



Insights into the Sm/Zr co-doping effects on N₂ selectivity and SO₂ resistance of a MnO_x-TiO₂ catalyst for the NH₃-SCR reaction

Chuanzhi Sun^{a,b,*}, Hao Liu^a, Wei Chen^a, Dezhan Chen^a, Shuohan Yu^b, Annai Liu^b, Lin Dong^{b,*}, Shuai Feng^c

^a College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Institute of Materials and Clean Energy, Shandong Normal University, Jinan 250014, PR China

^b Jiangsu Key Laboratory of Vehicle Emissions Control, School of the Environment, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

^c College of Chemistry and Chemical Engineering, Taishan University, Taian 271021, PR China

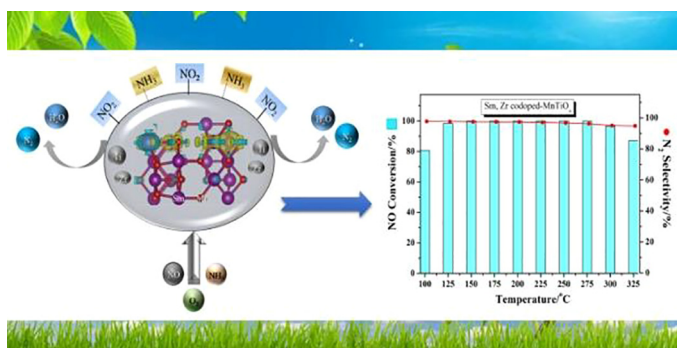


HIGHLIGHTS

- Sm, Zr co-doped MnO_x-TiO₂ catalysts were prepared by inverse co-precipitation.
- Excellent N₂ selectivity and SO₂ resistance are achieved by Sm and Zr co-doping.
- Redox cycle of Mn⁴⁺ + Sm²⁺ ↔ Mn³⁺ + Sm³⁺ is responsible for the good N₂ selectivity and SO₂ resistance.

GRAPHICAL ABSTRACT

Sm, Zr co-doped MnO_x-TiO₂ catalysts exhibited excellent N₂ selectivity and SO₂ resistance ability. Redox cycle of Mn⁴⁺ + Sm²⁺ ↔ Mn³⁺ + Sm³⁺ is responsible for the good N₂ selectivity and SO₂ resistance ability.



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ABSTRACT

A series of Sm- and/or Zr-doped MnO_x-TiO₂ catalysts were prepared, and the catalysts exhibited better N₂ selectivity and SO₂ resistance than the undoped MnO_x-TiO₂ catalyst for the selective catalytic reduction of NO by NH₃ (NH₃-SCR). The reasons for the good N₂ selectivity and SO₂ resistance of the catalysts were proposed. X-ray photoelectron spectroscopy (XPS) combined with density functional theory (DFT) calculations suggested that electron transfer between the manganese and samarium species by Mn⁴⁺ + Sm²⁺ ↔ Mn³⁺ + Sm³⁺ redox cycles occurred in the Sm-containing catalysts. Furthermore, electron transfer from Sm²⁺ to Mn⁴⁺ suppressed electron transfer from NH₃ to Mn⁴⁺, inhibiting the formation of NH₂ or NH. Thus, the pathway for NH generation was removed, and the reaction of 2NH + 4NO → 3N₂O + H₂O was prevented. Consequently, the N₂ selectivity of the NH₃-SCR reaction was enhanced. *In situ* diffused reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) combined with thermogravimetry, differential scanning calorimetry and mass spectrometry (TG-DSC-MS) results revealed that the deposition rate of sulfate species decreases after Sm doping,

* Corresponding authors at: College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Institute of Materials and Clean Energy, Shandong Normal University, Jinan 250014, PR China (C. Sun).

E-mail addresses: suncz@sdu.edu.cn (C. Sun), donglin@nju.edu.cn (L. Dong).

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which was also attributed to the suppressed electron transfer from SO_2 to Mn^{4+} , i.e., the oxidation of SO_2 to SO_3 . Thus, the catalysts exhibited better SO_2 resistance.

1. Introduction

Nitrogen oxides (NO_x) emitted from stationary sources (such as coal-fired power plants, and industrial furnaces) are major pollutants in the atmosphere [1–3], which can lead to acid rain, ozone depletion, the greenhouse effect, and photochemical smog and directly harm to human health [4,5]. The selective catalytic reduction of NO_x with ammonia (NH_3 -SCR) in the presence of excess oxygen is considered one of the best available approaches to control the emissions of NO_x produced from stationary sources. Commercial deNO_x technology, which employs $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ as a catalyst [6], has exhibited excellent catalytic performance in the NH_3 -SCR reaction in the temperature range of 300–400 °C. However, some inevitable disadvantages, such as a narrow operating temperature range, poor low-temperature activity and toxicity of the vanadium species, pose a barrier to its further application [7,8]. Thus, the development of a highly active catalyst for low-temperature SCR (< 300 °C) that works downstream of the electrostatic precipitator and desulfurization would be highly valuable and lead to improved economics for the SCR process.

$\text{MnO}_x\text{-TiO}_2$ catalysts have attracted much attention for the low-temperature selective catalytic reduction of NO with ammonia, and numerous works have been reported [9–15]. Wu et al. [9] studied $\text{MnO}_x\text{-TiO}_2$ mixed oxide synthesized using a CTAB-assisted method, which achieved ~100% NO conversion at 125 °C. Park et al. [16] reported a $\text{MnO}_x/\text{TiO}_2$ catalyst prepared by a chemical vapor condensation (CVC) method, which showed high SCR activity in the range of 100–250 °C, and the abundant quantity of amorphous Mn_2O_3 played an important role in the high activity. However, two flaws limit the application of the $\text{MnO}_x\text{-TiO}_2$ catalyst. First, the N_2 selectivity of this catalyst is relatively low and undesired N_2O always forms in the NH_3 -SCR process [4,6,9]. Second, the catalyst usually suffers from deactivation by SO_2 and H_2O [10,12,16]. To solve these problems, researchers have performed many works to modify the Mn-based catalyst. For example, Fe [4,17], Co [5,18], Ni [13,19], W [20], Ce [14,21,22] and other metal elements have been employed to modify the Mn-based catalyst to improve the N_2 selectivity and H_2O and/or SO_2 resistance of the catalyst. Yang et al. [8] suggested that the main reason for the high N_2 selectivity of the Mn/Fe-Ti spinels was that NH_3 was mainly adsorbed on the support of the catalyst, and therefore, it was not over-activated by Mn^{4+} , and the formation of N_2O was inhibited. Jin et al. [23] found that Mn-Ce/ TiO_2 catalysts prepared by a sol-gel method showed improved SO_2 tolerance compared with Mn/ TiO_2 , as the addition of Ce made the surface sulfate groups decompose more easily. Although many outstanding works have been reported, the results obtained thus far still cannot meet the needs of H_2O and SO_2 resistance at low temperature, and therefore, further studies should be carried out. Recently, Sm-doped mixed oxide catalysts were shown to exhibit considerably enhanced catalytic activity and SO_2 tolerance [2,24,25]. Meng et al. [2] found that a $\text{SmO}_x\text{-MnO}_x$ catalyst had an ideal SO_2 tolerance at low temperature, and they suggested that the incorporation of Sm could induce the formation of bulk-like sulfate on the Sm sites and weaken the influence of SO_2 on the Mn sites. However, the origins for the effect of Sm doping into the catalysts on the SO_2 tolerance are still unclear, and an in-depth study is still urgently needed. In addition, the effect of Sm doping into the catalysts on the N_2 selectivity of the NH_3 -SCR reaction should also be investigated.

In this study, Zr is used to adjust the surface acidic properties of the catalyst to pursue a higher catalytic activity [26,27]. Individual Sm- and Zr-doped $\text{MnO}_x\text{-TiO}_2$ catalysts and a Sm/Zr co-doped catalyst are synthesized, and the doping effects of Sm and/or Zr are studied.

Generally, the NH_3 -SCR reactivity of a catalyst is closely related to its redox and acidic properties. Therefore, the influences of Sm and/or Zr doping on the redox and acidic properties of catalysts are explored, and the relationships between these chemical properties and the activities are discussed. The main purpose of this work is to investigate the effects of Sm doping on the N_2 selectivity and SO_2 resistance of the $\text{MnO}_x\text{-TiO}_2$ mixed oxide catalyst for the NH_3 -SCR reaction. Accordingly, the interaction mechanisms of NH_3 , $\text{NO} + \text{O}_2$ and SO_2 with the catalyst surfaces are investigated deeply, and the essential reasons of the good N_2 selectivity and SO_2 resistance performance of the catalysts are proposed.

2. Experimental

2.1. Catalyst preparation

The Zr and Sm co-doped $\text{MnO}_x\text{-TiO}_2$ mixed oxide catalyst was prepared by an inverse co-precipitation method. Suitable amounts of a 50 wt% $\text{Mn}(\text{NO}_3)_2$ solution (50% solution, Sinopharm Chemical Reagent Co., Ltd), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aladdin, China), Zr $(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (98%, Sinopharm Chemical Reagent Co., Ltd) and Ti $(\text{SO}_4)_2$ ($\geq 96\%$, Sinopharm Chemical Reagent Co., Ltd), at a molar ratio of Mn:Sm:Zr:Ti = 0.2:0.1:0.1:1, were dissolved in deionized water and stirred for 0.5 h. Then, an equal volume of a CTAB ($\geq 99.0\%$, Sinopharm Chemical Reagent Co., Ltd) solution (60 mmol/L) was mixed with the solution and stirred for 1 h. The resulting solution was added dropwise to excess aqueous ammonia (25 wt%), and the solution during the entire process was maintained at $\text{pH} \geq 11$. After stirring for 5 h, the solution was aged for 24 h, washed five times with deionized water and placed in an oven at 110 °C overnight for drying. The sample was placed in a muffle furnace in an air atmosphere, heated to 500 °C at a temperature ramp rate of 2 °C·min⁻¹ and maintained at this temperature for 6 h. The obtained sample was compressed and sieved (40–60 meshes) to prepare the catalyst. For comparison, we also synthesized $\text{ZrO}_x\text{-TiO}_2$, $\text{SmO}_x\text{-TiO}_2$, $\text{MnO}_x\text{-TiO}_2$, and $\text{MnO}_x\text{-SmO}_x(\text{ZrO}_x)\text{-TiO}_2$ samples with the same method, and these samples are denoted as ZTO_x , STO_x , MTO_x , MZTO_x , MSTO_x and MSZTO_x , respectively. In addition, taking MTO_x as an example, the used sample tested in the presence of SO_2 for 24 h is denoted as $\text{MTO}_x\text{-U}$.

2.2. Catalyst characterization and DFT calculations

X-ray powder diffraction (XRD) measurements were performed at room temperature with a Rigaku D/max2000 diffractometer employing $\text{Cu K}\alpha$ (40 kV, 100 mA) radiation ($\lambda = 1.5406 \text{ \AA}$). Inductively coupled plasma-optical emission spectrometry (ICP-OES) was performed on a Thermo Scientific iCAP 7000 apparatus to determine the actual concentrations of the various elements in the samples. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by physical adsorption measurements of N_2 at -196 °C using a Micromeritics ASAP 2020/TriStar 3000 instrument. Each sample was degassed for 4 h at 350 °C under vacuum prior to the BET determination. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a PHI 5300 Versa Probe high performance electron spectrometer using monochromatic Al $\text{K}\alpha$ radiation (1486.6 eV) operating at an accelerating power of 15 kW.

Temperature programmed reduction by H_2 (H_2 -TPR) was carried out in a quartz U-tube reactor connected to a TCD with a $\text{H}_2\text{-Ar}$ mixture (7% H_2 by volume) as a reductant. An amount of 100 mg of each sample was used for each measurement. Before introducing the sample to the $\text{H}_2\text{-Ar}$ stream, the sample was pretreated in a N_2 stream at 300 °C for 1 h. TPR started from room temperature to 700 °C at a rate of

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