Gd-modified MnO\textsubscript{x} for the selective catalytic reduction of NO by NH\textsubscript{3}: The promoting effect of Gd on the catalytic performance and sulfur resistance

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HIGHLIGHTS

• Gd doped MnO\textsubscript{x} de-NO\textsubscript{x} catalyst was explored for the first time.
• Gd doping can inhibit the crystalline of manganese oxide.
• GdO\textsubscript{x} with abundant acid sites can enhance the surface acidity of MnO\textsubscript{x}.
• The catalyst with a 0.1 mol ratio of Gd/Mn delivered the best de-NO\textsubscript{x} performance.
• The SO\textsubscript{2} resistance of MnO\textsubscript{x} was enhanced by Gd doping.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Selective catalytic reduction
MnO\textsubscript{x}
de-NO\textsubscript{x}
Gadolinium
SO\textsubscript{2} resistance

ABSTRACT

Gadolinium (Gd) has been used as a dopant to modify MnO\textsubscript{x} for enhanced catalytic performance and sulfur resistance in the application of the selective catalytic reduction (SCR) of NO\textsubscript{x} with NH\textsubscript{3} for the first time. The results show that the introduction of Gd with proper amount can effectively restrain the crystallization of MnO\textsubscript{x}, enhance the specific surface area, increase the concentrations of surface Mn\textsuperscript{4+} and chemisorbed oxygen species, and enhance the amount and the strength of surface acid sites. The MnGdO-2 catalyst (Gd-modified MnO\textsubscript{x} with the molar ratio of Gd/Mn = 0.1) exhibits optimal catalytic performance among all prepared catalysts with a 100% NO conversion performance in a wide temperature window from 120 to 330 °C and a 100% N\textsubscript{2} selectivity from 150 to 300 °C under a high space velocity of 36,000 h\textsuperscript{−1}. In-situ DRIFT spectra reveal that the Gd doping can promote the NH\textsubscript{3} adsorption on the catalyst pre-adsorbed with NO\textsubscript{x} species, facilitating the reactive NH\textsubscript{4}\textsuperscript{+} species taking part in the SCR reaction. More importantly, MnGdO-2 catalyst presents stronger resistance to water vapor or sulfur poisoning in comparison with pure MnO\textsubscript{x} catalyst, which can be ascribed to these facts that Gd-modification restrains the transformation of MnO\textsubscript{2} to Mn\textsubscript{2}O\textsubscript{3} and the generation of MnSO\textsubscript{4}, impedes the decrease in Lewis acid sites and the increase in Brønsted acid sites, and alleviates the competitive adsorption between the NO and SO\textsubscript{2}. This work may provide new insights into the effects of rare earth modification on the de-NO\textsubscript{x} mechanism and the SO\textsubscript{2} resistance mechanism of MnO\textsubscript{x} catalysts.

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https://doi.org/10.1016/j.cej.2018.05.038
Received 6 February 2018; Received in revised form 20 April 2018; Accepted 7 May 2018
Available online 08 May 2018
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1. Introduction

As one of the most harmful pollutants in the atmosphere, nitrogen oxides (NO\(_x\), \(x = 1, 2\)) originated mainly from the coal-fired power plants, diesel engines and industrial heaters can lead to a series of environmental problems, such as photochemical smog, acid rain, ozone depletion and greenhouse effects, which directly pose a threat to the human health [1]. In the last few decades, the selective catalytic reduction (SCR) with ammonia has long been the most effective and economic technology for NO\(_x\) abatement from stationary source where an efficient \(\text{V}_2\text{O}_5\)-\(\text{WO}_3\) catalyst has been utilized since 1970s [2,3]. However, this classical formulation is confronting great challenges because of the toxicity of vanadium pentoxides, narrow working temperature window (300–400°C), SO\(_2\) oxidation to SO\(_3\) and the over-oxidation of NH\(_3\) to N\(_2\)O. In addition, due to the high working temperature, the catalysts have to be placed upstream of the dust remover and desulfurization units to avoid the reheating of the catalysts where the catalysts are susceptible to be deactivated by the dust accumulation and SO\(_3\) poison. Thus, it is highly imperative to develop low-temperature (<250°C) vanadium-free SCR catalysts with suitable working temperature window [4–6].

In recent years, plenty of transition metal oxides have been extensively studied and exhibited promising de-NO\(_x\) performance. Particularly, the manganese oxide (MnO\(_x\)) based catalysts outperform the others in the aspect of the low-temperature SCR performance and eco-friendliness, earth-abundant and low-priced advantages [7–12]. Nevertheless, the monometalllic MnO\(_x\) suffers from a few undesired properties, including the low specific surface area, thermal instability and poor resistance to water vapor and sulfur poison [12–14]. Therefore, several strategies have been proposed to enhance the comprehensive catalytic performance of MnO\(_x\), such as the utilization of support materials (\(\text{TiO}_2\), \(\text{Al}_2\text{O}_3\), \(\text{SiO}_2\) or carbon-based materials) to optimize the dispersion of MnO\(_x\) [15–19] or the modification with a secondary element (Mn-Fe, Mn-Co etc.) to induce synergetic effect [20–26]. Sometimes the two conventional methods are further combined to generate a supported bimetalllic oxide catalyst for better catalytic performance [27–30].

Rare earth elements with incompletely occupied 4f and empty 5d orbitals can be used as the active component or as the promoter of the catalyst [31]. It has been previously reported that the combination of CeO\(_2\) with MnO\(_x\) can give rise to enhanced de-NO\(_x\) performance, including catalytic performance, thermal stability and resistance to water vapor and sulfur poison [32–34]. Recently, Meng et al. demonstrated that the addition of suitable amount of samarium (Sm) to MnO\(_x\) (Sm/Mn = 0.1) can improve the low-temperature performance of MnO\(_x\) as well as the stability against water vapor and sulfur poison [35]. After that, Sun et al. found that the addition of europium (Eu) into MnO\(_x\) can enhance the SCR performance and resistance to water vapor and sulfur poison, accompanied by broadened operating temperature window [36], and a similar conclusion was drawn from the work performed by Zhu et al. where the catalytic performance of Fe-Mn/TiO\(_2\) catalyst was promoted by the doping of holmium (Ho) [37]. These successful research precedents confirm that rare earth elements are promising option to construct MnO\(_x\)-based composite oxide catalysts with excellent catalytic performance for the SCR of NO\(_x\) with NH\(_3\).

Gadolinium (Gd) is a lanthanide located in the middle of the periodic table which has been applied in various fields, especially for the magnetic resonance imaging contrast agents due to the unique magnetic properties of the Gd (III) ion [38]. In detail, the Gd (III) has seven unpaired electrons on each orbit which can give rise to large magnetic moments [38]. In addition, Gd as dopant can also be conducive to improving the photocatalytic performances of \(\text{TiO}_2\), \(\text{MoO}_3\), and \(\text{Bi}_2\text{MoO}_6\) [39–42], the ethanol oxidation and ethylene production of \(\text{Cr}_2\text{O}_3\) [43] and the dry reforming of methane for \(\text{Ni/ZSM}-5\) catalysts [44]. However, to the best of our knowledge, the Gd-modified MnO\(_x\) for the SCR of NO\(_x\) with NH\(_3\) has not been reported yet.

In this work, a series of Gd-modified MnO\(_x\) catalysts (MnGdO\(_x\)) with different mole ratios of Gd/Mn were successfully prepared for the first time, and their catalytic performances were evaluated by the NH\(_3\)-SCR of NO\(_x\). The influences of Gd doping on the physicochemical properties and de-NO\(_x\) performance were systematically investigated. Meanwhile, the catalyst with the best de-NO\(_x\) performance was further tested under vapor poisoning, sulfur poisoning, prolonged running time and higher GHSV to evaluate its potential in practical use. Moreover, based on in-situ DRIFTS, the effects of Gd modification on the de-NO\(_x\) mechanism and the SO\(_2\) resistance mechanism of the catalysts were investigated in detail.

2. Experimental section

2.1. Material synthesis

All reagents were analytical grade and used as received without further purification. The Gd-modified MnO\(_x\) catalysts were prepared by a co-precipitation method. In a typical synthesis, a certain amount of Gd(NO\(_3\))\(_3\)-6H\(_2\)O and Mn(NO\(_3\))\(_2\)-4H\(_2\)O with three different Gd/Mn molar ratios (0.05, 0.1 and 0.3, respectively) were completely dissolved in 50 mL distilled water by stirring for 30 min. Then the resultant solution was added dropwise to an ammonia solution (25 wt%) to initiate the co-precipitation reaction. During the reaction, the pH value of the solution was consistently maintained at 11. After continuously stirring at 500 rpm for 2 h, the resulting product was separated by filtrate and washed with distilled water for 3 times at least, and then was dried in an oven at 60°C overnight. Finally, the product was calcined in a muffle furnace in air at 400°C for 2 h, resulting in Gd-modified MnO\(_x\) catalysts with three different Gd/Mn molar ratios (0.05, 0.1 and 0.3, designated as MnGdO-1, MnGdO-2 and MnGdO-3 for convenience, respectively). For comparison, pure MnO\(_x\) and gadolinium oxide (GdO\(_x\)) were also prepared by using the same method without the addition of the other salt.

2.2. Catalyst characterization

The morphology of the catalyst was characterized by scanning electron microscopy (SEM, SU6600 Hitachi, Japan). X-ray diffraction (XRD) measurements were carried out on an X-ray Diffractometer (D2Phaser, Bruker, Germany) with Cu Ka radiation (λ = 0.15418 nm) at 30 kV and 10 mA. Thermogravimetric analysis (TGA) was carried out on a TGA/DSC-1 system (Mettler-Toledo, Switzerland) under oxygen (60 mL/min) and N\(_2\) (20 mL/min) flow at a heating rate of 10°C/min. N\(_2\) adsorption–desorption isotherms were conducted on a Autosorb IQ (Quantachrome, America) at liquid N\(_2\) temperature (∼196°C). The specific surface area was determined from the linear portion of the Brunauer-Emmett-Teller (BET) plot, and the average pore diameter was calculated from the desorption branch of the N\(_2\) adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method. Samples were degassed in vacuum at 150°C for 6 h prior to taking the surface area and pore volume measurement. X-ray photoelectron spectroscopy (XPS) analyses were tested on a PHI5300 analyzer (Perkin Elmer, America) with aluminum K\(_\alpha\) radiation. All the XPS curves were calibrated according to the standard C1s peak (284.6 eV). The Temperature-programmed reduction (H\(_2\)-TPR) experiments were conducted on a chemisorption analyzer (ChemBET Pulsar, Quantachrome, America) under a 10% H\(_2\)/Ar gas flow (20 mL/min) at a rate of 10°C/min up to 800°C. Temperature programmed desorption of NH\(_3\) (NH\(_3\)-TPD) was also carried out on the same apparatus as that for H\(_2\)-TPR. 20 mg of the catalyst was preheated in a pure He flow (20 mL/min) at 140°C for 30 min. Prior to the desorption at a heating rate 10°C/min up to 950°C, the catalyst was pre-treated in a 5% NH\(_3)/\text{He}\) flow (20 mL/min) at 140°C for 30 min and then under the purging in a pure He flow (20 mL/min) to remove the weak physical adsorbed NH\(_3\) molecules.