



Visible light driven Z-scheme $\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{palygorskite}$ nanostructure for photo-SCR of NO_x

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ABSTRACT

Commercial V–Ti oxide catalysts are widely used in the selective catalytic reduction (SCR) of NO_x , however it requires high reaction temperature and poisonous V components. In addition, the deactivation induced by the SO_2 and H_2O in the flow gases has restricted its extensive applications. To address those problems, a series of $\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{palygorskite}$ (Pal) with various Fe/Sm molar ratios ($n_{\text{Fe}}/n_{\text{Sm}}$) were prepared by a sol–gel method for photocatalytic assisted SCR of NO_x at low temperature. The morphology and structural properties of as-prepared catalysts were characterized by various measurements. Results indicated that the rational addition of Fe species could not only formed Z-scheme heterostructure $\text{Fe}_2\text{O}_3/\text{SmFeO}_3$ with high redox property, but also effectively restrained the generation of sulfate species. The catalysts achieved the highest 95% conversion rate and 100% N_2 selectivity when the $n_{\text{Fe}}/n_{\text{Sm}} = 2$ with remarkable SO_2 and H_2O resistance.

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1. Introduction

With the rapid development of economic and industry, emission of NO_x has attracting more and more attention since NO_x have serious impacts on environment such as acid rain, photochemical smog and many other environmental hazards [1,2]. For decades, selective catalytic reduction (SCR) with NH_3 has been employed as one of the most promising technology for controlling NO_x emission [3,4]. Although the commercial NH_3 -SCR catalysts including $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$ [5] and $\text{V}_2\text{O}_5\text{--}\text{MoO}_3/\text{TiO}_2$ [6] have been widely applied in industrial plants, there still remain several limitations, such as the poor catalytic activity at low temperature (less than 300 °C), narrow operation temperature window, poor SO_2 and H_2O resistance and the toxicity of active components. Therefore, it is imperative to develop green and efficient catalysts [7,8], or alternatively adopt photo-SCR method to resolve these problems [9,10].

In recent years, as an emerging functional materials with wide potentials, rare earth perovskite (ABO_3) has attracted great scientific interest in the area of industrial catalysis and environmental remediation owing to its stable crystal structure, high redox property and photocatalytic activity [11]. Despite that the $\text{LaFeO}_3\text{--}$

SrTiO_3 [12], $\text{LaFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ [13] and $\text{La}(\text{Co}, \text{Mn}, \text{Fe})_{1-x}(\text{Cu}, \text{Pd})_x\text{O}_3$ perovskites [14] have been reported on removal of NO_x , the single perovskite particles are easy to aggregate resulting in the low catalytic activity. Hence, it is necessary to construct perovskite catalyst with suitable supports to address the issues. As a natural clay material consisted of hydrated magnesium aluminum silicate, Pal possess the special pore structure, fibrous morphology and large specific surface area [15]. Due to the presence of a large number of active sites on its surface, it has good physical adsorption capacity for the gas molecules making it as an ideal catalyst support. In our previous work, a series of Pal supported perovskites with various metal doping have been successfully prepared for photo-SCR of NO_x [16–18]. However, they form the traditional type of semiconductor heterojunctions, in which the oxidation–reduction capabilities of photogenerated electrons and holes are weakened after charge transfer. It should be noted that the artificial Z-scheme heterojunction systems can be good candidate to avoid the shortcomings [19,20], since it not only ensures the efficient spatial separation of electron–hole pairs but also guarantees the redox abilities of the electrons–holes pairs.

In this work, we synthesized the $\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{Pal}$ nanocomposites by a facile sol–gel method. By rational tuning the molar ratio of Fe/Sm, extra Fe_2O_3 was formed to construct coherent Z-scheme heterojunction with SmFeO_3 . The photo-SCR of NO_x was performed to unveil the removal mechanism of the nanocomposite, in addition, the resistance of SO_2 and H_2O was also investigated.

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2. Experimental

2.1. Chemicals

Samarium nitrate hexahydrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), iron nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and ethylene glycol ($(\text{CH}_2\text{OH})_2$) were provided by Shanghai Linfeng Chemical Reagent Co., Ltd., China. Pal clay was provided by Nanjing University Zijin Co., Ltd. (China). All reagents were of analytical grade and used without further purification.

2.2. Catalysts preparation

$\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{Pal}$ nanocomposites catalysts were synthesized via sol-gel method. An appropriate amount solutions of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were dissolved in deionized water and dispersed by ultrasonic stirring. Ethylene glycol and the purified Pal were added into the mixed solution after a few minutes. The mixture was evaporated in a water bath at 80°C to obtain wet gel. After dried at 100°C for 12 h in an oven, the dry gel was calcined at 600°C for 2 h in muffle furnace to get the $\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{Pal}$ nanocomposites. The $\text{Fe}_2\text{O}_3/\text{SmFeO}_3/\text{Pal}$ nanocomposites catalysts were denoted as FS-1/Pal ($n_{\text{Fe}}/n_{\text{Sm}} = 1$), FS-1.5/Pal ($n_{\text{Fe}}/n_{\text{Sm}} = 1.5$), FS-2/Pal ($n_{\text{Fe}}/n_{\text{Sm}} = 2$), FS-2.5/Pal ($n_{\text{Fe}}/n_{\text{Sm}} = 2.5$), and FS-3/Pal ($n_{\text{Fe}}/n_{\text{Sm}} = 3$), respectively. SmFeO_3 and Fe_2O_3 counterpart were prepared by the same method without Pal.

2.3. Catalysts characterization

The XRD patterns were taken on an X-ray diffractometer equipped with a Cu anode (D/Max 2500 PC, Rigaku Corporation, Japan), running at 60 kV and 30 mA in the range between 5° and 80° . The binding energy of the elements was measured by X-ray photoelectron spectroscopy (XPS) with a Quantum 2000 Scanning ESCA Microprobe instrument using Al-K α . The C 1s signal was set to a position of 284.6 eV. The morphology was observed using a transmission electron microscope working at 200 kV (JEM-2100, JEOL, Japan). The BET and N_2 adsorption measurement were performed using Micromeritics ASAP 2010 at 77 K. The UV–vis diffuse reflection spectrum was obtained using a scanning UV–vis spectrophotometer (UV–vis DRS, UV-2700, Japan) equipped with an integrating sphere assembly using 100% BaSO_4 as a reflectance sample. The Photoluminescence (PL) spectra were measured on a Fluorescence photometer (LS45). The redox properties of the samples were measured by H_2 temperature-programmed reduction (H_2 -TPR) on a Micromeritics ASAP 2920 instrument (Micromeritics, USA). 50 mg sample was heated from 30°C to 700°C with a linear heating rate of $10^\circ\text{C}/\text{min}$ and a mixture of H_2 (10 vol%)/Ar was employed as a reducing atmosphere at a flow rate of 30 mL/min. The acid distribution of the catalysts was measured by NH_3 temperature-programmed desorption (TPD) on the same instrument. Approximately 0.3 g catalyst sample was pretreated for 30 min in N_2 at 400°C and then cooled down to room temperature under N_2 atmosphere. Then the sample was saturated with anhydrous NH_3 (in N_2 , flowrate = 30 mL/min) for about 30 min. Desorption experiment under N_2 (30 mL/min) was then performed at 30 – 500°C with a heating rate of $10^\circ\text{C}/\text{min}$.

2.4. Photo-SCR activity

The photo-SCR of NO_x was performed in a fixed-bed quartz flow reactor as shown in Fig. 1. The light source was a 500 W xenon lamp which can simulate sunlight. The simulated flue gas was: 1000 ppm NO , 1000 ppm NH_3 , 3% O_2 , N_2 as balance gas

with the total flow rate of 2 L/min corresponding to gas hourly space velocity (GHSV) of $40,000\text{ h}^{-1}$. Adequate sample was loaded in the fixed bed at a reaction temperature of from 30 to 200°C . The concentrations of the effluent gas, including NO , NO_2 and N_2O were continually monitored by the KM9106 flue gas analyzer. Correspondingly, the NO_x conversion and N_2 selectivity in the reaction could be calculated as follows [21,22]:

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

$$\text{N}_2 \text{ selectivity} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% \quad (2)$$

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction (XRD) patterns of samples Pal, Fe_2O_3 , SmFeO_3 and FS/Pal with various $n_{\text{Fe}}/n_{\text{Sm}}$ are shown in Fig. 2. The diffraction peak of pure Pal at 8.36° is ascribed to the characteristic basal plane for Pal clay [23]. The pure Fe_2O_3 and SmFeO_3 agree well with the standard card (JCPDS Nos. 87-1165 and 39-1490). The typical diffraction reflections observed at $2\theta = 24.15^\circ$, 33.16° and 35.63° correspond to the primary diffraction of the (012), (104), (110) crystal planes of hematite Fe_2O_3 , while SmFeO_3 occur at 22.87° , 25.63° and 32.71° correspond to the primary diffraction of (101), (111), (121) crystal planes of rhombohedra SmFeO_3 , respectively. As for FS/Pal, the characteristic diffraction peaks of Pal and SmFeO_3 are identified, indicating that SmFeO_3 has been loaded onto the Pal. With the increase of $n_{\text{Fe}}/n_{\text{Sm}}$ from 1.5 to 3, the peak intensity of the SmFeO_3 phase is weakened while the Fe_2O_3 phase increases, suggesting the emerging of Fe_2O_3 in addition to perovskite SmFeO_3 phase.

3.2. XPS analysis

XPS was employed to further analyze the surface compositions and chemical states of the as-prepared catalysts. Fig. 3(A) presents the survey scan spectra of Pal, FS-1/Pal and FS-2/Pal, while Sm, Fe, Mg, Al, Si, O and C elements are observed in FS-2/Pal sample. Fig. 3(B) exhibits the high-resolution Sm 3d spectrum of the FS-2/Pal and FS-1/Pal sample, which consists of two peaks with binding energies around 1083 and 1110 eV corresponding to the signals from the doublets of Sm $3d_{5/2}$ and Sm $3d_{3/2}$ in the trivalent oxidation state [24]. Further observation shows that the FS-2/Pal sample has slight higher binding energies than the FS-1/Pal counterpart. This indicates that the SmFeO_3 has strong interaction with extra Fe_2O_3 , which leads to the enhanced density of electron cloud of Sm^{3+} . Moreover, the chemical environment around the SmFeO_3 species is altered, suggesting the precipitation of Fe_2O_3 on the surface of SmFeO_3 [25]. Fig. 3(C) shows the high-resolution Fe 2p spectra of the three samples. It can be observed that the Fe 2p spectra present the characteristic Fe $2p_{3/2}$ and Fe $2p_{1/2}$ spin-orbit peaks at binding energies around 711 and 724 eV, respectively. The peaks of FS-2/Pal are stronger than the counterpart of Pal and FS-1/Pal, which could be ascribed to formation of iron oxides on the FS-2/Pal composites surface [26]. Fig. 3(D) shows the high-resolution Si 2p spectra of the three samples, where the peaks located at 102 eV correspond to the Si $2p_{3/2}$ [27]. It should be noted that the FS-1/Pal and FS-2/Pal sample exhibits shift trend to lower energy and weaker intensity than that of pure Pal, implying the formation of Si–O–Sm chemical bonds on the composite surface [23].

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