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Ce-Mn mixed oxides supported on glass-fiber for low-temperature selective catalytic reduction of NO with NH_3

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Abstract: Samples of cerium-manganese oxides supported on modified glass-fiber with different Ce/Mn molar ratios (Ce-Mn/GF) were prepared by an impregnation method and tested for low-temperature (80–180 ºC) selective catalytic reduction (SCR) of NO with ammonia. This brand-new technology could remove NO and particles matter from coal-fired flue gas. The surface properties of the catalysts were examined by means of Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The experimental results showed that the catalyst with a Ce/Mn molar ratio of 0.2 obtained high activity of 87.4% NO conversion at 150 ºC under a high space velocity of 50000 h^{-1}. Deactivation poisoned by SO_2 still occurred, but the Ce-Mn/GF(0.2) catalyst performed desirable tolerance to SO_2 with decreasing 50% in 40 min and then maintaining at about 30% NO conversion. Characterization results indicated that the excellent low-temperature catalytic activity was related to the high specific surface area, pore structure, and amorphous phase.

Keywords: Mn-Ce mixed oxides; glass-fiber; NO; low-temperature SCR by NH_3; SO_2 poisoning; rare earths

Selective catalytic reduction (SCR) of NO_x with ammonia is an efficient technology for reducing NO_x emitted from stationary sources[1]. The general reaction is as follows: $4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O$. Commercial catalysts for the above process are V_2O_5/TiO_2 catalyst promoted by WO_3[2]. However, this catalyst is active within a narrow temperature range of 300–400 ºC, while in order to avoid the deactivation by SO_2 and dust, SCR reactor is suggested to be located after the particle control and the desulfurizer devices, where the flue gas temperature is usually below 150 ºC[3,4]. Flue gas preheating causes increasing of installation and operation casts. Besides, there are still residual particle and SO_2 remaining after the particle control and desulfurizer devices. Therefore, there is a great interest to develop superior catalysts with high activities at low temperature (150–160 ºC). And such a catalyst would also possess the advantage of de-dusting capability and SO_2 resistance.

Manganese oxides (MnO_x) have been studied extensively as low-temperature SCR catalysts because of their multivalent nature and various types of labile oxygen, which are necessary to complete a catalytic cycle[5]. The MnO_x or Mn-based catalysts, such as MnO_x/CNTs[6], MnO_x/TiO_2 [7], and unsupported MnO_x [8] have shown to be active at low-temperature for NO removal. However, these catalysts are easily deactivated in the presence of SO_2. As a promoter, CeO_2 has attracted considerable interest because of its large oxygen storage capacity and unique redox properties, which stores and releases oxygen via the redox shift between Ce^{3+} and Ce^{4+} under oxidizing and reducing conditions. Ceria should enhance the oxidization of NO to NO_2, thereby increases the activity of SCR of NO by ammonia[9]. Gu et al.[10] indicated that CeO_2 had strong SO_2 resistance due to its surface sulfation. Moreover, catalyst supports are also believed to be important for SCR performance as they possess high surface areas, good thermal stability, and high active substance dispersion on surfaces[11,12]. Chen et al.[13] modified the glass-fiber with 2 mol/L hydrochloric acid and found that mild corrosion could generate steady nonmicropore on the surface of glass-fiber, which is propitious for catalyst carriers. They also proved high efficiency of fiber catalyst. Glass-fiber has been selected as catalyst supports in some areas due to its reasonable price, good physical and chemical properties, such as CO removing and hydrosilylation reactions[14,15], but reports focused less on its application of NO removing.

For the reason above, Ce-Mn mixed oxides supported on glass-fiber are believed to be a potential catalyst with high activity, de-dusting capability, and SO_2 resistance.

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However, there have been few reports that focused on selecting glass-fiber as Ce-Mn mixed oxides carriers, so the great challenge of this work is to obtain good loading effects and achieve high NO conversion in the low-temperature window of 100–180 ℃. In this study, a series of cerium-manganese oxides were supported on modified glass-fiber by impregnation method, and the activity of these catalysts were tested. The results showed that the most active catalyst yielded 87.4% NO conversion at 150 ℃ under GHSV=50000 h^{-1}.

1 Experimental

1.1 Catalysts preparation

The Ce-Mn/GF catalysts were prepared by impregnation method using cerium nitrate, manganese nitrate and alkali-free glass-fiber. After HCl pretreatment, glass-fiber generated some rough non-micropores, which was suitable for catalyst carrier[16].

The modification step of glass-fiber is as follows: Seven samples of 1.2 g glass-fiber were firstly marinated in soapy water for 20 min, then washed, dried and weighted. These samples were pretreated by 2 mol/L hydrochloric acid for 30 min at 50 ℃ to get a weight loss of 7.5%.

The aqueous solution of manganese nitrate ($Mn(NO_3)_2$, 0.02 mol) and cerium nitrate ($Ce(NO_3)_3$, 0–0.01 mol) was mixed in 100 mL deionized water under stirring at room temperature. Then modified glass-fibers were impregnated with the prepared solution for room temperature for 24 h and 50 ℃ for 24 h to reach adequate loading purpose. Finally, the samples were pyrolyzed at 200 ℃ for 4 h in air. The catalyst was denoted as Ce-Mn/GF(x), where x represents the molar ratio of Ce to Mn, e.g. Ce-Mn/GF(0–0.2).

1.2 Characterization of catalysts

Surface area and pore size distribution for the catalysts were measured by Brunauer-Emmett-Teller (BET) method. Barrett-Joyner-Halenda (BJH) method was used to analyze the successive pore size distribution (PSD) curves of macropores. The surface atomic state of the catalysts was determined by X-ray photoelectron spectroscopy (XPS) using a Thermo escalab 250Xi spectrometer equipped with a monochromated Al Kα radiation (1486.6 eV) (Thermo Electron, USA). Crystal structure of the catalysts were characterized by X-ray diffractometry using Rigaku D/max-2550 PC with a diffractometer operated at 40 kV and 200 mA (Japan, Cu K α radiation, 0.154056 nm), and the scans were taken over a range of 5° to 60° at a speed of 5 (°)/min. A scanning electron microscope (SEM) Quanta-250 was used to observe the supporting imaging of the catalysts.

1.3 Activity test

Catalyst activity measurements were carried out in a quartz tube reactor of diameter 20 mm. In typical conditions, 1 g sample was used in each run. The feed gases consisting of 500 ppm NO, 550 ppm NH_3, 5 vol.% O_2, and 550 ppm SO_2 (when used) in N_2 were adjusted by a rotameter and introduced into the reactor with a total flow rate of 1000 mL/min, yielding a gas hourly space velocity(GHSV) of 50000 h^{-1}. The feed gases except NH_3 were mixed in a mixing tank before entering the reactor, and NH_3 was directly into the quartz tube reactor to avoid possible reaction with SO_2 (when used). All catalyst activity tests were performed at the temperature of 80–180 ℃ with a heating rate of 5 ℃/min. In order to avoid the impact of gas adsorption on the catalyst samples, the test data were recorded after the reactions had been kept in stable states for each reaction temperature. NO conversion was obtained by the following equation:

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

2 Results and discussion

2.1 Activity test

Fig. 1 shows the NO conversion at various temperatures for the SCR of NO by NH_3 over Ce-Mn/GF catalysts with different Ce/Mn molar ratios. Mn/GF catalyst without Ce showed relatively low activity and 78% NO conversion was obtained at 160 ℃. It should be noted that the addition of Ce caused a significant enhancement of the catalytic activity. With the Ce/Mn molar ratios increasing from 0 to 0.33, the NO conversion was enhanced in the low temperature range (100–150 ℃), and the maximum NO conversion shifted towards lower temperature. For Ce-Mn/GF(0.2), over 87% NO conversion was obtained at a low temperature of 150 ℃. However, further increase of the molar Ce/Mn ratios from 0.2 to 0.5 lowered the NO conversion. This phenomenon apparently occurred in Ce-Mn/GF(0.5), which declined the NO conversion both at low and high temperatures compared with pure Mn/GF without Ce. It can be

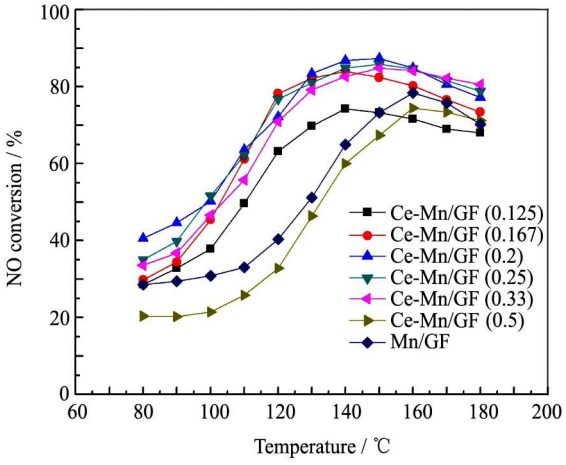

Fig. 1 NO Conversion of Ce-Mn/GF(x) with different Ce/Mn molar ratios (Reaction conditions: 500 ppm NO, 550 ppm NH_3, 5% O_2, and balance N_2, GHSV=50000 h^{-1})