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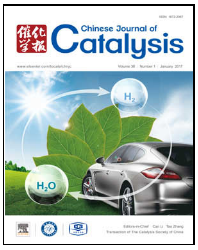

Article

Influence of preparation methods on the physicochemical properties and catalytic performance of MnO_x-CeO_2 catalysts for NH_3-SCR at low temperature

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ABSTRACT

This work examines the influence of preparation methods on the physicochemical properties and catalytic performance of MnO_x-CeO_2 catalysts for selective catalytic reduction of NO by NH_3 (NH_3-SCR) at low temperature. Five different methods, namely, mechanical mixing, impregnation, hydrothermal treatment, co-precipitation, and a sol-gel technique, were used to synthesize MnO_x-CeO_2 catalysts. The catalysts were characterized in detail, and an NH_3-SCR model reaction was chosen to evaluate the catalytic performance. The results showed that the preparation methods affected the catalytic performance in the order: hydrothermal treatment > sol-gel > co-precipitation > impregnation > mechanical mixing. This order correlated with the surface Ce^{3+} and Mn^{4+} content, oxygen vacancies and surface adsorbed oxygen species concentration, and the amount of acidic sites and acidic strength. This trend is related to redox interactions between MnO_x and CeO_2. The catalyst formed by a hydrothermal treatment exhibited excellent physicochemical properties, optimal catalytic performance, and good H_2O resistance in NH_3-SCR reaction. This was attributed to incorporation of Mn^{n+} into the CeO_2 lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). Strengthening of the electronic interactions between MnO_x and CeO_2, driven by the high-temperature and high-pressure conditions during the hydrothermal treatment also improved the catalyst characteristics. Thus, the hydrothermal treatment method is an efficient and environment-friendly route to synthesizing low-temperature denitrification (*de*NO_x) catalysts.

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1. Introduction

Recently, the harmful nature of nitrogen oxides (NO_x) has become a serious environmental issue that has attracted public attention. It has been recognized that NO_x are major atmospheric pollutants, mainly emitted from stationary sources, such as coal-fired power plants, and mobile sources, such as motor vehicles. These emissions not only cause acid rain and photochemical smog, but also act as a precursor for airborne particulate matter ($PM_{2.5}$), which can damage human health and plant growth [1–3]. Elimination of NO_x is an urgent environmental concern. Among currently available technology, selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) has been proved to be an efficient, reliable, and economical way to control NO_x emissions [4].

A V_2O_5/TiO_2 sample promoted by WO_3 or MoO_3 is the commercial catalyst for NH_3-SCR process, which exhibits excellent catalytic performance between 300 and 400 °C [5–7]. However, to reach these operating temperatures, the NH_3-SCR device has to be located upstream of electric precipitator and desulfurizer units in a power station setting. Under these conditions, the catalyst may become blocked and deactivated by dust and sulfur-containing compounds in flue gas [3,5,8]. Furthermore, there may not be enough space to place an NH_3-SCR device before the electric precipitator and desulfurizer units in old coal-fired power plants. Therefore, there is demand for low-temperature (below 200 °C) NH_3-SCR catalysts that would allow the NH_3-SCR device to be placed downstream of the electrostatic precipitator and desulfurizer units, after dust and SO_2 have been eliminated [3,9,10].

In recent years, considerable efforts have been devoted to developing novel NH_3-SCR catalysts that show good low-temperature catalytic performance. Some examples include supported noble-metal catalysts [11], metal-ion exchanged molecular sieves [12–14], and manganese-based catalysts [5,8,9,15–18]. Among these, manganese-based catalysts have attracted considerable attention owing to their good redox properties and excellent oxygen migration ability, which are beneficial for oxidation of NO to NO_2, and lead to relatively high conversion of NO_x at low temperatures through a "fast NH_3-SCR" route [3,19]. However, the low N_2 selectivity, poor H_2O resistance, and narrow operating temperature window of manganese-based catalysts require further improvements [20–22]. Efficient low-temperature NH_3-SCR catalysts are required, which not only exhibit high catalytic activity at low temperatures, but also have a wide operation temperature window, good H_2O resistance and high N_2 selectivity at low temperatures.

Ceria (CeO_2) has been widely used to eliminate NO_x owing to its good redox properties and high oxygen storage/release capacity associated with oxygen vacancies in the material and the Ce^{4+}/Ce^{3+} redox couple [2,23–29]. It has also been reported that CeO_2 can promote adsorption of NO_x, provide stronger Brønsted acidic sites, enhance oxidation of NO to NO_2, and improve the water and sulfur resistance of catalysts, which would be particularly beneficial for the NH_3-SCR model reaction [10,19,26,30]. Therefore, a combination of manganese oxide (MnO_x) and CeO_2 to form MnO_x-CeO_2 catalysts might improve the materials catalytic performance for the NH_3-SCR of NO_x. This is because of the synergistic interaction between MnO_x and CeO_2, and other advantages. Shen *et al.* [31] synthesized a supported MnO_x/CeO_2 catalyst for the low-temperature NH_3-SCR model reaction, which showed more than 90% NO conversion between 120 and 220 °C owing to a high dispersion of MnO_x, favorable redox properties, and good adsorption of oxygen species. However, the operating temperature window, H_2O resistance, and N_2 selectivity of this catalyst need further improvement.

It has been widely reported that the physicochemical properties and catalytic performance of redox catalysts are highly dependent on their preparation methods [22,32]. In the present work, we synthesized a series of MnO_x-CeO_2 (MnCe) catalysts for a low-temperature NH_3-SCR model reaction, using several different preparation methods. The obtained samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, N_2 physisorption, H_2 temperature-programmed reduction (TPR), NH_3 temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS). Moreover, a $NO+NH_3+O_2$ model reaction was chosen to evaluate the catalytic performance of these catalysts. The purpose of this paper is to first examine the influence of different preparation methods on the physicochemical properties and catalytic performance of MnO_x-CeO_2 catalysts and to screen for an optimal preparation method. Second, we investigate the interaction of NH_3 and $NO+O_2$ with these catalysts by *in situ* DRIFTS in the temperature range of 25–350 °C to further understand the reaction mechanism of NH_3-SCR over MnO_x-CeO_2 catalysts.

2. Experimental

2.1. *Catalyst preparation by different methods*

2.1.1. *Mechanical mixing method (MMM)*

The MnCe-MMM catalyst was prepared by a mechanical mixing method. MnO_x and CeO_2 were obtained by separate thermal decompositions of $Mn(NO_3)_2$ and $Ce(NO_3)_3{\cdot}6H_2O$ at 500 °C for 5 h in air, after grinding the precursors in an agate mortar. The desired amounts of MnO_x and CeO_2 were then mixed together in an agate mortar for 1 h to prepare the sample.

2.1.2. *Impregnation method (IM)*

The MnCe-IM catalyst was prepared by an impregnation method. CeO_2 (obtained by thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ at 500 °C for 5 h in air) was impregnated with an aqueous solution containing the desired amount of $Mn(NO_3)_2$ for 2 h. The resulting solid was then heated at 100 °C using an oil bath to evaporate residual water. The sample was dried at 110 °C in an oven for 12 h and finally calcined at 500 °C for 5 h in air.

2.1.3. *Hydrothermal treatment method (HTM)*