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Article

Promotional effects of Er incorporation in $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ for selective catalytic reduction of NO by NH_3

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ABSTRACT

A series $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ catalysts were modified with Er using a sol-gel method. The catalytic activity of the obtained catalysts in the selective catalytic reduction (SCR) of NO with NH_3 was investigated to determine the appropriate Er dosage. The catalysts were characterized using X-ray diffraction, N_2 adsorption, NH_3 temperature-programmed desorption, H_2 temperature-programmed reduction, photoluminescence spectroscopy, electron paramagnetic resonance spectroscopy, and X-ray photoelectron spectroscopy. The results showed that the optimum Er/Ce molar ratio was 0.10; this catalyst had excellent resistance to catalyst poisoning caused by vapor and sulfur and gave more than 90% NO conversion at 220–395 °C and a gas hourly space velocity of 71 400 h^{-1} . Er incorporation increased the Ti^{3+} concentrations, oxygen storage capacities, and oxygen vacancy concentrations of the catalysts, resulting in excellent catalytic performance. Er incorporation also decreased the acid strength and inhibited growth of TiO_2 and CeO_2 crystal particles, which increased the catalytic activity. The results show that high oxygen vacancy concentrations and oxygen storage capacities, large amounts of Ti^{3+} , and low acid strengths give excellent SCR activity.

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1. Introduction

Nitrogen oxides are major contributors to worsening environment problems such as acid rain, photochemical smog, and the greenhouse effect [1–3]. Selective catalytic reduction (SCR) of NO with NH_3 is the most widely used technique for the abatement of NO emissions. Currently, commercial $\text{V}_2\text{O}_5(\text{WO}_3, \text{MO}_3)/\text{TiO}_2$ catalysts are mainly used [4]. However, the operating temperature window for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts is narrow. V_2O_5 -based catalysts suffer from low N_2 selectivity and sublimation of V_2O_5 at high temperatures, even after modification

with Mo and W species [5,6]. Increasing attention is therefore being paid to the development of novel environmentally friendly deNO_x catalysts with high efficiencies and broad active temperature windows.

Because of its redox properties and high oxygen storage capacity, CeO_2 has attracted much interest as a catalyst for a broad range of applications, e.g., fuel cells [7], photocatalysis [8], and oxygen permeation membranes [9]. For NH_3 -SCR, the oxygen storage capacity of CeO_2 can be increased by the introduction of other transition and non-transition metal ions, and many CeO_2 -based catalysts have been developed, e.g., Ce-Zr- O_x

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[10–13], CeO₂/TiO₂ [14–16], Ce-W-O_x/TiO₂ [17–20], CeO₂/Al₂O₃ [21–23], CeO₂/TiO₂-SiO₂ [24,25], Ce-Zr-O_x/TiO₂ [26], Mn-Ce/TiO₂ [27–31], Cu-Ce/TiO₂ [32], Ce-Mo/TiO₂ [33] and Mn-Fe-Ce/Al₂O₃ [34]. These catalysts have broad temperature windows for effective denitration activity.

There have been various reports of the promotional effects of Er addition [35,36]. However, the promotional effects of Er incorporation on NH₃-SCR of NO over Ce-based metal oxide catalysts have not been investigated. Er₂O₃ can interact with CeO₂, and the defect concentration increases with increasing Er incorporation; Er₂O₃ addition therefore improves the NH₃-SCR activities of catalysts. In this work, the promotional effects of Er incorporation in CeO₂(ZrO₂)/TiO₂ (CZT) as a catalyst for NH₃-SCR were investigated. CZT catalysts and CZT catalysts with added Er (ECZTs) were prepared using a sol-gel method. The catalysts had good redox properties, high defect concentrations, and large oxygen storage capacities, and therefore had high SCR activities.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by thermal decomposition of aged Ce-Zr/Ti and Er-Ce-Zr/Ti composite gels calcined at 500 °C for 2 h. A Ce-Zr/Ti composite sol, with Ti:Zr:Ce molar ratios of 4:1:1, was synthesized using Ti(OC₄H₉)₄ (CP, LingFeng, Shanghai, China), ZrOCl₂·8H₂O (AR, Sinopharm, Beijing, China), and Ce(NO₃)₃·6H₂O (AR, Ruibo, Zibo, China) as precursors. Ti(OC₄H₉)₄ and ethanol were mixed under vigorous stirring at room temperature to form a composite solution A, and composite solution B was synthesized by mixing glacial acetic acid, deionized water, ethanol, and nitric acid. Solution B was added dropwise to solution A, and then the required amounts of ZrOCl₂·8H₂O and Ce(NO₃)₃·6H₂O were dissolved in the AB mixed solution under vigorous stirring for 1 h to obtain the CZT composite sol. Er(NO₃)₃·5H₂O (GR, Xiya, Chengdu, China) was added to the CZT mixed solution to obtain the ECZT composite sol. Aged gels were obtained by aging the sols, and drying in air at 80 °C for 24 h and 110 °C for 12 h. The solid was calcined at 500 °C for 2 h.

2.2. Catalytic activity and selectivity measurements

The catalytic activities of the prepared catalysts in NH₃-SCR of NO were investigated using a fixed-bed quartz reactor (6 mm inner diameter), 0.7 mL of catalyst (particle size 0.3–0.45 mm), and a gas flow rate of 833 mL/min, corresponding to a gas hourly space velocity (GHSV) of 71 400 h⁻¹. The reactant gas typically consisted of 600 ppm NO, 600 ppm NH₃, 6 vol% O₂, and balance N₂. The NO concentrations at the inlet and outlet of the reactor were monitored online using a flue gas analyzer (MRU VarioPlus, Germany). The catalytic activity (X_{NO}) in NH₃-SCR of NO is expressed by equation (1). Analysis was performed at selected temperatures after 30 min, when the reactor temperature had stabilized.

$$X_{\text{NO}} = ([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}) / [\text{NO}]_{\text{inlet}} \times 100\% \quad (1)$$

The temperature range in which the catalytic activity is equal to or more than 90% of the maximum catalytic activity is defined as the catalytically active temperature window, denoted by T_r . The lowest T_r is denoted by T_{r-L} , and the highest by T_{r-H} [2].

The N₂ concentration at the reactor outlet was monitored online by gas chromatography (GC2014, Japan), using a 5 Å molecular sieve column (length 2 m, sorbent particle size 60–80 mesh); a single-point corrected external standard method was used. We selected two representative samples (CZT and ECZT-0.10) and collected data at various temperatures. The detecting conditions were as follows: injection volume 1 mL, injector temperature 90 °C, chromatographic column temperature 80 °C, thermal conductivity detector operated at 120 °C, carrier gas Ar, and H₂ flow rate 30 mL/min. We obtained the peak area for a known standard, i.e., N₂/Ar (600 ppm, and balance Ar), and defined this area as S_0 . We then determined the peak area for N₂ detected at the outlet and defined this area as S . Based on the reaction

the consumed NO_x is converted to N₂, i.e., $[\text{NO}_x]_{\text{N}_2\text{consu}} = [\text{N}_2] = 600 S/S_0$ ppm, and the total NO_x conversion is $[\text{NO}_x]_{\text{conv}} = [\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}$. To facilitate quantitative analysis and determine the N₂ selectivity of the catalysts in NH₃-SCR of NO_x, the N₂ selectivity is expressed as [37]:

$$\eta = [\text{NO}]_{\text{N}_2\text{consu}} / [\text{NO}]_{\text{conv}} \times 100\% = 600S / (S_0[\text{NO}]_{\text{inlet}} - S_0[\text{NO}]_{\text{outlet}}) \times 100\% \quad (3)$$

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a D/MAX-RB X-ray diffractometer (Rigaku, Japan) with Cu K_α radiation. The 2θ scans covered the range 10°–80°, and the accelerating voltage and applied current were 40 kV and 40 mA, respectively. Electron paramagnetic resonance (EPR) spectroscopy was performed at -163 °C, using a Bruker EMX-10/12 spectrometer, at the X-band. Photoluminescence (PL) spectra were obtained at room temperature using a Labram-HR800 spectrophotometer (Jobin Yvon Co., France) with a He-Cd laser (λ = 325 nm) as the light source. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra DLD instrument, with monochromatic Al K_α radiation as the excitation source. After complete removal of moisture from the catalysts by drying at 100 °C for 24 h, the catalysts were analyzed without surface sputtering or etching so that the degree of vacuum in the XPS equipment was maintained at 1 × 10⁻⁷ Pa.

The numbers of acid sites in, and acid strengths of, the catalysts were evaluated using temperature-programmed NH₃ desorption (NH₃-TPD; CHEMBET-3000, Quantachrome). The samples were preheated to 450 °C in a He stream for 1 h, and then cooled to 100 °C for NH₃ adsorption; NH₃ was desorbed using He at a flow rate of 30 mL/min from 100 to 800 °C at a heating rate of 10 °C/min. The NH₃ desorption was monitored online using a Thermo ONIX ProLab mass spectrometer. Temperature-programmed H₂ reduction (H₂-TPR) was performed using a semiautomatic Micromeritics TPD/TPR 2900 appa-

ratus. The samples were treated at 400 °C for 1 h in an Ar flow and then cooled to 50 °C before the H₂-TPR experiments. Reduction profiles were obtained using 5% H₂/Ar at a flow rate of 20 mL/min. The temperature was increased from 50 to 900 °C at a rate of 10 °C/min. The specific surface areas and average pore diameters of the samples, determined using the Brunauer-Emmett-Teller (BET) method, were determined from the N₂ adsorption/desorption isotherms at -196 °C, obtained using a surface area analyzer (2020M V3.00H, Micromeritics). All the samples were degassed at 350 °C under vacuum for 3 h prior to the adsorption experiments.

3. Results and discussion

3.1. Effects of calcination temperature on catalytic performance of CZT

Fig. 1 shows the NO conversion over catalysts calcined for 2 h at 450, 500, 550, and 600 °C, denoted by CZT-450, CZT-500, CZT-550, and CZT-600, respectively. The catalytic activity decreased slightly with increasing calcination temperature from 450 to 550 °C. The low-temperature (190–350 °C) catalytic activity of the catalyst calcined at 600 °C was clearly lower than those of the other catalysts, but the catalytic activities were similar at higher temperatures. These results suggest that anatase transformation to rutile occurred at about 600 °C, therefore the catalytic activity decreased. Precursor decomposition may be incomplete at a calcination temperature of 450 °C, resulting in carbonation of CZT. Based on the test results, CZT and ECZT calcined at 500 °C were used; CZT-500 is referred to as CZT for brevity.

3.2. Effects of Er incorporation on catalytic performance

The catalytic activities of CZT and ECZT were investigated; the NO conversions as a function of temperature are shown in Fig. 2(a). The results show that CZT and ECZT were effective catalysts for NH₃-SCR of NO, and Er incorporation strongly affected the catalytic activity. Fig. 2(a) shows that the maximum catalytic activity of CZT was 94.28% at 320 °C, and the catalytic

Fig. 1. NO conversions over CZT catalysts; reaction conditions: 600 ppm NO, 600 ppm NO, 6% O₂ in N₂, GSHV 71 400 h⁻¹.

Fig. 2. NO conversion (a) and N₂ selectivity (b) of Er-promoted CZT samples at GSHV 71 400 h⁻¹.

cally active temperature window was 230–390 °C. However, addition of a small amount of Er (Er/Ce = 0.05:1) to CZT clearly increased the activity. This suggests that Er incorporation plays an important role in promotion of the catalytic activity. ECZT-0.10 (Er/Ce = 0.10:1) showed the best catalytic activity (98.85%) and the catalytically active temperature window was 220–395 °C. The catalytic activity of ECZT decreased with further increases in the Er/Ce molar ratio, possibly because of a decrease in the number of active Ce sites on the catalyst surface.

Fig. 2(a) shows that all the catalytic activity versus temperature curves was parabolic: at temperatures lower than T_{r-L} , the quantity of activated molecules and the effective collision frequency on the catalyst surface increased with increasing temperature, which increased the reaction rate [2]. In addition, NH₃ was oxidized at temperatures higher than T_{r-H} , which directly decreased the amount of reducing agent, therefore the catalytic activity in NO_x reduction decreased with increasing temperature. Fig. 2(b) shows the N₂ selectivity of the CZT and ECZT-0.10 catalysts in NH₃-SCR of NO at various temperatures. The N₂ selectivity decreased slightly on Er incorporation and the ECZT-0.10 catalyst showed high N₂ selectivity at all test temperatures.

3.3. Effects of H₂O and SO₂

Fig. 3 shows the NO conversions over CZT and ECZT-0.10 under the reaction conditions 5 vol% H₂O and/or 200 ppm SO₂

Fig. 3. NO conversion over CZT (a) and ECZT-0.10 (b) catalysts in presence of H₂O and SO₂ at GHSV 71 400 h⁻¹ and 320 °C.

at 320 °C. The total catalytic activities of CZT and ECZT-0.10 were unchanged when water vapor was introduced separately during the tests, possibly because competitive adsorption among water vapor and NH₃ or NO on the catalyst surface was weak. When 5 vol% H₂O and 200 ppm SO₂ were added, the NO conversions over CZT and ECZT-0.10 dropped by 18% and 13%, respectively, in 5 h. In the next 13 h, the NO conversions over CZT and ECZT-0.10 were almost unchanged. When SO₂ and H₂O additions were stopped, the NO conversions over CZT and ECZT-0.10 quickly recovered to 82% and 91%, respectively. The anti-sulfur ability was therefore enhanced slightly by Er addition, and ECZT-0.10 showed excellent resistance to catalyst poisoning caused by vapor and sulfur.

3.4. XRD and BET analyses

Fig. 4 shows the XRD patterns of the CZT and ECZT catalysts. All the patterns showed the reflections for anatase TiO₂ (PDF 71-1168) and Ce_{0.5}Zr_{0.5}O₂ (PDF 38-1436). In terms of the effect of the ionic radius, the ionic radii of Zr⁴⁺ and Ce⁴⁺ are 0.086 and 0.101 nm, respectively, therefore they satisfy equation (4). CeO₂ could therefore react with ZrO₂ and form a continuous solid solution [38–40].

$$(r_1 - r_2)/r_1 < 15\% \quad (4)$$

Fig. 4 shows that the intensities of the anatase TiO₂ peaks decreased and the Ce_{0.5}Zr_{0.5}O₂ peaks widened as a result of Er incorporation, i.e., crystallization of a CeO₂-ZrO₂ solid solution and TiO₂ was inhibited by Er incorporation. In addition, no

Fig. 4. XRD patterns of Er-promoted CZT samples.

diffraction peaks attributable to Er species were detected in the XRD patterns, implying that the Er species were well dispersed in the ECZT samples or were present as amorphous species. The catalytic activities of the CZT and ECZT samples suggest that the catalytic activity can be increased by appropriate inhibition of TiO₂ and CeO₂-ZrO₂ solid solution crystallization.

The BET surface areas, pore volumes, and pore sizes are listed in Table 1. The surface area of the CZT catalyst was 105.52 m²/g. The data in Table 1 show that the surface area decreased with increasing Er incorporation, possibly because of the small surface area of Er₂O₃ and because the small pores in CZT collapsed to form larger pores on Er incorporation. This could be one reason why the catalytic activities of ECZT-0.20 and ECZT-0.60 were lower than that of CZT at low temperatures.

3.5. NH₃-TPD analysis

Four samples, CZT, ECZT-0.10, ECZT-0.20 and ECZT-0.60, were examined using NH₃-TPD. Fig. 5 shows the NH₃-TPD pro-

Table 1
Physical properties of various catalysts.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore Diameter (nm)
TiO ₂	104.65	0.204	7.80
CZT	105.52	0.196	7.44
ECZT-0.10	100.17	0.197	7.87
ECZT-0.20	96.84	0.196	7.94
ECZT-0.60	87.31	0.183	8.65

Fig. 5. NH_3 -TPD profiles of various catalysts.

files. All the profiles showed two distinct regions: one desorption peak centered at a low temperature, representing weak acid sites, and another centered at a higher temperature, representing strong acid sites. Two desorption peaks were observed in the NH_3 -TPD profiles of the CZT and ECZT samples.

Fig. 5 shows that the areas of the NH_3 desorption peaks decreased in the order $\text{CZT} \approx \text{ECZT-0.10} > \text{ECZT-0.20} > \text{ECZT-0.60}$ at low temperatures, implying that the number of weak acid sites decreased in this order. The areas of the NH_3 desorption peaks at high temperatures clearly decreased on Er incorporation, indicating that the total amount of acid sites in CZT was higher than those in the ECZT catalysts. For ECZT-0.10, the low-temperature NH_3 desorption peak shifted from 223 to 186 °C, and the high-temperature peak shifted from 630 to 610 °C. These observations indicate that the strengths of the weak and strong acid sites both decreased when a small amount of Er was added to the CZT catalyst. The low-temperature NH_3 desorption peak shifted from 223 to 236 °C for ECZT-0.60; this could be one reason why the catalytic activity of ECZT-0.60 was lower than that of CZT. The catalytic activity therefore showed a parabolic trend on Er addition.

3.6. H_2 -TPR analysis

Fig. 6 shows the H_2 -TPR results for CZT and ECZT-0.10. For CZT, the broad peak at around 461 °C is assigned to reduction of surface oxygen in $\text{Ce}^{4+}\text{-O-Ce}^{4+}$ [18,41]. The weak peak at around 611 °C is attributed to reduction of TiO_2 and surface oxygen in $\text{Ce}^{3+}\text{-O-Ce}^{4+}$ [42,43]. The peak at around 848 °C corresponds to reduction of bulk CeO_2 , which only occurs above 750 °C [44,45]. However, ECZT-0.10 gave three clear reduction peaks, at about 480, 700 and 824 °C, suggesting that Er incorporation adversely affects the redox properties. The integral areas of H_2 -TPR profiles are usually used to compare the oxygen storage capacities of catalysts, which is a significant parameter in the SCR activity of CeO_2 -based catalysts [46]. The total H_2 consumption by ECZT-0.10 was higher than that by CZT, which indicates that the number of surface oxygen defects increased, i.e., the oxygen storage capacity of the catalyst increased on Er incorporation. This may be one reason why the

Fig. 6. H_2 -TPR profiles of the catalysts.

catalytic activity of ECZT-0.10 was better than that of CZT.

3.7. PL spectroscopic analysis

PL emission spectra have been widely used to investigate surface defects [1]. When the defect concentration increases, more electrons are trapped and recombine with holes through nonradioactive paths. The PL intensity decreases with increasing number of surface defects [11]. Fig. 7 shows that the PL spectra of CZT and ECZT-0.10 are similar. Peak 1, at 558 nm, arises from surface defects, and peak 2, at 633 nm, results from the polarizability of the lattice ions surrounding the defects [47,48]. The PL peak intensity decreased on Er incorporation, i.e., Er incorporation increased the number of surface defects. These results suggest that an increase in the number of surface defects improves the catalytic activity.

3.8. EPR analysis

Fig. 8 shows the EPR spectra of CZT and ECZT-0.10. Both catalysts gave a strong and broad peak at $g = 2.006$, which is attributed to oxygen vacancies [49,50]. The EPR intensity of ECZT-0.10 at $g = 2.006$ was higher than that of CZT, i.e., the oxygen vacancy concentration in the CZT catalyst increased on Er incorporation, and this provides active oxygen species for the NH_3 -SCR reaction, and improves the catalytic activity. The

Fig. 7. PL spectra of CZT and ECZT-0.10 catalysts.

Fig. 8. EPR spectra of the catalysts at $-196\text{ }^{\circ}\text{C}$.

signal at $g = 1.977$ is attributed to Ti^{3+} , and the EPR intensity increased on Er incorporation [51]. This suggests that Er incorporation increased the Ti^{3+} content. The presence of a large Ti^{3+} amount is beneficial in the SCR reaction because Ti^{3+} can create a charge balance, and form oxygen vacancies and unsaturated chemical bonds on the catalyst surface, leading to an increased amount of chemisorbed oxygen [52].

3.9. XPS analysis

High-resolution Ce 3d, Ti 2p, Zr 3d, and O 1s XPS profiles of CZT and ECZT-0.01 were obtained to identify the states of surface species on the catalysts; the spectra are shown in Fig. 9. The spectra of CZT and ECZT-0.10 showed peaks at binding energy of 903 and 885 eV in Fig. 9(a), attributed to Ce^{4+} and Ce^{3+} [53]. The O 1s peaks Fig. 9(d) were fitted to a peak from

Table 2

Surface atomic ratios for CZT and ECZT-0.10 catalysts.

Sample	Surface atomic ratio		
	$\text{O}_{\alpha}/(\text{O}_{\alpha} + \text{O}_{\beta})$	$\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$	$\text{Ti}^{3+}/(\text{Ti}^{3+} + \text{Ti}^{4+})$
CZT	0.22	0.24	0.06
ECZT-0.10	0.42	0.23	0.12

chemisorbed oxygen (O_{α}) and one from lattice oxygen (O_{β}) [54]. The Ti 2p Fig. 9(b) spectra had peaks attributable to Ti^{3+} and Ti^{4+} [55]. The Ce 3d, O 1s, Ti 2p, and Zr 3d core levels shifted to higher binding energies on Er incorporation, indicating that interactions among Ce, Ti, O, and Zr increased slightly.

Table 2 shows the surface atomic ratios for CZT and ECZT-0.10. The atomic ratios of O_{α} , Ce^{3+} , and Ti^{3+} on the CZT catalyst surface were 0.22, 0.24, and 0.06, respectively, and the atomic ratios of O_{α} , Ce^{3+} , and Ti^{3+} on the ECZT-0.10 catalyst surface were 0.42, 0.23, and 0.12 respectively. The atomic ratio of Ce^{3+} did not change much. The atomic ratios of O_{α} and Ti^{3+} increased on Er incorporation; this is in agreement with the EPR results. It has been reported that surface chemisorbed oxygen is the most active form of oxygen and plays an important role in oxidation [56]. The catalytic activity of ECZT-0.10 in oxidation of NO should therefore be higher than that of CZT, because an increase in the amount of surface chemisorbed oxygen has a positive effect on the catalytic activity.

CZT is a solid acid catalyst, and there is a strong correlation between catalytic activity and acid properties. As stated above, the strengths of the weak and strong acid sites decreased when Er was added to the CZT catalyst, and this is why Er incorporation widened the catalytically active temperature window. In

Fig. 9. High-resolution XPS profiles of CZT and ECZT-0.10 catalysts: (a) Ce 3d; (b) Ti 2p; (c) Zr 3d, and (d) O 1s.

addition, Ti^{3+} can create a charge balance, and form oxygen vacancies and unsaturated chemical bonds on the catalyst surface, and surface chemisorbed oxygen plays an important role in NO oxidation. Er incorporation increased the concentrations of chemisorbed oxygen and Ti^{3+} , resulting in an excellent catalytic performance of ECZT-0.10. The oxygen storage capacity of the catalyst is also increased by Er incorporation, and this may be one of the reasons why the catalytic performance of ECZT-0.10 was better than that of CZT.

4. Conclusions

Er incorporation greatly improved the catalytic performance of CZT in NH_3 -SCR of NO. The ECZT-0.10 catalyst, with an Er/Ce molar ratio of 0.10, showed the highest catalytic activity and excellent resistance to catalyst poisoning by vapor and sulfur. The reasons for these results are as follows: (1) Er incorporation increased the oxygen storage capacity and decreases the acid strength; (2) the surface defect (oxygen vacancies and Ti^{3+} concentrations increased on Er incorporation; (3) Er incorporation inhibited growth of TiO_2 and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ crystal particles. All these features contribute to the excellent catalytic performance of ECZT.

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Graphical Abstract

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Promotional effects of Er incorporation in $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ for selective catalytic reduction of NO by NH_3

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Er addition increased the concentrations of oxygen vacancies and Ti^{3+} , which improved the catalytic activity of $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ for selective catalytic reduction of NO by NH_3 .

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Er 掺杂对 CeO₂(ZrO₂)/TiO₂ 催化剂脱硝性能的影响

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摘要: 氮氧化物 (NO_x) 是大气污染的主要因素之一, 对其排放的治理成为较为迫切的需求. 氨气选择性催化还原法 (NH₃-SCR) 是目前减少 NO_x 排放中应用最为广泛的技术. 目前, 商业 SCR 催化剂主要是 V₂O₅(WO₃, MO₃)/TiO₂, 但其具有活性温度窗口窄、N₂ 选择性低和对环境影响大等缺点. 因此, 新型的催化活性高且活性温度窗口宽的环境友好催化剂成为脱硝催化剂的研究热点. CeO₂ 因其独特的氧化还原性能和优异的储释氧能力在催化领域具有广泛应用, 在 NH₃-SCR 中也研发出较多类型的铈基催化剂. 我们课题组前期研发了具有优异脱硝性能的 CeO₂(ZrO₂)/TiO₂ 催化剂, 为拓展其应用范围, 需要进行更深入的研究. 理论上, Ti⁴⁺, Ce⁴⁺ 以及 Zr⁴⁺ 离子的价态均高于 Er³⁺, 且离子半径相近. 换言之, Er₂O₃ 能够与 TiO₂ 以及 CeO₂ 产生缺陷反应增大催化剂的缺陷浓度, 进而提高催化剂的催化活性.

本文以溶胶-凝胶法制备了一系列 Er 掺杂 CeO₂(ZrO₂)/TiO₂ 催化剂, 测试了样品的 NH₃-SCR 催化活性和 N₂ 选择性, 并且在 320 °C 下连续 24 h 测试了水蒸气、SO₂ 以及两者混合作用对催化剂活性的影响. 使用 X 射线衍射 (XRD)、N₂ 等温吸附-脱附 (N₂-BET)、NH₃ 程序升温脱附 (NH₃-TPD)、H₂ 程序升温还原 (H₂-TPR)、光致发光光谱 (PL)、电子顺磁共振 (EPR) 以及 X 射线光电子能谱 (XPS) 对催化剂进行了表征.

XRD 结果显示, Er 掺杂后催化剂的结晶程度降低, 且图谱中没有出现明显的 Er₂O₃ 衍射峰, 即 Er 在催化剂上有较好的分散度且掺杂抑制了催化剂的晶化. NH₃-TPD 和 H₂-TPR 结果表明, Er 掺杂降低了酸强且提高了储释氧能力, 催化剂的氧化还原能力则有所减弱. PL 和 EPR 测试结果显示, 掺杂后的催化剂氧空位浓度和 Ti³⁺ 浓度有所增加, 与前期理论设计一致. XPS 测试结果表明, 掺入 Er 后催化剂的化学吸附氧含量和 Ti³⁺ 浓度增加, Ce³⁺ 浓度基本不变, 推测是 CeO₂(ZrO₂)/TiO₂ 催化剂中掺入的 Er 主要与载体 TiO₂, 而不是与活性组分 CeO₂ 或助剂 ZrO₂ 产生缺陷反应的结果.

CeO₂(ZrO₂)/TiO₂ 催化剂最高活性为 94.28%, 其活性温度窗口为 230–390 °C, 掺入 Er (Er:Ce = 0.10:1) 后, 催化剂的整体活性尤其是 350 °C 以下的催化活性具有明显提升, 最高活性达到 98.85%, 活性温度窗口也拓展为 220–395 °C. 单独的水

蒸气对催化活性影响很小, SO_2 会部分降低催化剂活性, 而当两者混合作用时, 催化剂活性下降最为显著, 且 Er 掺杂后 $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ 催化剂的抗中毒能力有所增强.

Er 掺杂 $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ 催化剂显示出较好的抗硫抗水中毒能力以及较高的 $\text{NH}_3\text{-SCR}$ 催化活性和 N_2 选择性, 应该是一种具有应用前景的 SCR 催化剂. Er 掺杂降低了催化剂的酸强, 抑制了 TiO_2 和铈锆固溶体的晶化, 提高了 Ti^{3+} 和氧空位浓度并增强了储释氧能力, 是 $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ 催化剂活性提高的主要原因.

关键词: $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$; 铒掺杂; 选择性催化还原; 氮氧化物; 催化性能

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