Synthesis and Denitration Performance Research of Manganese Oxide Nanowires Loaded by Cerium Oxide as Low Temperature SCR Catalyst

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Abstract: The MnO_x nanowires loaded by cerium oxide are synthesized using hydrothermal method and impregnation method. The products exhibit excellent performance on selective catalytic reduction denitration experiments at low temperature. Meanwhile, the obtianed Mn Ce composite oxide are characterized by X-ray power diffraction(XRD) and scanning electron microscopy(SEM), effects of molar ratio of Mn to Ce, catalyst calcination temperature and temperature window on catalytic activity of cerium manganese compound catalyst were also investigated. Activity measurement results indicate that when Mn/Ce mole ratio is 10:4, calcination temperature is 550 °C, catalyst shows optimal performance. When the temperature is 150°C and air velocity is 10 000 h^{-1}, NO conversion rate can reach 88.5%.

Introduction

Nitrogen oxide is the most ordinary pollutant in environment for human activities. NO will be oxidized into NO_2 by photochemical effect forming nitrite, nitrite thus be the main cause of acid rain [1]. Furthermore, with the influence of sunshine, NO_x and hydrocarbon organic compounds will generate several severely poisonous secondary pollutants such as photochemical smog [2] and cause a series of environmental pollution problems.

Nowadays, NH_3 selective catalytic reduction is one of valid methods flue gas denitration and is widely used in thermal power plants. On account of vanadium titanium catalyst whose active temperature window is between 350-400 °C is widely used currently [3-4], SCR device needs to be installed before the air preheater and the flue gas with high sulfur and high dust will pull down the activity of the catalysts and service life [5]. So the development of low temperature (120-250 ˚C), highly active catalyst and place it after dust collector is full of significance.

An approach to decrease the catalytic reaction temperature is that utilize resourceful transition metal and rare earth oxides as low temperature denitration catalyst [6], such as manganese oxide. Pefie's [7, 8] research shows that in 120 °C, the catalytic activity of metal oxide order is as follow: Mn＞Cu≥Cr≥Co＞Fe≥V＞Ni, catalyst crystallization degree and various oxidation state decide the catalytic activity and selectivity [9]. Kapteijn etc. [10] found manganese oxide has many oxidation state, which is helpful to realize catalytic cycle and cerium oxide (CeO_2) with the characteristics of high oxygen capacity is able to provide more oxygen vacancies increasing the adsorption capacity of NH_3. Hence, we synthesize MnO_x nanowires loaded by cerium oxide, greatly improve the chemical stability, surface acidic or alkaline feature of low temperature (100-200°C) catalyst, endow it capability to remove acid and alkali as well as efficiently promote the catalytic reaction.

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Experimental

catalysts preparation. The MnO_x nanowires were prepared by the hydrothermal method, and the $MnCeO_x$ catalysts with different ratios were prepared by impregnation method. Typically, 0.008 mol $MnSO_4 \cdot H_2O$ and 0.015 mol $(NH_4)_2SO_4$ were added into 32 ml demineralized water, after constant stirring for 10min, the solution were transferred into a 50 ml Teflon-sealed autoclave and age at 120 ˚C for 24 h. The obtained product were washed with DI water and dried at 60 ˚C overnight. Then the samples were firstly marinated in HCl solution (1 mol/L) for 30 min, washed by DI water. The MnO_2 nanowires surface were acidized, which was suitable for adsorption of Ce^{3+}. Then dip 0.6 g samples in 50 ml $Ce(NO_3)_3$ solution (0-0.15 mol/L) at 50 ˚C for 24 h. Finally, the samples were calcined at 550 ˚Cfor 4 h in air. The catalyst was denoted as $MnCeO_x$(y), y represents the molar ratio of Ce to Mn.

Characterization of catalysts. Crystal structure of the catalysts were characterized by X-ray diffractometry using Shimadzu XRD7000 with a diffractometer operated at 40 kV and 200 mA, and the scans were taken over a range of 5° to 85° at a speed of 8°/min. Support imaging of the catalysts were observed by a scanning electron microscope(SEM) JSM6510A.

Activity test. The SCR activity measurements were carried out in a U quartz tube reactor with the inner diameter of 8 mm. In typical conditions, 0.5 g sample was used in each run. The feed gases consisting of 500 ppm NO, 550 ppm NH_3, 3 vol.% O_2, and balanced N_2 with a total flow rate of 200 ml/min, yielding a gas hourly space velocity(GHSV) of 10000 h^{-1}. Before entering the reactor, the feed gases were mixed in a mixing tank in the temperature range of 80–180 ºC with a heating rate of 8 ˚C/min. In order to avoid the impact of gas adsorption on the catalyst samples, the test data were recorded after the temperature was stabilized at the desired temperature. NO conversion was obtained by the following equation: $\eta_{NO} = \frac{C_{NO,in} - C_{NO,out}}{C_{NO,in}} \times 100\%$

Results and discussion

Catalytic activity performance. Fig. 1 shows the NO conversion at different temperatures for the SCR of NO by NH_3 over $MnCeO_x$ catalysts with different Ce/Mn molar ratios. MnO_x catalyst without Ce showed relatively low catalytic activity and obtain 75.3% NO conversion at 160 ˚C. With the Ce/Mn molar ratios increasing from 0 to 0.4, the NO conversion enhance obviously in the low temperature range (100–150 ˚C), it note that add the Ce could enhance the catalytic activity significantly, and the $MnCeO_x$(0.4) catalyst afford highly catalytic activity, it obtained 88.5% NO conversion at 150 ºC. However, further increase of the molar Ce/Mn ratios from 0.4 to 0.8 lowered the NO conversion. It can be interpreted as more Ce addition could inhabit the redox activity at low temperature. Fig. 1 also shows the SCR activity decreased in the following sequence: $MnCeO_x$(0.4)>$MnCeO_x$(0.2)> $MnCeO_x$(0.6)>$MnCeO_x$(0.8)>MnO_x

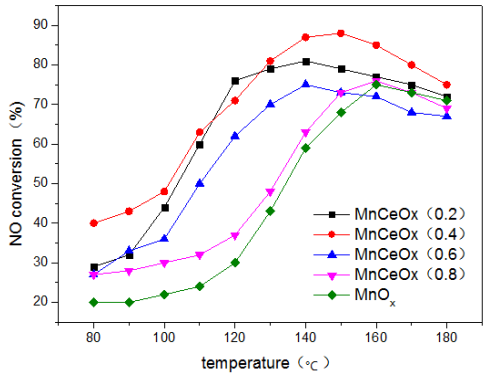

Fig. 1 NO Conversion of $MnCeO_x$(y) with different Ce/Mn molar ratios

XRD analysis. Fig. 2 shows the X-ray diffraction patterns $MnCeO_x$ with different Ce/Mn molar ratios. Several diffraction peaks observed at23.131°, 32.951°, 38.234°, 55.189° and 65.806° match the supporter Mn_2O_3 very well (PDF#41-1442). While, the appearance of the peaks at 28.549°, 33.083°, 47.486° and 56.346° is due to the cubic CeO_2 crystal (PDF#75-0120). In addition, the peak of CeO_2 becomes visible when the Ce/Mn molar ratios increasing from 0.2 to 0.8, which indicates that CeO_2 mainly existed on the surface. However, this peak is relatively invisible for low Ce/Mn ratios catalyst, indicating that CeO_2 is highly dispersed on the MnO_x nanowires.

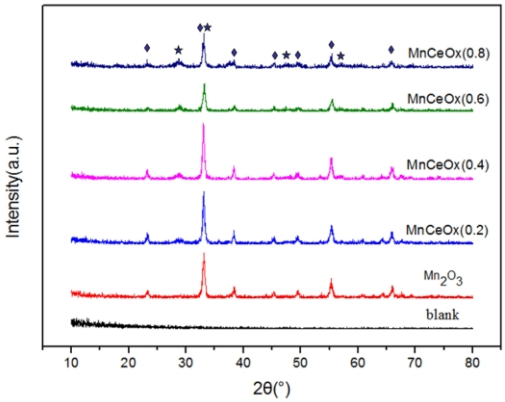

Fig. 2 X-ray diffraction patterns of $MnCeO_x$ with different Ce/Mn molar ratios
（♦, Mn_2O_3; ★, CeO_2）

SEM analysis. Fig. 3(a) shows the MnO_x nanowires. In Fig. 3(b), the CeO_2 has been loaded on the surface of the nanowires. Fig.3 is the support imaging in high magnification, clearly shows the nanowires has been agglomerat and the CeO_2 were well supported on the nanowires， This phenomenon was consistent with the X-ray diffraction analysis.

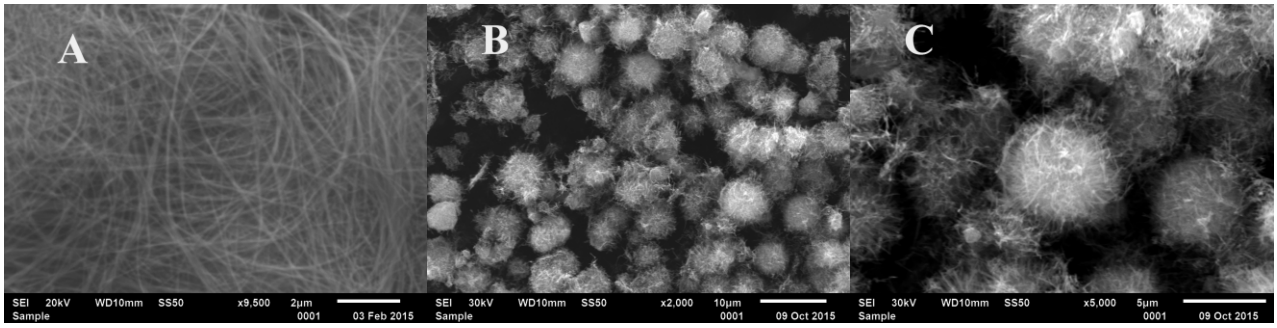

Fig.3 SEM photographs of MnCeOx(y) catalyst
（A）MnOx nanowire, (B) MnCeOx(0.8) in low magnification,
(C) MnCeOx(0.8) in high magnification

Conclusions

It has been demonstrated that $MnCeO_x$ catalyst exhibited high catalytic activity for the NH_3-SCR of NO_x at low temperature. Compared with MnO_x catalysts, $MnCeO_x$ catalyst shows excellent NH_3-SCR catalytic performance of deNO_x, this in mainly dual to the manganese oxide has many oxidation state(+2,+3,+4, and+7), and the materials have large surface area. The present results have practical implications, as they may open new pathways for NO_x reduction at low temperatures, the SCR system can be set up after the electric precipitator system and desulfurization system. Besides its application in power plant, this catalyst is also promising for a number of SCR applications.

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