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Short communication

Functional-membrane coated Mn-La-Ce-Ni-O_x catalysts for selective catalytic reduction NO by NH_3 at low-temperature

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ABSTRACT

Functional-membrane coated Mn-La-Ce-Ni-O_x catalysts for NH_3-SCR at low-temperature were designed and prepared. The catalytic activity for NO removal and the anti-poison ability of catalyst were also investigated and discussed. Result showed that functional-membrane coated Mn-La-Ce-Ni-O_x catalysts had the highest NO removal efficiency of 93% at 180 °C and after injecting 10 vol% H_2O and 300 ppm of SO_2, the NO removal efficiency still reached about 80%. The functional membrane could not only prevent H_2O absorbing on the surface of catalyst and produce sulfur ammonium salt, but also effectively isolate the poison contacting catalyst active sites.

1. Introduction

Nitrogen oxides (NO_x) is one of the major pollutant in the atmosphere. If inhaled NO_x directly, it can irritate the lungs, cause respiratory diseases, and lead to permanent changes in the lung as a result. So, it is very harmful to human body. A series of policies and regulations for limiting NO_x emissions are being implemented which has driven the development and utilization of a number of NO_x control technologies. In these technologies, because of its high efficiency and reliability, selective catalytic reduction (SCR) became the most mature technology for controlling NO_x in the industry [1].

The SCR catalyst is significant for SCR technology. At present, the operating temperature of the commercial SCR catalyst is 250–410 °C. However, for those industrial boilers which flue gas temperature is below 250 °C, the commercial SCR catalyst is difficult to meet the needs of such industrial boilers currently and it requires using of an SCR catalyst which can be used at low-temperature [2–4]. Therefore, the key to making low-temperature SCR technology practical application is making SCR catalysts as efficient and stable as possible at low-temperature.

Mn-based complex oxides are a hot spot due to its excellent performance for NO removal at low-temperature. Zhihang Chen [5] prepared an $Fe_3Mn_3O_8$ catalyst using the citric acid method and the molar ratio of Fe / (Fe + Mn) was 0.4. The results showed that the NO removal efficiency of the $Fe_3Mn_3O_8$ catalyst reached 98.8% at 120 °C. Under these conditions the existence of H_2O and SO_2 inhibited the removal activity. Roy et al. [6] also prepared a series of $Ti_{0.9}Mn_{0.1}O_{2-\delta}$ and $Ti_{0.9}Mn_{0.05}Fe_{0.05}O_{2-\delta}$ catalyst by using the solvent combustion method. These catalysts had good performance for NO removal. The NO removal efficiency was over 90% at 140 °C. However, the NO removal efficiency decreased rapidly after injecting SO_2. The SO_2 caused the irreversible inactivation on the surface of the catalyst. Haoxi Jiang et al. [7] doped CeO_2 into an Mn-based catalyst to improving the stability. The results showed that the MnO_x-CeO_2 catalyst had a greater rate of diffusion of oxygen and a larger surface area which gives it excellent NO removal performance at low-temperature. However, the MnO_x-CeO_2 catalyst is still poisonous under the existence of H_2O and SO_2. Despite Mn-based catalyst has excellent NO removal performance at low-temperature, but the poisonous effect of SO_2 and H_2O is a biggest bottleneck for the practical application of low-temperature SCR catalyst.

The Polytetrafluoroethene (PTFE) has high strength, toughness and self-lubrication properties. It can be used long-term at a maximum temperature of 250 °C. In addition, it also has excellent performance as a waterproof oil repellent and stain-resistor [8,9]. In our early studies, our research team has doped lanthanum, and nickel oxide in a Mn—Ce based catalyst and developed the Mn-La-Ce-Ni-O_x catalyst for NH_3-SCR of NO at the low-temperature. Our previous work [10] showed that the Mn-La-Ce-Ni-O_x (Mn/La/Ce/Ni = 2.5:2.5:1:1 in mol) catalyst had good

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SCR activity at 100–200 °C. In this study, in order to further improve the anti-poison ability of low-temperature SCR catalyst, a membrane coated Mn-La-Ce-Ni-O_x catalyst for NH_3-SCR of NO at low-temperature was designed and prepared. A layer of anti-corrosion, abrasion resistance, and water-repellent functional coating (PTFE-based membrane) will be applied to the surface of the catalyst. The structure schematic of the functional-membrane coated Mn-La-Ce-Ni-O_x catalyst was presented in Fig. 1. The catalytic activity for NO removal and the anti-poison ability of the functional-membrane coated Mn-La-Ce-Ni-O_x catalyst will also be investigated and discussed.

2. Experimental

2.1. Catalyst preparation

The functional-membrane was made of a layer of PTFE-based foam coating. In order to insure the gas molecules could contact with the active site through the functional coating, the functional-membrane was prepared of a porous structure by adding to pore former (using ethanol as pore former). The solution of PTFE-based foam coating was mixed using hydroxyethyl cellulose (AR, Sinopharm Chemical Group Co., Ltd.), Methyl alcohol Silicon sodium (AR, Sinopharm Chemical Group Co., Ltd.), ethanol (AR, Sinopharm Chemical Group Co., Ltd.) and 3% of polytetrafluoroethylene (Sigma-Aldrich Co., Ltd.) under continuous stirring for 30 min at 60 °C.

The Mn-La-Ce-Ni-O_x catalyst was prepared by the thermal decomposition method. The precursor solution was mixed using $Mn(NO_3)_2$(AR, Sinopharm Chemical Group Co., Ltd.), $La(NO_3)_2 \cdot 6H_2O$ (AR, Sinopharm Chemical Group Co., Ltd.), $Ce(NO_3)_2 \cdot 6H_2O$ (AR, Sinopharm Chemical Group Co., Ltd.), $Ni(NO_3)_2 \cdot 6H_2O$ (AR, Sinopharm Chemical Group Co., Ltd.) and deionized water under continuous stirring for 20 min at 60 °C. The precursor solution was dried at 120 °C for 2 h and calcined at 550 °C for 6 h. Then, the Mn-La-Ce-Ni-O_x particles were made about 200 mesh powder. In order to simulate the working of the catalyst, catalyst particles were formed as a monolithic honeycomb (30 mm × 30 mm × 120 mm) catalyst with a wall thickness of 1.1 mm and a channel diameter of 9.0 mm by an extruder.

The Mn-La-Ce-Ni-O_x monolithic honeycomb catalyst was immersed into the PTFE-based solution for 5 min. Then the catalyst was calcined at 350 °C for 5 min and rapidly cooled to room temperature after calcination. Repeating the above steps until the quantity of sulfur functional coating accounted for 1% of mass of the Mn-La-Ce-Ni-O_x catalyst.

2.2. Characterization

The Micro-morphology of membrane coated Mn-La-Ce-Ni-O_x catalysts were analyzed by scanning electron microscope(SEM) using a JEOL model JSM-5900. Fourier infrared spectrum was recorded by a Nexus 670 model FT-IR equipment.

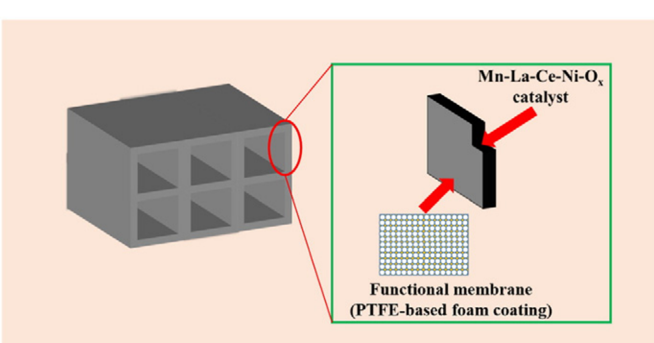

Fig. 1. Structure schematic of the membrane coated Mn-La-Ce-Ni-O_x catalyst.

2.3. Measurement of catalytic activity

The SCR activity of catalysts was measured using a fixed bed reactor made of a quartz reactor tube (the diameter of the reaction tube was 45 mm) and a tube temperature programmed furnace (Nabertherm) composition. The test gas was made of simulate flue gas concentration of each component (NO, O_2, SO_2 and H_2O), according to actual working conditions (N_2 as balance gas). The gas flow rate was controlled by mass flow meters (HORIBA METRON, S48 32/HMT). The test condition was presented in Table 1. NO concentration before and after the catalytic reaction was detected by using flue gas analyzer (Ecom, Germany), and then the NO conversion rate was calculated according to equation (Eq. 1).

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

The N_2 selectivity of catalysts was calculated by detecting the concentrations of NO, NH_3, NO_2 and N_2O. And the concentrations of NO, NH_3, NO_2 and N_2O were analyzed by an FTIR spectrometer (Nexus 670, Nicolet, USA), which equipped with a 2 m multiple-path gas cell. The N_2 selectivity of catalysts was expressed by the equation (Eq. 2):

$$\eta = \frac{[NO]_{in} - [NO]_{out} + [NH_3]_{in} - [NH_3]_{out} - [NO_2]_{out} - 2[N_2O]}{[NO]_{in} - [NO]_{out} + [NH_3]_{in} - [NH_3]_{out}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Micro-morphology of the functional-membrane coated Mn-La-Ce-Ni-O_x catalyst

The Micro-morphology of the functional-membrane coated Mn-La-Ce-Ni-O_x catalyst was presented in Fig. 2. As shown in Fig. 2, there was a coating on the surface of Mn-La-Ce-Ni-O_x catalyst obviously. This coating can prevent the dust from flue gas impacting the catalyst effectively. In addition, due to the use of a porous former, there were lots of pores and channels (diameter was less than 1 μm) existing in the coating. These pores and channels insured the contact between gas molecules with the active site of Mn-La-Ce-Ni-O_x catalysts.

3.2. SCR activity of the functional-membrane coated Mn-La-Ce-Ni-O_x catalyst

The NO removal efficiency of Mn-La-Ce-Ni-O_x catalyst and membrane coated Mn-La-Ce-Ni-O_x catalyst was investigated at different temperatures and presented in Fig. 3. As shown in Fig. 3, the trend of NO removal efficiency over two catalyst was similar and the high activity temperature window was between 140 and 200 °C. The change of NO removal efficiency with temperature could be divided into three stages. At 80–100 °C, the

Table 1
Test condition of catalytic activity for NO.

Items	Condition
Sample size	Monolithic honeycomb catalyst 30 mm × 30 mm × 120 mm, Wall thickness = 1.1 mm, channel diameter = 9.0 mm
NH_3/NO molar ratio	1
GHSV	5000 h^{-1}
Inlet NO gas concentration	600 ppm
O_2 concentration	6%
Reaction temperature	80–240 °C
SO_2 concentration	300 ppm
H_2O concentration	10 vol%