

Manganese oxide catalysts for NO_x reduction with NH₃ at low temperatures

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Abstract

Manganese oxide catalysts prepared by a precipitation method with various precipitants were investigated for the low temperature selective catalytic reduction (SCR) of NO_x with NH₃ in the presence of excess O₂. Various characterization methods such as N₂ adsorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and X-ray absorption near edge structure (XANES) were conducted to probe the physical and chemical properties of MnO_x catalysts. The active MnO_x catalysts, precipitated with sodium carbonate and calcined in air at moderate temperatures such as 523 K and 623 K, have the high surface area, the abundant Mn⁴⁺ species, and the high concentration of surface oxygen on the surface. The amorphous Mn₃O₄ and Mn₂O₃ were mainly present in this active catalyst. The carbonate species appeared to help adsorb NH₃ on the catalyst surface, which resulted in the high catalytic activity at low temperatures.

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1. Introduction

The emission control of nitrogen oxides (NO, NO₂ and N₂O) from various combustion processes has been a major environmental concern related to the air quality because nitrogen oxides have been reported as one of the most serious pollutants causing acid rain along with sulfur dioxide and play a major role in the photochemical chain reaction leading to the formation of photochemical smog. The primary nitrogen oxides (NO_x) produced from combustion processes with fossil fuel are nitric oxide (NO) and nitrogen dioxide (NO₂), which are 90–95% of the total NO_x emission from automotive exhausts and stationary sources such as thermoelectric power plant and incinerator [1].

The removal of nitrogen oxides from stationary or mobile sources has become an important issue and a variety of reduction methods to minimize the emission of NO_x such as a combustion control and a post-combustion control technology have been developed. Among the proposed post-combustion methods for NO_x removal, the technologies using the catalysts are known as one of most efficient methods in terms of relatively low cost and high efficiency. Especially, the selective catalytic reduction (SCR) of nitrogen oxide has been generally recognized as the most effective and widely commercialized removal technology of NO_x emitted from the stationary sources [1–3].

In order to convert NO contained in the flue gas into N₂, the reducing agent must be employed. NH₃, CO, H₂ and a variety of hydrocarbons such as methane, propylene, and ethane have been employed as reductants for NO removal reaction [4]. Although a number of reducing agents can be utilized in SCR, ammonia is the most effective and widely commercialized, which is called NH₃-SCR, for stationary sources such as power

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plants and nitric acid plants [5]. The selective catalytic reduction (SCR) is a process in which a reducing agent, e.g. NH_3 , reacts selectively with NO_x to produce N_2 without consuming an excess O_2 .

In the past few decades, the backbone of SCR technology is the development of SCR catalysts such as noble metals [6], supported metal oxides [7], zeolites [8] and others [1,9,10]. Among them, vanadia supported on titania is known to be the most effective and widely used commercial SCR catalyst due to its high activity and durability to sulfur compounds. Because this catalyst exhibits high conversions only in the temperature range of 573–673 K, the SCR should be applied before units for particle removal and desulfurization where the gas temperature decreases [11]. However, when the flue gas has high concentrations of particles and other contaminants which are deleterious for the catalyst, proper units should be located at the upstream of the catalyst bed to resolve above problems, which causes the decrease of the exit gas temperature. Therefore, there is a great interest in the development of SCR catalysts active at low temperatures (<573 K).

A number of catalysts consisted of various transition metal (V, Cr, Mn, Fe, Co, Ni and Cu) oxides on different commercial supports such as silica and alumina have been studied. Among these catalysts, manganese oxides such as $\text{MnOx}/\text{Al}_2\text{O}_3$ [12], MnOx/NaY [13], MnOx/USY [14] and MnOx/TiO_2 [15,16] have attracted much interests due to their high catalytic activities. These catalysts were prepared by the solution impregnation method on supports using manganese nitrate or acetate. In case of unsupported metal oxides, only limited works have been reported because unsupported MnOx catalysts suffer from very low surface areas [17]. Some additives such as citric acid were added in the preparation step to increase the surface area as well as the catalytic activity [18].

Recently, we found that MnOx catalysts prepared by a simple precipitation method with sodium carbonate showed the high catalytic activity for low temperature NH_3 -SCR [19]. This catalyst also appeared to be stable in the presence of excess water vapor. In the present study, we investigated the effect of preparation methods including kinds of precipitants and calcinations temperatures of the MnOx catalysts on their structural features and catalytic performance for selective catalytic reduction of NO_x with ammonia.

2. Experimental

2.1. The preparation of catalysts

The various kinds of manganese oxides were prepared by a precipitation method with different precipitants such as ammonium carbonate (AC), potassium carbonate (PC), sodium carbonate (SC), ammonium hydroxide (AH), potassium hydroxide (PH) and sodium hydroxide (SH). Each catalyst is denoted as MnOx-AC , MnOx-PC , MnOx-SC , MnOx-AH , MnOx-PH and MnOx-SH , respectively. 0.5 M ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$, DAEJUNG, 99.5%) aqueous solution, 0.5 M potassium carbonate (K_2CO_3 , DAEJUNG, 99.5%) aqueous solution, 0.5 M sodium carbonate (Na_2CO_3 , SHINYO,

99.5%) aqueous solution, ammonium hydroxide (NH_4OH , DAEJUNG, 25.0–28.0%) solution, potassium hydroxide (KOH , DAEJUNG, 99%) or sodium hydroxide (NaOH , SAMCHUN, 99%) was continuously added to 500 ml of 0.5 M manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich, 98.0+%) aqueous solution until the pH of the solution reached 8. The resulting precipitate was aged at 298 K for 1 h, filtered, and washed several times with distilled water. The cake was dried in air at 393 K for 12 h and calcined in static air at different temperatures such as 523 K, 623 K, 723 K and 823 K.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAC-III using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm), operated at 50 kV and 30 mA (1.5 kW). BET surface areas were calculated from N_2 adsorption data that were obtained using Autosorb-1 apparatus (Quantachrome) at liquid N_2 temperature. Before the measurement, the sample was degassed for 12 h at 150 °C. The amount of adsorbed NH_3 and NO was measured at 300 K by a pulse adsorption method using helium as a carrier gas. X-ray photoelectron spectroscopy (XPS) data were obtained with an $\text{Mg K}\alpha$ (1253.6 eV) X-ray source using ESCA2000 (VG Microtech) instrument. The binding energy of C 1s (284.7 eV) was used as an internal standard. The thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer Series 7 thermal analysis system under a flow of dry air. The temperature was raised from room temperature to 1173 K using a linear programmer at a heating rate of 40 K min^{-1} . The X-ray absorption near edge structure (XANES) spectra were taken in a transmission mode for the K-edge of Mn at beamline 3C1 of the Pohang light source (PAL) operating at 2.5 GeV with ca. 100–150 mA of stored current. The detector gas was N_2 for the incident beam and the transmitted beam. In addition to catalyst samples, XAFS data were also obtained for Mn foil, MnCO_3 , MnO , Mn_2O_3 , Mn_3O_4 , and MnO_2 as references. They were analyzed by using ATHENA [20].

2.3. Activity measurements

Catalytic activities were measured over a fixed bed of catalysts in a tubular flow reactor of 8 mm i.d. Reactant gases were fed to the reactor by means of electronic mass flow controller (MKS).

The reactant gas typically consisted of 500 ppm NO , 500 ppm NH_3 , 5 vol.% O_2 , and N_2 or He. The NO_x concentration in the inlet and outlet gas was analyzed by means of a NO/NO_2 combustion gas analyzer (Euroton). The N_2 and N_2O in the effluent were separated at 353 K with HeySep D column and their concentrations were analyzed with a thermal conductive detector (TCD) in a gas chromatography (Hewlett-Packard, HP 5890). From the concentration of the gases at steady state both the conversion and the selectivity are calculated according to the following formula [12,17]:

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

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