



Novel manganese oxide confined interweaved titania nanotubes for the low-temperature Selective Catalytic Reduction (SCR) of NO_x by NH₃



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ABSTRACT

A series of manganese confined titania nanotubes (Mn/TNT) prepared by alkaline hydrothermal synthesis technique and were investigated for the Selective Catalytic Reduction (SCR) of NO_x with NH₃ in the presence of excess (10 vol.%) oxygen. Remarkably, the surface texture and tubular morphology of Mn/TNT-H catalyst greatly promote the NO_x conversions in the temperature regime of 100–300 °C. The existence of abundant surface Mn⁴⁺ species apparently contributes to the remarkable low-temperature SCR activity, and additionally the increased surface area, high dispersion and numerous Lewis acid sites distribution contribute to broaden temperature window over Mn/TNT-H catalyst with 0.25 Mn/Ti atomic ratio. The impregnation of MnO_x over TNT-SA catalyst occurs bare minimum because of the low specific surface area and low pore volume, and this leads to poor deNO_x activity. The Mn⁴⁺/Mn³⁺ fraction deduced by XPS found to be considerably high for the Mn(0.25)/TNT-H catalyst (Mn⁴⁺/Mn³⁺ = 2.15) while in other catalysts the fraction is typically in the range of 0.36–1.34. Raman scattering reveals a redshift of 13 cm⁻¹ from 640 cm⁻¹ (TiO₂-Hombikat) to 627 cm⁻¹ in Mn/TNTs-H sample, which indicates the formation of a new phase or structural difference. In comparison with the Mn supported on TiO₂ (Hombikat) nanoparticles, the Mn species on the developed tubular Mn/TNT-H were less pronounced to coagulate under the reaction temperatures. It is interesting to note that the relative atomic ratios of Mn⁴⁺/Ti and Mn⁴⁺/Mn³⁺ as well as the existence of surface Mn⁴⁺ species in the titania nanotube appear to be directly correlated with the deNO_x performance of the catalysts.

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1. Introduction

The Selective Catalytic Reduction (SCR) of NO_x using ammonia (NH₃) as the reducing agent is a well-established and efficient process for the abatement of nitrogen oxide (NO_x) emissions. The prevailing commercial catalytic formulation consists of V₂O₅ supported on TiO₂ (anatase), frequently promoted by WO₃ or MoO₃, having an operating temperature window from 300 to 400 °C [1,2]. The high temperature required for the operation of the catalyst influences its performance due to the presence of SO₂ and soot. The development of catalytic formulations active in low temperature region will help to resolve issues caused by SO₂ oxidation and poisoning, and moreover will assist the widespread utilization of SCR units by the automotive industry in order to achieve the abatement of NO_x emitted by automobile sources.

Selective catalytic reduction of NO_x by urea (urea/SCR) is the most efficient technology for the aftertreatment of NO_x from diesel engine exhaust to meet stringent emission regulations, including EURO VI and SULEV [3]. An SCR catalyst is required to be active, particularly in the low temperature regimes, since the normal exhaust gas temperature from a diesel engine ranging from 100 to 250 °C for light duty to 200–350 °C for heavy duty diesel engines is significantly lower than that from a gasoline engine, and the exhaust temperature from an advanced diesel engine for high fuel efficiency is foreseeable to become even lower [4,5].

It has been well reported in the literature that the manganese oxide-based catalysts supported on TiO₂ nanoparticles exhibit promising deNO_x potential in the low temperature region [1,6–9]. Manganese oxide-based catalysts supported on various TiO₂ (anatase, rutile and mixed phases) exhibit higher catalytic activities. In our earlier studies, we have reported high surface area (309 m²/g) anatase TiO₂ (Hombikat) as a superior support compared to other types of commercially available TiO₂ [7–10].

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Subsequently, novel titania nanotubes prepared by alkaline hydrothermal treatment can provide a high surface area and a unique nanotubular structure which can be beneficial for the higher dispersion of the active species and improve the deNO_x potential of manganese oxide-based formulations.

Recently, titania nanotubes have been attracted significant attention for their utilization in catalysis [11–13]. Metal oxide-based catalysts supported on titania nanotubes utilized for the low-temperature SCR of NO_x by NH₃ is a research in primary stages. Some researchers reported copper oxide [14,15], ceria [16–20], and vanadia [21] supported on titania nanotubes for the SCR of NO by NH₃. However, most of the reported nanotubes have shown activity in the medium and high temperatures regimes. To date, no manganese confined titania nanotubes have been synthesized and investigated for the remarkable low-temperature (100–300 °C) SCR of NO_x with NH₃ in the presence of excess (10 vol.%) oxygen.

In the present work, various TiO₂ nanoparticles with numerous crystallographic phases, particle size and surface area were used to prepare titania nanotubes via the alkaline hydrothermal treatment method. The resulting titania nanotubes possess different morphological features such as specific surface area, length and diameter due to the different characteristics of TiO₂ nanoparticles used for their synthesis. The main objective of our present work is not only to screen titania nanotube supports and optimize the manganese content for the SCR of NO_x reaction, but more significantly, it seeks to elucidate the structural-performance correlation of the catalyst. These factors allow a broad variation of the manganese loading together with an excellent anchoring of the manganese species onto the various titania nanotubes.

The catalytic activity of the manganese confined titania nanotubes (Mn/TNTs) was investigated for the low temperature SCR of NO_x by NH₃ at a GHSV of 50,000 h⁻¹ in the presence of excess oxygen. The Mn/TNT-H catalyst exhibits remarkable deNO_x potential at temperatures as low as 100 °C and a wide temperature window up to 300 °C. Our X-ray photoelectron spectroscopy studies illustrate that the relative atomic percentage value of Mn⁴⁺/Mn³⁺ characterized by deconvoluted XPS spectra was considerably high for the Mn(0.25)/TNT-H catalyst (Mn⁴⁺/Mn³⁺ = 2.15) whereas, surface Mn³⁺ species are in equivalence with MnO₂ phase in other catalysts (Mn⁴⁺/Mn³⁺ = 0.36–1.34). For the layered tubular structures, existence of abundant surface Mn⁴⁺ species contributes to the remarkable low-temperature SCR activity, additionally increased surface area, and high dispersion and rich Lewis acid sites distribution contribute to broad temperature window over Mn(0.25)/TNT-H catalyst. This contribution demonstrates the use of spectroscopic, physicochemical techniques to study the effect of various supports in the nanotubular structure, reduction profiles and surface atomic compositions for the remarkable selective catalytic reduction at low-temperatures.

2. Experimental

2.1. Synthesis of TiO₂ nanoparticles from titanium oxysulfate

A required amount of the precursor was dissolved in deionized water and then stirring and heating were applied. The resulting solution was washed with deionized water in order to remove sulfates and the precipitant was dried in oven at 80 °C, finally grinded in mortar and then sieved using a mesh with 300 μm opening.

2.2. Synthesis of titania nanotubes

Various TiO₂ nanoparticles (Hombikat, Ishihara, Sigma–Aldrich, P25 Degussa, Kemira, and TiO₂ prepared using titanium oxysulfate)

with numerous crystallographic phases, particle size and surface area were used as precursors for the titania nanotubes synthesis. Hereafter, these titania nanotubes were denoted as TNT-H, TNT-I, TNT-SA, TNT-P25, TNT-K, and TNT-TOS, respectively.

The synthesis of the titania nanotubes was achieved by dissolving 2 g of TiO₂ in 70 mL of 10 M NaOH solution and hydrothermally treated at 130 °C for 24 h in a Teflon-lined stainless steel autoclave. After the thermal treatment, the content of the autoclaves was filtered and washed initially with deionized water followed by 2 L of 0.2 M HCl aqueous solution until the pH reached approximately 1–2 and finally washed again with deionized water until the pH was resorted to neutral. The resulting nanotubes were dried at the low temperature of 80 °C for 18 h in order to avoid agglomeration of the structure. Finally, the material was grinded in mortar and sieved in a mesh with 300 μm openings. The resulting titania nanotubes are denoted as TNT-X where X indicates the TiO₂ precursor used for the preparation as can be observed in Table 1 along with the corresponding specific surface area (m²/g) of the materials.

2.3. Synthesis of Mn(0.25)/TNT-X (X = H, SA, I, P25, K, and TOS) and Mn(x)/TNT-H (x = Mn/Ti atomic ratio) nanotube catalysts

2.3.1. Screening of nanotube supports and optimization of manganese content for the SCR of NO_x

Initially, we have prepared a series of titania nanotubes by alkaline hydrothermal synthesis method using various titania precursors such as TiO₂ (Ishihara), TiO₂ (Kemira), TiO₂ P25 (Degussa), TiO₂ (Sigma–Aldrich), TiO₂ (Hombikat), and TiO₂ synthesized from titanium oxysulfate (TOS). Consequently, manganese oxide confined titania nanotube catalysts were prepared by adopting the incipient wetness technique. In a typical synthesis procedure, manganese nitrate hydrate (MnN₂O₆·xH₂O 99.99% trace metal basis from Sigma–Aldrich) was an active metal precursor. For the first family of catalysts, we have screened by aiming at the pre-eminent nanotube support for the SCR of NO_x reaction by altering the titania precursor. For this purpose, the manganese loadings were selected as 15 wt.% and the support titania nanotubes (TNT-H, TNT-I, TNT-SA, TNT-P25, TNT-K, and TNT-TOS) varied as described in the earlier section. For the second family of catalysts, we have synthesized a series of manganese oxide confined titania nanotube (Mn/TNT-H) catalysts with different manganese to titania atomic ratio (Mn/Ti = 0.15, 0.20, 0.25, 0.30, and 0.35) by adopting the incipient wetness technique.

For this purpose, the required amount of precursor was added to a 100 mL beaker containing 1.0 g of support in 50 mL deionized water. The excess water was then slowly evaporated on a water bath with continuous stirring at 70 °C. For comparison purposes, we also prepared conventional Mn/TiO₂ (Hombikat) catalyst. The resulting materials were oven dried at 120 °C for 12 h, and were ground and sieved (80–120 mesh) to obtain homogeneous powder. Prior to the reaction studies, the powder was calcined in a tubular oven at 400 °C for 2 h under continuous air flow (150 mL min⁻¹). The metal components of the catalysts are denoted as atomic ratios. All the ratios of the catalysts in this study are Mn/Ti = 0.15, 0.20, 0.25, 0.30, and 0.35. For example, Mn(0.25)/TNT-H indicates that the atomic ratio of manganese/titania is 0.25 and the titania nanotube support was synthesized by alkaline hydrothermal treatment of TiO₂ Hombikat.

2.4. Materials characterization

The specific surface area (m²/g), pore volume (cm³/g), average pore diameter (nm), adsorption desorption isotherms and pore size distribution of the synthesized titania nanotubes and the resulting manganese oxide based catalytic formulations were obtained from N₂ adsorption isotherms at liquid nitrogen temperature (77 K)

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