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# Catalytic hydrolysis of carbonyl sulfide in blast furnace gas over Sm-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst†

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Carbonyl sulfur (COS) is a prominent organic sulfur pollutant commonly found in the by-product gas generated by the steel industry. A series of Sm-doped CeO<sub>x</sub>@ZrO<sub>2</sub> catalysts were prepared for the hydrolysis catalytic removal of COS. The results showed that the addition of Sm resulted in the most significant enhancement of hydrolysis catalytic activity. The 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst exhibited the highest activity, achieving a hydrolysis catalytic efficiency of 100% and H<sub>2</sub>S selectivity of 100% within the temperature range of 90–180 °C. The inclusion of Sm had the effect of reducing the acidity of the catalyst while increasing weak basic sites, which facilitated the adsorption and activation of COS molecules at low temperatures. Appropriate doping of Sm proved beneficial in converting active surface chemisorbed oxygen into lattice oxygen, thereby decreasing the oxidation of intermediate products and maintaining the stability of the hydrolysis reaction.

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## 1. Introduction

Carbonyl sulfide (COS) is widely present in the by-product gas (blast furnace gas, coke oven gas, converter gas) of the iron and steel industry.<sup>1–3</sup> Its acidity and polarity are weaker than H<sub>2</sub>S, but its properties are more stable, making the removal of COS an important part of achieving gas fine desulfurization.<sup>4,5</sup> COS removal methods mainly include pyrolysis, hydrogenation, hydrolysis, chemical absorption and so on.<sup>6,7</sup> Pyrolysis is greatly affected by temperature, so the hydrogenation conversion method is widely used in industry, but the hydrogenation method requires higher temperature, and is prone to side reactions.<sup>8–10</sup> The catalytic hydrolysis method has high conversion efficiency and few side reactions. It is a hot research field at present and the core aspect is the research and development of hydrolysis catalysts.<sup>11,12</sup>

COS hydrolysis catalyst are based on γ-Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, etc.<sup>13–16</sup> The H<sub>2</sub>S produced by hydrolysis is easily oxidised to monosulfur or

further oxidised to sulphate, which is deposited on the surface of the catalyst, thus clogging up the holes of the catalyst.<sup>17,18</sup> γ-Al<sub>2</sub>O<sub>3</sub> is strongly acidic, which reduces the surface alkalinity of aluminium-based catalysts, making the catalysts inadequate in low-temperature hydrolysis performance and stability.<sup>19</sup> In contrast, TiO<sub>2</sub> has stronger resistance to sulfate, and TiO<sub>2</sub> itself has better catalytic hydrolysis ability for COS, but the relatively small specific surface area of TiO<sub>2</sub> will limit its application to some extent.<sup>20,21</sup> Studies have shown that ZrO<sub>2</sub> has higher hydrolysis catalytic activity and stability than Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Previous studies found that the hydrolysis activity of nano-TiO<sub>2</sub> and ZrO<sub>2</sub> is much higher than that of commercial nano-Al<sub>2</sub>O<sub>3</sub>, and that the increase in the activity is due to the decrease in surface hydrophilicity of the catalyst and increase in free surface basic hydroxyl groups.<sup>22–24</sup> However, the low-temperature hydrolysis activity of ZrO<sub>2</sub> was insufficient, and the loaded metal oxides were proved to be effective in enhancing the hydrolysis activity of the catalysts.<sup>25,26</sup> Consequently, the catalyst for the hydrolysis catalytic removal of carbonyl sulfur should be bifunctional, which means catalyst should have both ox-red and acid-base sites. Moreover, acid sites should be medium strength. One of the ways of such type catalyst's design is based on the application of oxide composites.

Alkali metals and alkaline earth metals regulate the alkali content and alkali strength distribution on the catalyst surface, but they do so in slightly different ways.<sup>27,28</sup> Alkali metals have a significant modulating effect on alkali content, while alkaline earth metals have a significant modulating effect on alkali strength. Rare earth elements such as La, Ce and Pr, which have a unique 4f electron layer structure, are used as excellent catalytic materials and co-catalysts, and they exhibit unique catalytic properties in chemical reactions. When they are used in

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combination with components such as metals or their oxides, they have obvious synergistic effects and show reaction activities that far exceed the expected ones.<sup>29–32</sup>

Consequently, this study utilized CeO<sub>2</sub> as the primary active component of the catalyst and ZrO<sub>2</sub> as the catalyst carrier. The aim was to evaluate various metal oxides (Sm, Y, Na, K) for doping modification. After screening the optimal metal oxides for doping, the doping amount was adjusted to determine the most effective ratio. The morphology and structure of the catalyst were characterized, and the reasons behind the improvement in hydrolysis catalytic efficiency and anti-poisoning ability were analyzed. Additionally, the preparation conditions and process parameters of the catalyst were investigated to determine the optimal ones.

## 2. Experimental

### 2.1 Catalyst preparation

In this experiment, a specific quantity of nano-ZrO<sub>2</sub> and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was carefully measured and placed in a beaker. Deionised water was then added to the mixture, followed by a certain amount of Sm<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Y(NO<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>, with a doping concentration of 1%. The mixture was stirred at a temperature of 80 °C for a duration of 8 h. The dried solid product was removed by spatula into a quartz crucible. Subsequently, the solid material was calcined in an air atmosphere at 600 °C for a period of 2 h, resulting in the formation of catalyst samples. These catalysts were given the names Sm-CeO<sub>x</sub>@ZrO<sub>2</sub>, Y-CeO<sub>x</sub>@ZrO<sub>2</sub>, Na-CeO<sub>x</sub>@ZrO<sub>2</sub>, and K-CeO<sub>x</sub>@ZrO<sub>2</sub>, respectively. Furthermore, additional catalyst samples were prepared by adjusting the amount of Sm<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, resulting in different doping concentrations of Sm. These samples were designated as 1% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>, 2% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>, 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>, 4% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>, and 5% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>. The detail qualification about the reagents was provided in ESI†.

### 2.2 Catalytic activity test and characterization

The detail information of characterization and catalytic activity test was provided in ESI†.

## 3. Results and discussion

### 3.1 Screening catalysts

In order to optimize the performance of catalyst, an investigation was conducted to examine the influence of doping with rare earth metals Sm and Y, as well as alkali metals Na and K. The experimental findings presented in Fig. 1 illustrated the COS conversion and H<sub>2</sub>S selectivity of the 1% MO<sub>x</sub> dopant on a 15% CeO<sub>x</sub>@ZrO<sub>2</sub> catalyst. The results clearly demonstrated that, within the temperature range of 60 to 180 °C, the impact of rare earth metal doping on the hydrolysis performance of the catalyst surpassed that of alkali metals. Notably, Sm as a dopant exhibited the most substantial enhancement in the hydrolysis activity, achieving a hydrolysis efficiency of 100% at 180 °C. This positive outcome could be attributed to the reinforcement of the synergistic interaction between the active component of the catalyst and the carrier through the addition of Sm, resulting in an increased abundance of hydroxyl groups on the catalyst and ultimately enhancing the hydrolysis efficiency.<sup>33</sup>

### 3.2 Catalytic properties of Sm-based catalysts

Fig. 2 presented the performance of catalysts containing different amounts of Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub>. The evaluation was based on COS conversion and H<sub>2</sub>S selectivity. The findings indicated that the catalytic activity was most favorable when the doping amount of Sm<sub>2</sub>O<sub>3</sub> constituted 3% of the carrier mass fraction. Specifically, the COS conversion of 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> is 13.7% higher than that of 1% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> at 60 °C. Moreover, the H<sub>2</sub>S selectivity of 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> reaches 90.7% at 60 °C. This outcome was attributed to the enhanced synergistic effect among Sm, Ce, and Zr metals resulting from the increased doping amount of Sm.<sup>34</sup>

The dispersion state of the active component in the catalyst and the interaction between the active component and the carrier were greatly influenced by the calcination temperature, thus altering the catalytic activity of the catalyst.<sup>35,36</sup> Fig. 3 showed the curves of the COS hydrolysis conversion and H<sub>2</sub>S selectivity for 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts calcined at different temperatures. The results indicated that the optimal

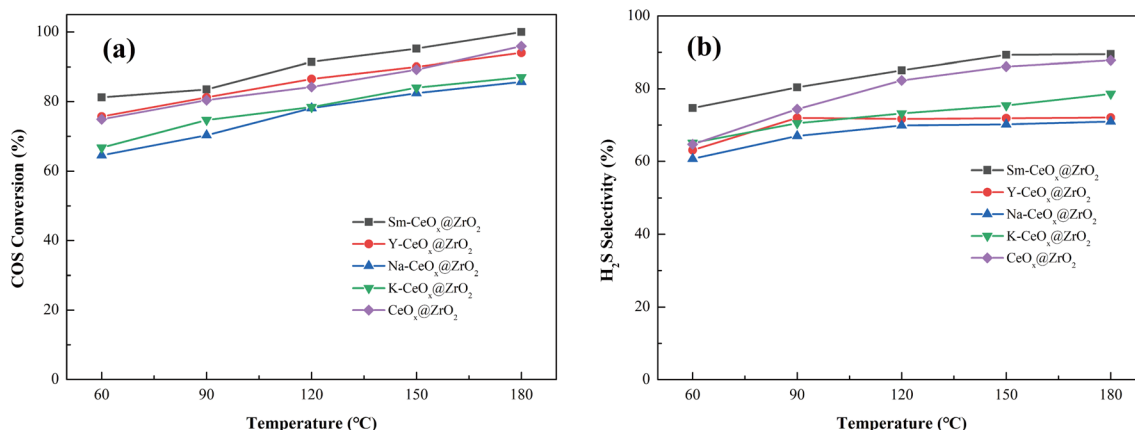


Fig. 1 (a) COS conversion, (b) H<sub>2</sub>S selectivity of M-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts.



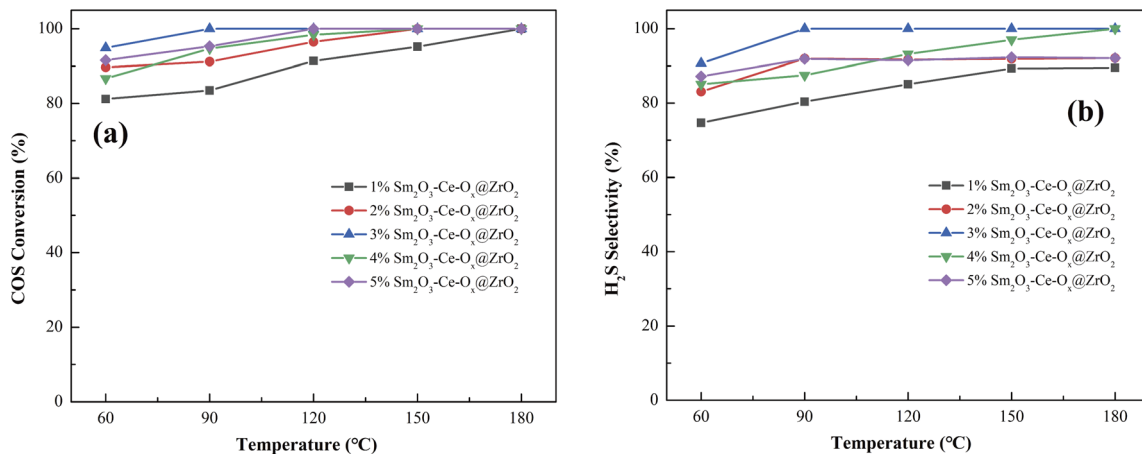


Fig. 2 (a) COS conversion, (b) H<sub>2</sub>S selectivity of Sm-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts with different Sm contents.

calcination temperature for the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst was 600 °C. When the calcination temperature was increased from 300 °C to 600 °C, the COS conversion and H<sub>2</sub>S selectivity of the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst both increased. The COS conversion increased from 71.1% to 94.9%, and the H<sub>2</sub>S selectivity increases from 71.7% to 90.7% at 60 °C. However, when the calcination temperature was 700 °C, the catalytic performance of the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst decreased. This might be attributed to the fact that excessively high calcination temperatures were unfavorable for the dispersion of the active component on the catalyst surface, while also leading to the destruction of the catalyst structure, thereby resulting in a decrease in the catalytic performance of the catalyst.<sup>37,38</sup>

The calcination time of catalyst had an impact on both the COS conversion and H<sub>2</sub>S selectivity of the catalyst. Fig. 4 illustrated the catalytic performance and H<sub>2</sub>S selectivity of catalysts prepared with different calcination times at 600 °C. It can be observed that the hydrolysis activity of the catalyst first increased and then decreased with increasing calcination time. The optimal calcination time for the catalyst was 2 h, with a COS conversion of 94.9% at 60 °C and an H<sub>2</sub>S selectivity of 90.7%.

Compared to a calcination time of 1 h, the hydrolysis efficiency increased by 25.6% and the H<sub>2</sub>S selectivity increased by 23.1%. The hydrolysis efficiency and H<sub>2</sub>S selectivity both remained at 100% after 90 °C. This was because a too short calcination time cannot form a Sm-Ce-Zr solid solution, reducing the redox properties of the catalyst and subsequently affecting its acidity and basicity. With further prolongation of the calcination time, the COS conversion decreased to 82% at 60 °C when the calcination time was 3 h, and further decreased to 78.4% when the calcination time was 4 h. An excessively long calcination time led to a decrease in COS conversion and a corresponding decrease in H<sub>2</sub>S selectivity, possibly due to the destruction of the pore structure caused by the prolonged calcination time, resulting in a decrease in hydrolysis activity.

### 3.3 Efficiency of Sm-based catalysts

The stability of catalyst was one of the factors used to evaluate the performance of a catalyst.<sup>39,40</sup> Fig. 5 illustrated the stability test results for different catalysts. From Fig. 1(a), it could be observed that the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst exhibited the best stability, maintaining 90% hydrolysis efficiency even after continuous testing

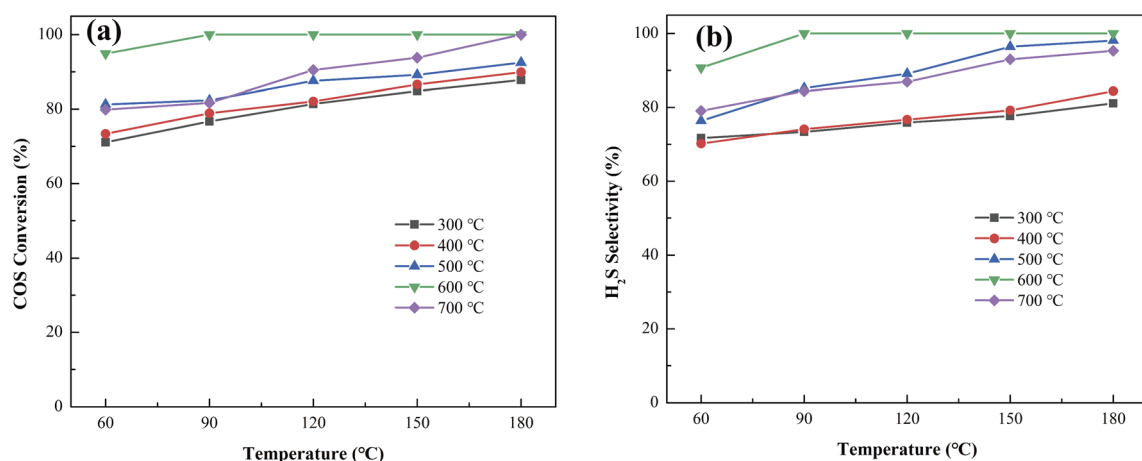


Fig. 3 (a) COS conversion, (b) H<sub>2</sub>S selectivity of 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts under different calcination temperatures.



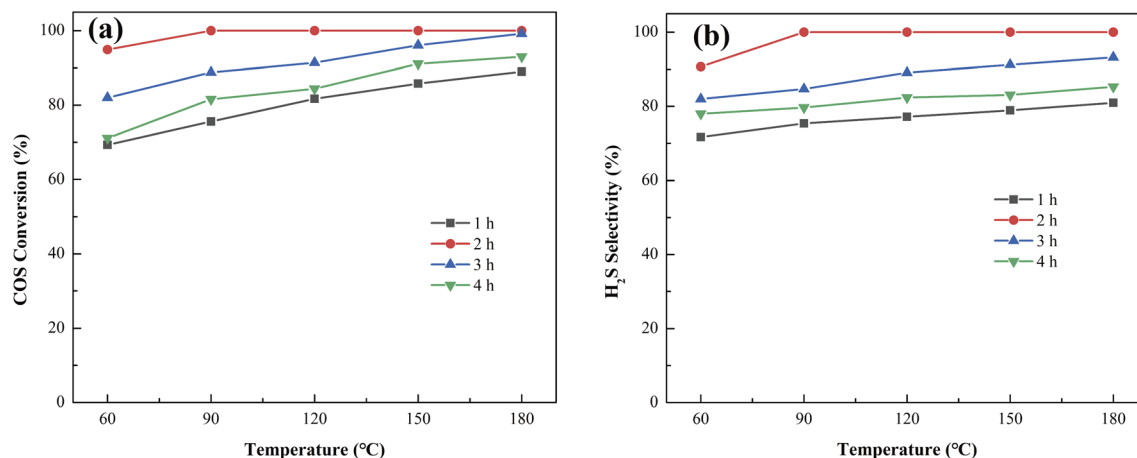


Fig. 4 (a) COS conversion, (b) H<sub>2</sub>S selectivity and of 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts under different calcination time.

for 20 h. This indicated that the addition of Sm enhanced the stability of the CeO<sub>x</sub>@ZrO<sub>2</sub> catalyst. Based on this, the stability of the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst under different temperature conditions was investigated. Fig. 5(b) depicted the test curves for the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst at three different temperatures: 60 °C, 90 °C, and 120 °C. It can be seen that the COS conversion rate dropped to 90% after continuous testing for 7 h at 60 °C. This might be attributed to the condensation of H<sub>2</sub>O in the reaction gas, which covered the catalyst surface and reduced the hydrolysis activity. The catalyst maintained a 90% COS conversion for 30 h at 120 °C, which demonstrated the significant stability improvement of the catalyst with increased temperature.

The 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst demonstrated superior catalytic performance in COS hydrolysis at lower temperatures (<90 °C) compared to both Al-based catalysts and activated carbon series catalysts (Table 1). This suggested that the addition of Sm<sub>2</sub>O<sub>3</sub> effectively enhanced the basicity of the catalyst surface, increasing the number of active sites. As a result, the catalyst was able to promote the conversion of COS to H<sub>2</sub>S even at lower reaction temperatures, with the hydrolysis reaction playing a dominant role in the surface reaction.

### 3.4 Analysis of components

The X-ray diffraction patterns of different catalysts were presented in Fig. 6. From the graph, it can be observed that the catalysts exhibited diffraction peaks at  $2\theta = 17.3^\circ, 24.1^\circ, 28.2^\circ, 31.5^\circ, 34.1^\circ, 35.2^\circ, 38.5^\circ, 40.8^\circ, 46.2^\circ, 50.5^\circ, 54.2^\circ, 55.6^\circ, 59.9^\circ, 63.1^\circ,$  and  $65.8^\circ$ . These peaks corresponded to the crystal planes (001), (110), (-111), (111), (002), (-201), (120), (-112), (201), (-121), (221), (-311), (-203), (113), and (023) of ZrO<sub>2</sub> (PDF-ICDD 37-1484).<sup>45,46</sup> The diffraction peak at  $2\theta = 47.5^\circ$  corresponded to the crystal plane (220) of CeO<sub>2</sub> (PDF-ICDD 43-1002).<sup>47</sup> However, characteristic diffraction peaks of Sm<sub>2</sub>O<sub>3</sub> were not observed in the XRD pattern of the catalysts. This could be due to the low mass fraction of Sm in the catalyst or the highly dispersed or amorphous nature of Sm<sub>2</sub>O<sub>3</sub> on the catalyst surface.

### 3.5 Specific surface area analysis

The N<sub>2</sub> adsorption and desorption curves, pore size distribution, and specific surface area of five catalyst groups were shown in Fig. 7 and Table 2. According to Table 2, when the doping amount was 3%, the specific surface area of the catalyst Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> increased from 27 m<sup>2</sup> g<sup>-1</sup> to 30 m<sup>2</sup> g<sup>-1</sup>. The larger

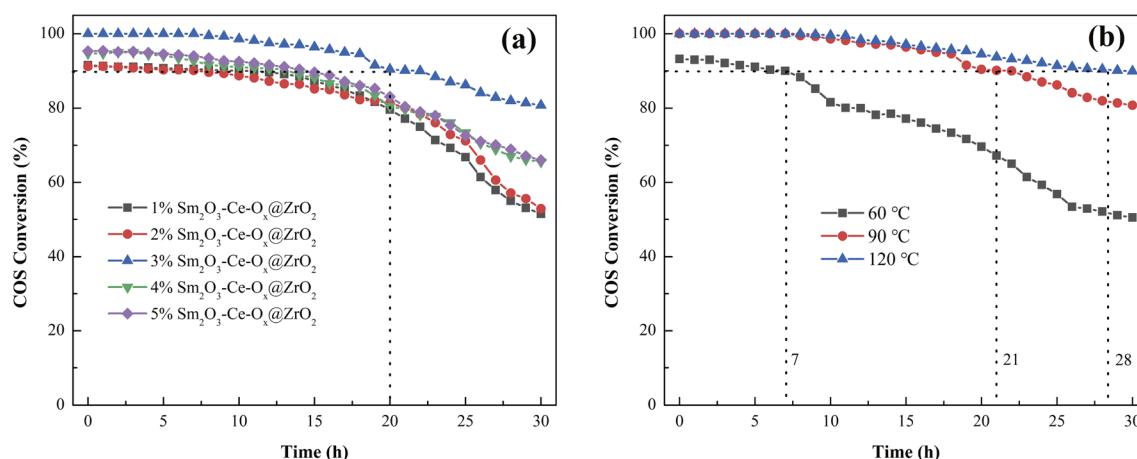
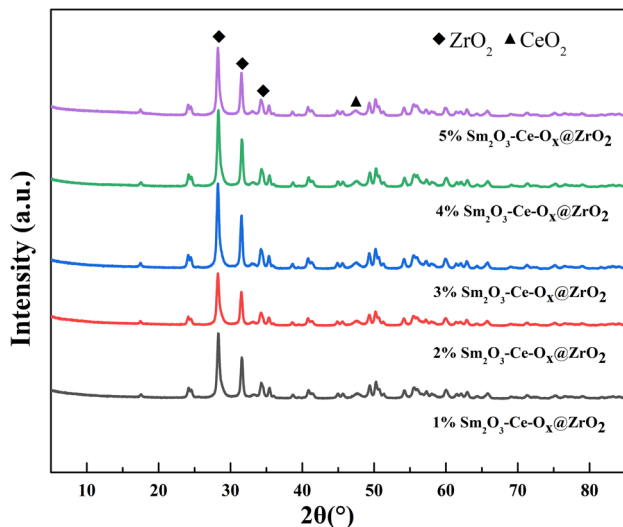


Fig. 5 Stability of Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst: (a) different Sm contents, (b) different reaction temperature.



Table 1 The summary results of published catalysts performance

| Catalyst                                     | Concentration (ppm) | Temperature (°C) | GHSV (h <sup>-1</sup> ) | Conversion (%) | Ref. |
|--|---------------------|------------------|-------------------------|----------------|------|
| 0.5% Pt/5% Ba/Al <sub>2</sub> O <sub>3</sub> | 500–1000            | 200              | 7000                    | 100            | 41   |
| 5% K/Mo-Al <sub>2</sub> O <sub>3</sub>       | 150                 | 120              | 17 000                  | 100            | 42   |
| Fe <sub>1</sub> Cu <sub>4</sub> /AC          | 150                 | 130              | 10 000                  | 70             | 43   |
| 10Ni/AC                                      | 340                 | 160              | 20 000                  | 100            | 44   |

Fig. 6 XRD patterns of Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts with different Sm contents.

specific surface area increased the effective contact area between the reactants and the catalyst, which was beneficial for the adsorption and diffusion of reactant molecules on the catalyst surface. Meanwhile, the number of active sites of the catalyst were increased, thereby enhancing the hydrolysis activity of the catalyst. Although the catalysts with different Sm additions had different average pore diameters, the average

pore diameters of each catalyst were still much larger than the molecular dynamic diameters of COS (0.34 nm) and H<sub>2</sub>O (0.27–0.32 nm), which suggests that COS and H<sub>2</sub>O can enter the internal pores of the catalysts for hydrolysis reactions.<sup>48</sup>

### 3.6 Microscopic morphology analysis

SEM images of catalysts with different Sm contents were shown in Fig. 8. From Fig. 8(f), it can be observed that the catalysts composed of a series of irregular nanospheres, all of which exhibited irregular geometric shapes. Specifically, the 1% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts agglomerated together to form a block-like structure with a relatively large volume, thus exhibiting a smaller specific surface area. With increasing Sm doping level, the block-like structure of the catalysts became smaller and more numerous, resulting in an increased specific surface area. When the Sm<sub>2</sub>O<sub>3</sub> doping level reached 3%, the catalyst surface was enriched with a large number of spherical particles, and more obvious large pores were observed between the particles.<sup>49</sup> When the Sm<sub>2</sub>O<sub>3</sub> doping level reached 3%, the catalyst surface was enriched with a large number of spherical particles, and more obvious large pores were observed between the particles. The porous structure contributed to an increased specific surface area of the catalyst, which was also confirmed by BET test results. A larger specific surface area facilitated the adsorption and reaction of flue gas on the catalyst surface, leading to improved hydrolysis activity. However, the 5% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts exhibited a significantly increased block-like volume and reduced quantity.

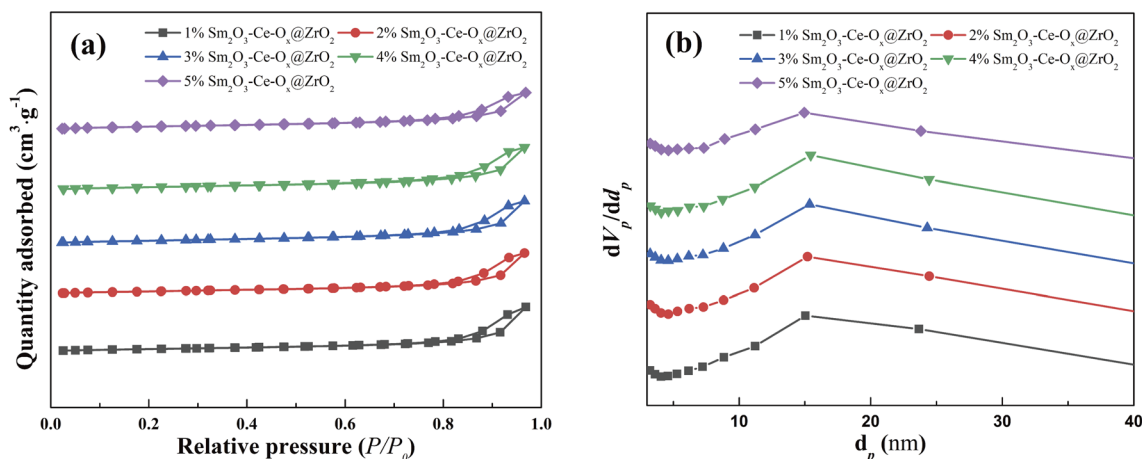
Fig. 7 (a) N<sub>2</sub> adsorption–desorption and (b) pore size distribution curves of Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts with different Sm contents.

Table 2 Structural parameter of  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalysts with Sm contents

| Sample  | BET surface area/( $\text{m}^2 \text{g}^{-1}$ ) | Pore volume/( $\text{cm}^3 \text{g}^{-1}$ ) | Average pore diameter/nm |
|---|---|---|--------------------------|
| 1% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 27  | 0.10  | 15.6                     |
| 2% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 27  | 0.10  | 14.1                     |
| 3% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 31  | 0.10  | 13.2                     |
| 4% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 30  | 0.100                                       | 13.2                     |
| 5% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 33  | 0.09  | 10.9                     |

### 3.7 Surface element composition analysis

The X-ray photoelectron spectroscopy (XPS) spectra of the Ce 3d, O 1s, and Zr 3d elements on different catalyst surfaces were depicted in Fig. 9. Fig. 9(a) illustrated the fitting curves of the Ce 3d peaks on different catalysts. The Ce 3d peaks can be divided into  $\text{Ce}^{3+}$  (902.7 eV and 885.1 eV) and  $\text{Ce}^{4+}$  (916.4 eV, 907.5 eV, 900.5 eV, 898.1 eV, 888.9 eV, 882.1 eV).<sup>50</sup> It can be observed that the intensity of the Ce 3d peaks remained relatively unchanged as the doping level increases. This might be due to the fact that the relative concentration of Sm in the catalyst did not increase significantly in terms of overall content. Furthermore, according to Table 3, the proportion of  $\text{Ce}^{3+}$  in the catalyst gradually decreased with increasing Sm doping. This was because the

relative content of  $\text{Ce}^{3+}$  decreased and some Sm was embedded in the Ce lattice, altering the structure and morphology of cerium oxide and forming a samarium–cerium solid solution, thereby enhancing the catalytic redox performance.<sup>51</sup> The coexistence of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  indicated a strong interaction between Ce and Sm, increasing the number of oxygen vacancies on the catalyst surface and promoting the redox cycling between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ . Consequently, the Sm doping can enhance the catalytic activity for hydrolysis.

Fig. 9(b) presented the peak fitting curves of different catalysts in the O 1s region. All catalysts exhibited peaks at 531.7 eV and 529.6 eV, with the peak around 531.7 eV attributed to chemisorbed surface oxygen ( $\text{O}_2$ ) and the peak around 529.6 eV

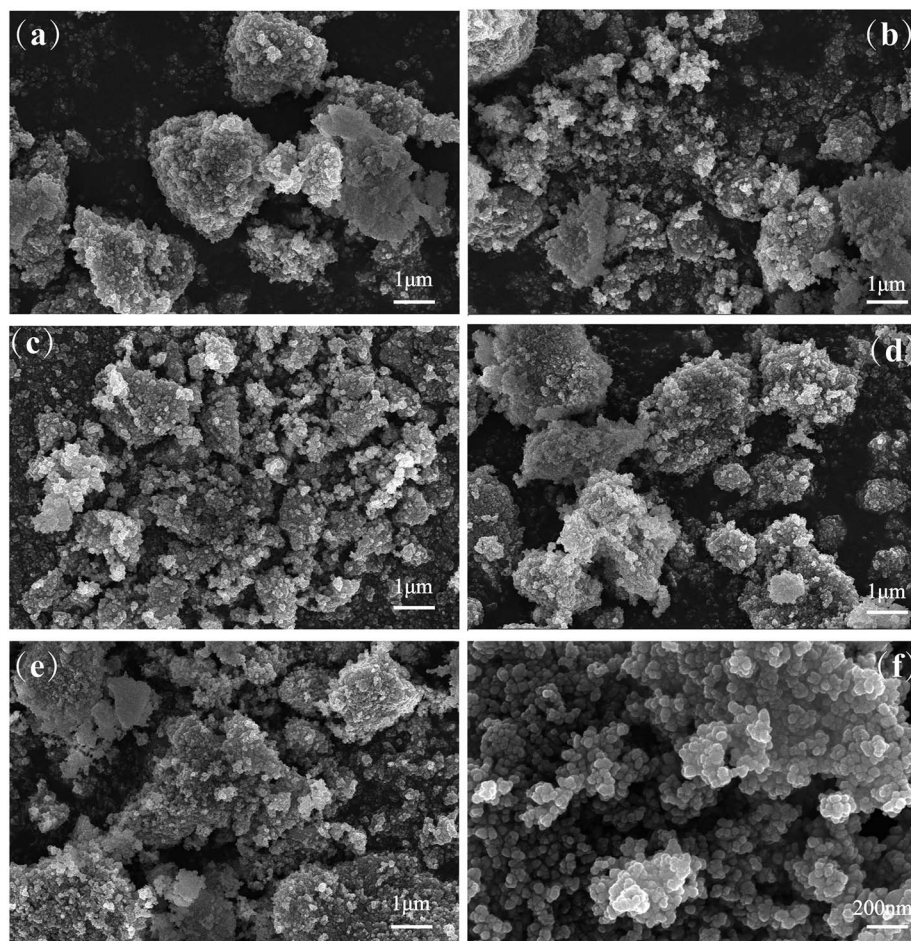


Fig. 8 SEM images of  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalysts with  $\text{Sm}_2\text{O}_3$  contents (a) 1%, (b) 2%, (c) 3%, (d) 4%, (e) 5%, (f) 5%–200 nm.



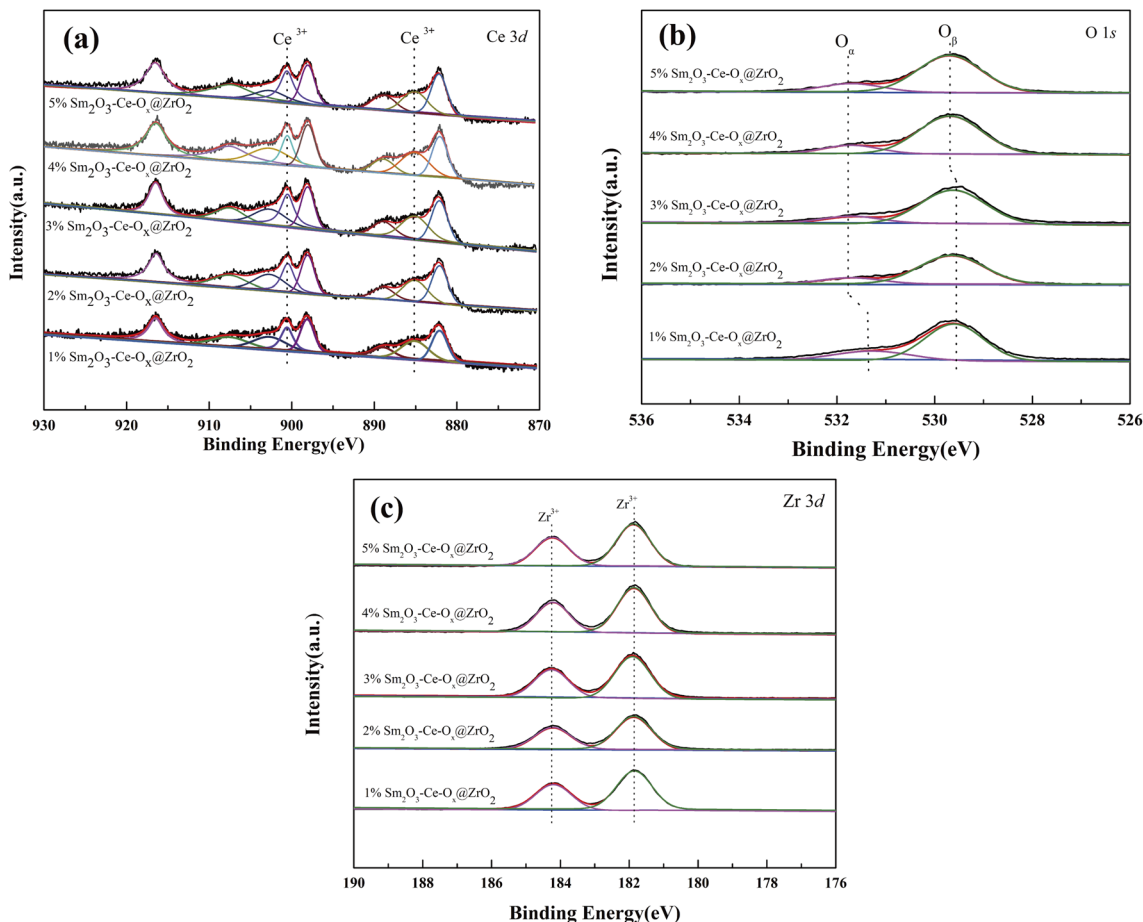


Fig. 9 XPS profiles of  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalysts with different Sm contents (a) Ce 3d, (b) O 1s, (c) Zr 3d.

attributed to lattice oxygen ( $\text{O}_\beta$ ).<sup>52</sup> With the introduction of Sm dopant, the O 1s spectral peaks shifted towards higher binding energies, indicating a strong interaction between Sm and O, which promoted catalytic activity. Chemisorbed surface oxygen was the most active oxygen species in catalytic reduction reactions, and studies had shown that oxygen adsorbed on the catalyst surface can oxidize intermediates generated during the hydrolysis of COS, leading to the formation of  $\text{SO}_4^{2-}$ . A large amount of sulfate species can poison the active sites on the catalyst surface, thereby impeding the long-term progress of the hydrolysis reaction. As shown in Table 3, the concentration of chemisorbed surface oxygen initially decreased and then increased with an increase in Sm doping concentration. When the doping level was 3%, the catalyst exhibited the lowest concentration of chemisorbed surface oxygen and the highest concentration of lattice oxygen. This indicated that appropriate Sm doping facilitated the conversion of active chemisorbed surface oxygen into more stable lattice oxygen, thereby reducing the oxidation of intermediate products and maintaining the stability of the hydrolysis reaction. This also explained the significant improvement in low-temperature hydrolysis activity and superior stability of the catalyst after Sm doping.

Fig. 9(c) displayed the fitted curves of the Zr 3d peaks for different catalysts. The binding energy of approximately

181.8 eV corresponds to the Zr  $3d_{5/2}$  peak, while the binding energy of approximately 184.2 eV corresponds to the Zr  $3d_{3/2}$  peak. It can be observed from the graph that the intensity of the Zr 3d spectral peaks decreases with an increase in the amount of Sm doping, possibly due to a decrease in the relative content of Zr in the catalyst.

### 3.8 Surface acid and alkaline analysis

$\text{NH}_3$ -TPD is a commonly used characterization method to investigate the acidity of catalysts. The hydrolysis of COS was a base-catalyzed reaction, therefore, the stronger the acidity of the catalyst surface, the less favorable the adsorption of

Table 3 Atomic distribution of  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalysts with different Sm contents

| Sample  | $\text{Ce}^{3+}/\text{Ce}^{n+}$ | $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ | $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ |
|---|---------------------------------|--|---|
| 1% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 0.257                           | 0.249  | 0.751   |
| 2% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 0.254                           | 0.167  | 0.833   |
| 3% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 0.244                           | 0.151  | 0.849   |
| 4% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 0.238                           | 0.161  | 0.839   |
| 5% $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$ | 0.185                           | 0.183  | 0.817   |



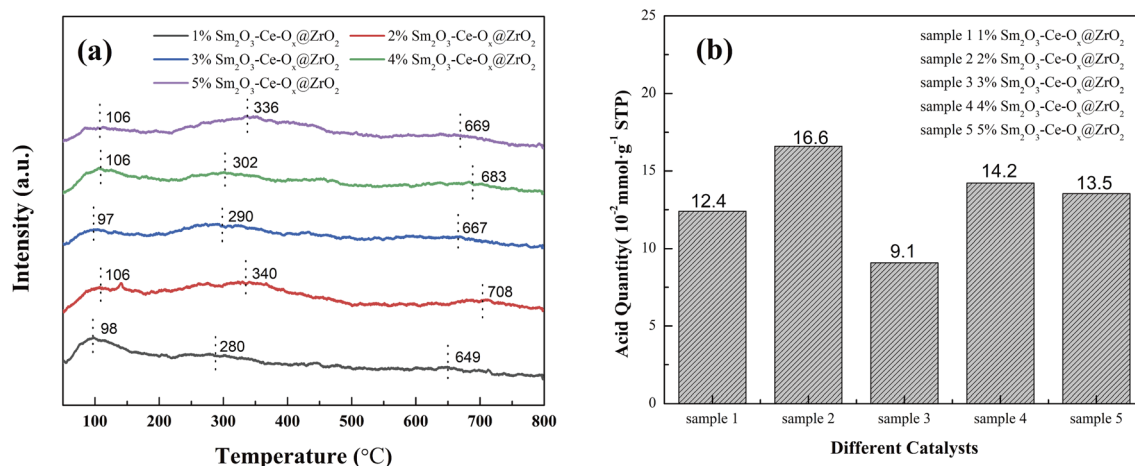


Fig. 10 (a) NH<sub>3</sub>-TPD profiles and (b) acid quantity of Sm-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts with different Sm contents.

reactants on the catalyst surface. Fig. 10 showed the NH<sub>3</sub>-TPD test results of five groups of catalysts. All five groups of catalysts exhibited three NH<sub>3</sub> desorption peaks within the temperature range of 100 °C, around 300 °C, and 600–700 °C, which can be attributed to weak acid sites, medium-strong acid sites, and strong acid sites.<sup>53</sup> Among them, the desorption peak area of weak acid sites generally decreased with the increase of Sm doping amount. This indicated that the doping of Sm can effectively reduce the number of weak acid sites on the catalyst surface, making it easier for acidic reactants to adsorb on the catalyst surface, thereby improving the catalytic activity. The integrated peak area of medium-strong acid sites and strong acid sites was the smallest for the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst, indicating the lowest acidity on the catalyst surface. The 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst had the lowest acid amount on the surface, which was beneficial for the adsorption and activation of COS molecules, thereby enhancing the catalytic activity of the catalyst for the hydrolysis of COS. Therefore, the 3% Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalyst exhibited the highest catalytic activity for COS hydrolysis.

The enhancement of catalyst surface alkalinity was beneficial to the adsorption of COS molecules on the catalyst surface, thereby improving the catalytic activity of hydrolysis reaction. As shown in Fig. 11, two desorption peaks were observed for all five catalyst groups at around 90 °C and 300 °C. The desorption peak around 90 °C was attributed to weak alkaline sites, which were manifested by hydroxyl groups (–OH) on the oxide surface. The desorption peak around 300 °C was attributed to medium-strong alkaline sites, which were manifested by lattice oxygen on the oxide surface. It was believed that the active centers for COS hydrolysis were mainly weak alkaline centers. As clearly seen from the figure, the desorption peak area of weak alkaline sites was greater than that of medium-strong sites for all samples, indicating that the number of weak alkaline centers in the catalyst was greater than the number of medium-strong alkaline centers, which also confirmed that weak alkaline centers play a major role in catalytic activity. In addition, the peak intensity of weak alkaline sites increased with the increase

of Sm loading, indicating that the doping of Sm effectively increased the number of weak alkaline centers in the catalyst and improved the catalytic efficiency of hydrolysis. Therefore, it can be concluded that the alkaline sites on the catalyst surface played a key role in the hydrolysis of COS.

### 3.9 Redox performance analysis

In order to investigate the redox performance of catalysts, the oxidation–reduction properties of five catalyst groups were characterized using H<sub>2</sub>-TPR. The characterization test results of the five catalyst groups were shown in Fig. 12. All catalysts exhibited three hydrogen consumption peaks at around 380 °C, 510 °C and 660 °C. Firstly, the reduction peaks around 660 °C should be attributed to the bulk oxygen reductions of CeO<sub>2</sub>.<sup>54</sup> Furthermore, the obvious shape changes reflected that the Sm doping had significant influence on the states of oxygen species. It is observed the shape changes of peaks around 380 and 510 °C

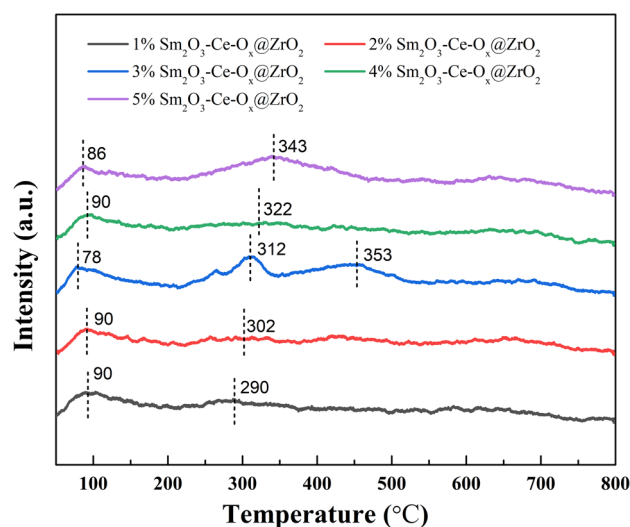


Fig. 11 CO<sub>2</sub>-TPD profiles of Sm<sub>2</sub>O<sub>3</sub>-Ce-O<sub>x</sub>@ZrO<sub>2</sub> catalysts with different Sm contents.





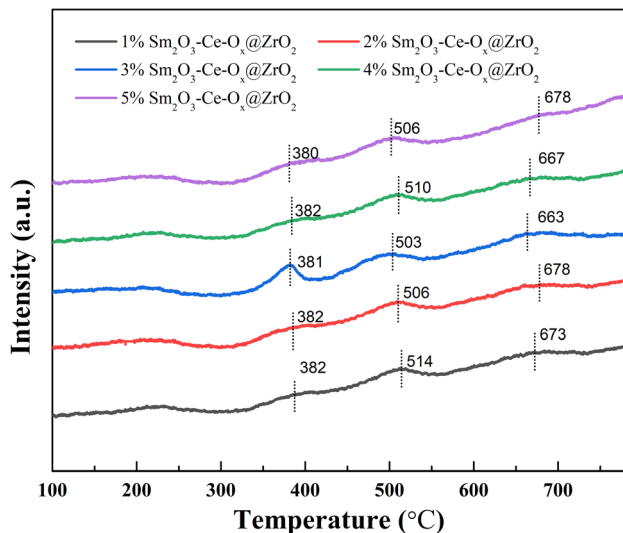


Fig. 12  $\text{H}_2$ -TPR profiles of  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalysts with different Sm contents.

C, the peak coming to an end beyond 600 °C, which represented that a small amount of oxygen species on the surface and in the bulk could be reduced in the catalysts. In other words, appropriate amount of Sm doping was conducive to promoting the evolution to the abundance subsurface oxygen species from the surface or in the bulk. The intensity of the hydrogen consumption peak around 380 °C showed an initial increase followed by a decrease. This can be attributed to the reduction of Sm species with different dispersion states on the  $\text{ZrO}_2$  particles. When the  $\text{Sm}_2\text{O}_3$  doping amount was 3%, the intensity of the hydrogen consumption peak reached its maximum. Additionally, the hydrogen consumption peak shifted to lower temperatures (from 514 °C to 503 °C). Notably, 3%  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalyst exhibited the lowest reduction peak temperature and consumed more amount of hydrogen, indicating that doping Sm improved the redox performance of the catalyst. This was also one of the reasons why the 3%  $\text{Sm}_2\text{O}_3\text{-Ce-O}_x\text{@ZrO}_2$  catalyst exhibited the best activity.

## 4. Conclusions

This study involved the selection of rare earth metals Sm and Y, as well as alkali metals Na and K, for doping in the  $\text{CeO}_x\text{@ZrO}_2$  catalyst system. Results showed that when the doping amount of  $\text{Sm}_2\text{O}_3$  reached 3%, the COS conversion and  $\text{H}_2\text{S}$  selectivity both reached 100% at 90 °C. The introduction of  $\text{Sm}_2\text{O}_3$  led to an increase in the specific surface area of the catalyst and the enlargement of some of its pores. Consequently, the adsorption and activation of reactant molecules at low temperatures were affected. Additionally, the doping of Sm reduced the number of weak acid sites on the catalyst, while increasing the number of weak basic sites. This change proved beneficial for the adsorption and activation of COS molecules at low temperature. Proper doping of Sm facilitated the conversion of active surface chemisorbed oxygen into more stable lattice oxygen, thus

decreasing the oxidation of intermediate products and maintaining the stability of the hydrolysis reaction.

## Author contributions

Jintao Yu: data curation, formal analysis, roles/writing – original draft, Yao Lu: data curation, formal analysis, roles/writing – original draft, Sheng Wang: data curation, Mutao Xu: data curation, formal analysis, Qijie Jin: methodology, investigation, funding acquisition, Chengzhang Zhu: methodology, investigation, Jisai Chen: supervision, validation, project administration, Haitao Xu: supervision, validation; funding acquisition, project administration.

## Conflicts of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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