide will form at approximately 500°C; however, at higher calcination temperatures, structural changes will occur, which will reduce the specific surface area.

According to literature, methane oxidation has a first-order kinetic model (with a methane concentration of less than 20%) [6,10]. The apparent activation energy ($E_a$) of samples 1, 4, and 5 was calculated, and the correlation coefficients of the obtained curves were all above 0.989, showing strong linearity. As shown in Figure 4b and Table 4, the $E_a$ for sample 4 is 97.02 kJ/mol, which is lower than that of sample 1 (112.24 kJ/mol) and sample 5 (136.77 kJ/mol). Thus, sample 4 has the highest catalytic activity for CH$_4$ combustion.

### Table 4: Catalytic activities and $E_a$ of the catalysts for CH$_4$ combustion

| Samples | $T_{10}$/°C | $T_{50}$/°C | $T_{90}$/°C | $E_a$ (kJ/mol) |
|---------|-------------|-------------|-------------|----------------|
| Sample 1 | 499         | 659         | 748         | 112.24         |
| Sample 2 | 485         | 637         | 697         | 111.56         |
| Sample 3 | 468         | 623         | 686         | 108.94         |
| Sample 4 | 435         | 586         | 663         | 97.02          |
| Sample 5 | 606         | 702         | 737         | 136.77         |

#### 3.3 XRD characterization analysis

XRD patterns of the original mine tailings and the subsequent catalysts calcined at different temperatures are shown in Figure 5a and b. The mineral composition...
of the mine tailings is extremely complex. According to literature, these REE-containing mine tailings contain 71 elements and 172 minerals [18]. The main components are iron mineral and fluorocarbons, of which the primary constituent is the fluorocarbon cerium ore.

Figure 5a shows that CaF$_2$, Fe$_2$O$_3$, and CeCO$_3$F are the main minerals in the mine tailings before calcination. The intensity of the diffraction peak of CaF$_2$ is the strongest, indicating that the CaF$_2$ content is high. The intensity of the CeCO$_3$F peak gradually decreases with increasing calcination temperature (Figure 5b). At the calcination temperature of 700°C, the diffraction peak of the fluorocarbon cerium ore disappears. According to literature, the fluorocarbon cerium ore is completely decomposed into CeO$_2$ at 700°C [21]. Furthermore, Fe$_3$O$_4$ in the mine tailings is converted into Fe$_2$O$_3$. Both CeO$_2$ and Fe$_2$O$_3$ can promote the catalytic combustion of methane. However, the conversion rate of methane decreases after calcination at 700°C.

3.4 Properties and microstructure analysis

As shown in the SEM results (Figure 6a), the original mine tailings have an irregular shape but smooth surface. Post calcination at 500°C, cracks appear on the surface of the mineral (Figure 6b). Post calcination at 600°C, further cracks are observed on the mineral, with the formation of a pore structure that increases the mineral’s specific surface area. At 700°C, the entire surface of the tailings is flocculent. In conclusion, surface roughness increases with the calcination temperature, resulting in a flocculated surface. This effect increases the specific surface area of the catalysts and exposes active sites, increasing the contact area between methane gas and the catalyst [22,23].

As shown in Figure 7, energy-dispersive X-ray spectroscopy (EDS) mapping of the catalyst calcined at 600°C reveals that Fe, Ce, Ti, O, and other active metal elements are evenly distributed on the catalyst surface.

3.5 XPS and oxygen species analysis

Figure 8a shows the Ce 3d XPS spectra for samples 1–5. Cerium mainly exists as Ce$^{3+}$ and Ce$^{4+}$ in the samples. The characteristic peaks of Ce$^{4+}$ approximately appear at the following binding energies: 882.20, 888.60, 898.00, 907.20, and 916.15 eV, labeled as $v_0$, $v_1$, $v_2$, $v_3$, $v_4$, and $v_5$, respectively. The characteristic peaks of Ce$^{3+}$ approximately appear at the following binding energies: 884.40, 880.00, 903.90, and 899.30 eV, labeled as $u_0$, $u_1$, $u_2$, and $u_3$, respectively [24–26]. The spectra for the mine tailings contain the characteristic peaks of both Ce$^{3+}$ and Ce$^{4+}$ before and after calcination. The conversion of Ce$^{3+}$ to Ce$^{4+}$ occurs in the calcined samples. Ce$^{3+}$ is beneficial owing to the production of oxygen vacancies and unsaturated chemical bonds, which can promote the adsorption and migration of oxygen and thereby improve the redox performance of the catalyst. The relative contents of Ce$^{3+}$/Ce$^{4+}$ are presented in Table 5. Sample 4 contained the highest Ce$^{3+}$ content, which confirms the above viewpoint. Therefore, the catalyst calcined at 600°C exhibits better catalytic performance owing to the presence of both Ce$^{3+}$ and Ce$^{4+}$.

Figure 8b shows the Fe 2p XPS spectra for samples 1–5. The binding energies of the characteristic peaks of Fe$^{3+}$ are observed at approximately 711 (W1) and 725 eV (W2). The binding energy for Fe$^{2+}$ is at approximately 718–721 eV [27]. From the spectrum, we can observe that Fe exists in the form of both Fe$^{2+}$ and Fe$^{3+}$. Interconversion between Fe$^{2+}$ and Fe$^{3+}$ provides unstable oxygen vacancies and increases mobility of the lattice oxygen species on the catalyst surface. Fe$^{3+}$ is easily reduced; thus, Fe$^{2+}$ is beneficial to the catalytic performance of the catalyst. Table 5 shows that the tailings calcined at 600°C contain more Fe$^{2+}$. The Fe$^{2+}$/Fe$^{3+}$ ratio in sample 4 was the highest among the five samples and reached 0.56, resulting in good catalytic performance.
Figure 8c shows the O 1s XPS spectra for samples 1–5. Two species of oxygen can be distinguished here. The characteristic peak for lattice oxygen \(O_{\text{latt}}\) can be found at approximately 529.5–530.5 eV, and the characteristic peak for adsorbed energy \(O_{\text{ads}}\) can be found at approximately 531.5–533.0 eV [28]. According to the
literature [29,30], lattice oxygen and adsorbed oxygen can be interconverted, whereby the reaction with adsorbed molecules on the catalyst surface can be achieved by converting lattice oxygen to adsorbed oxygen. The $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio can be used to describe the ratio of oxygen species: the higher the ratio, the more reactive oxygen species are present on the catalyst surface and the better is the activity. Table 5 shows a range of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ values for the samples in the following order: sample 4 (19.00) > sample 3 (11.50) > sample 2 (7.33) > sample 1 (4.56) > sample 5 (4.00). Therefore, the high content of $\text{Ce}^{3+}$, $\text{Fe}^{2+}$, and $\text{O}_{\text{ads}}$ contributes to the improvement of catalytic activity.

### 3.6 Reducibility and stability of catalyst

High mobility of oxygen in surface and bulk contributes to the high activity for hydrocarbon oxidation. $\text{H}_2$-TPR diagram shows (Figure 9) that sample 1 has only one hydrogen consumption peak at 665°C, samples 2 and 3 have two reduction peaks, and sample 4 has four reduction peaks. The first reduction peak of samples 2, 3, and 4 appears at approximately 400°C, and the first reduction peak of sample 4 appears at approximately 500°C; these peaks are due to the surface-active oxygen reduction of the $\text{Ce}^{4+}$–$\text{O}$–$\text{Ce}^{4+}$ bond. In samples 1–4, a reduction peak appears at approximately 650°C, which can be attributed to FeO [31–33]. The reduction peaks of samples 4 and 5 at approximately 650–800°C can be attributed to the surface lattice oxygen [34]. Among them, sample 4 has the largest number of reduction peaks, which are at low temperatures, revealing that the redox properties of the catalyst calcined at 600°C are relatively good, thus improving the corresponding catalytic performance.

Figure 10 shows the stability experiment results for samples 1, 3, and 4. The samples were evaluated on-stream for 3,500 min at $T_{90}$ (686°C). The methane conversion of sample 1 began to decline significantly around 260 min and consistently declined until 3,500 min. The methane conversion dropped from 63% to 31%. However, the methane conversion for samples 3 and 4 only started to gradually decline after 1,000 min. After 3500 min, the methane conversion rate remained above 80%. Therefore, a higher calcination temperature can increase the stability of the catalyst.

![Figure 9: H2-TPR diagrams before and after the calcination of mine tailings.](image)

![Figure 10: Methane combustion with time-on-stream for samples 1, 3, and 4.](image)
4 Conclusion

Mine tailings from an REE mine were used to prepare catalysts for the catalytic combustion of low-concentration CH₄. The mine tailings were calcined at 400°C, 500°C, 600°C, and 700°C to prepare the catalysts. Calcination at 600°C produced catalysts that exhibited the lowest apparent activation energy ($E_a$ is 79.02 kJ/mol) along with the highest performance for the catalytic combustion of methane ($T_{50}$ of 586°C and $T_{90}$ of 663°C). To further investigate the structural changes post calcination, various characterization methods were performed. The diffraction peak intensity of Fe₂O₃ in the mine tailings was enhanced, whereas the CeCo₁xF₄ peak intensities were reduced. Moreover, a series of beneficial properties were afforded upon the calcination of the catalyst. Cracks and holes appeared on the surface, which increased the specific surface area. Fe, Ce, Ti, O, and other active metal elements were evenly distributed throughout the catalyst. A high surface $O_{ads}/O_{latt}$ ratio was achieved, thus enhancing the reducibility. Ce coexisted in both Ce³⁺ and Ce⁴⁺ oxidation states, and Fe coexisted in the Fe³⁺ and Fe⁴⁺ oxidation states as active components in the mine tailings, which improved the catalytic activity. However, at 700°C, sintering occurred, which lowered the catalytic performance.

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