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Metal oxide-confined interweaved titania nanotubes M/TNT (M = Mn, Cu, Ce, Fe, V, Cr, and Co) for the selective catalytic reduction of NO_x in the presence of excess oxygen

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ABSTRACT

A series of metal oxide confined titania nanotube M/TNT (M = Mn, Cu, Ce, Fe, V, Cr and Co) catalytic formulations were successfully synthesized using hydrothermal method followed by wet impregnation technique. The resulting materials were investigated for the low temperature Selective Catalytic Reduction (SCR) of NO_x with NH_3 in the presence of excess oxygen (10 vol.%). The prepared catalysts exhibit remarkable deNO_x potential at temperatures as low as 100 °C and in a wide temperature range from 100 to 350 °C. Compared to manganese oxide supported on conventional TiO_2, the synthesized Mn/TNT catalyst exhibits superior activity. Interestingly, the surface texture and tubular morphology of Mn/TNT catalyst greatly promotes the NO_x conversion in the temperature regime of 100–300 °C. Our BET results of the as-prepared catalysts demonstrated that this is an effective synthesis for the generation of high specific surface area (421 m^2/g) titania nanotubes. High resolution transmission electron microscopy (HR-TEM) results revealed the formation of tubular structure and multi-walled layer construction in the pristine titania nanotube (TNT), Mn/TNT and Ce/TNT samples. The relative atomic percentage value of Mn^{4+}/Mn^{3+} and Ce^{3+}/Ce^{4+} characterized by deconvoluted XPS spectra was considerably high for the Mn/TNT ($Mn^{4+}/Mn^{3+} = 2.15$) and Ce/TNT catalysts ($Ce^{3+}/Ce^{4+} = 0.79$), respectively. The existence of abundant surface Mn^{4+} species apparently contributes to the remarkable low-temperature SCR activity over our Mn/TNT catalyst. The H_2-TPR results are in good accordance with our XPS results, with MnO_2 being the prevailing phase and the increased reduction potentials of manganese appear to be the reason for the high deNOx activity of the Mn/TNT catalyst at low-temperatures. Vanadia based catalyst (V/TNT) formulations exhibit monolayer isolated species present over the support where V^{5+} is the dominant oxidation state. Titania nanotubes confined vanadium oxide catalyst demonstrates a broad operation temperature window attributed to the high dispersion of active species on the support.

1. Introduction

Selective catalytic reduction using ammonia as reducing agent (NH_3-SCR) has drawn extensive attention as an advanced exhaust control technology to reduce NOx emissions [1,2]. NH_3-SCR technology has been commonly used for NOx control in stationary applications and more recently for diesel vehicle emissions. The current strategy of SCR by using ammonia as reducing agent, in particular for diesel-equipped vehicles [3–5] is nowadays considered as one of the most economical and effective NOx abatement catalytic technologies. SCR of NOx by urea (urea/SCR) is the most efficient technology for the after treatment of NOx from diesel engine exhaust to meet stringent emission regulations, including EURO VI and SULEV [6]. A SCR catalyst is required to be active, principally 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 considerably lower than that from a gasoline engine, and the exhaust temperature from an advanced diesel engine for high fuel efficiency is anticipated to become even lower [7,8].

Typically, transition metal oxides show good SCR activity in the low temperature range, such as Cr/TiO_2 [9], Co/TiO_2, Ni/TiO_2 [10], Mn/TiO_2 [1], Fe_xTiO_y [11], $V_2O_5/TiO_2–SiO_2–MoO_3$ [12], Cu/TiO_2 [13]. Particularly, Mn-based and Cu-based catalysts have attracted much interest due to their unique redox properties which make them significant for a variety of applications. In our earlier studies, we have developed Mn/TiO_2 catalysts [1,14–18] that exhibit promising deNO_x potential in the temperature range of 150–210 °C.

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Recently, titania nanotubes and nanowires have received a great deal of attention. These elongated structures possess large surface area and can be used to prepare novel 3D and highly crystalline structures exhibiting large porosity [19–21]. Interweaved titania nanotube structures have wide-ranging research interests due to the open structure which is beneficial to the mass and heat transfer. In addition to the desirable compositions, previous studies have already demonstrated that the catalytic behaviors of catalysts are also strongly dependent on the morphology and hierarchical structure of the materials. In particular, the nanotube architectures with uniform hollow structures and porous nature would greatly benefit the performance of catalysts by offering a high specific surface area, short diffusion length of reaction gases, and efficient channels for mass transport. As a result, the rational design and controllable synthesis of metal oxide-confined titania nanotubes (M/TNTs) with uniform compositions and hierarchically porous structures are highly desirable for the enhancement of its catalytic performance but still remain as a significant challenge. Metal oxide based catalysts supported on titania nanotubes utilized for the low-temperature SCR of NOx by NH_3 is a research in primary stages [22–30]. However, most of the reported nanotubes do not show high deNOx performance in the low-temperature regimes and suffer from other typical disadvantages at industrially relevant conditions.

In the present work, we report a successful synthesis route of homogeneously doped interweaved titania nanotubes (TNTs) with M^{n+} ions (M = Mn, Cu, Ce, Fe, V, Cr and Co) using scroll-type trititanate ($Na_2Ti_3O_7$) nanotube precursor produced by an alkali hydrothermal treatment of Hombikat TiO_2. These multi-walled nanotubes are composed of stepped or corrugated host layers of edge-sharing TiO_6 octahedrons having interlayer alkali metal cations. Further, we investigated these materials for the low temperature Selective Catalytic Reduction (SCR) of NO_x with NH_3 in presence of 10 vol.% oxygen at a gas hourly space velocity (GHSV) of 50,000 h^{-1}.

Our catalytic activity and characterization results revealed that the transformation of spherical nanoparticles of titania to open-ended tubular structures in the catalyst greatly promoted the SCR catalytic activities. Alkaline hydrothermal treatment of Hombikat TiO_2 led to the great enhancement in specific surface area (SSA = 421 m^2/g) compared to the primitive TiO_2 nanoparticles (SSA = 309 m^2/g). The Barrett–Joyner–Halenda (BJH) pore size distribution results illustrate that the pore size of the Mn/TNT samples centered at 2.4 nm and 6.5 nm which can be attributed to the native tube-like pores, and the pores constructed by interweaved connections. Our H_2-TPR results illustrate that the absence of the high-temperature (T_3) peak at 482 °C and relatively low peak area of T_2 imply that the dominant phase is MnO_2. This enormously prevailing MnO_2 phase appear to be the reason for the high deNOx potential of the Mn/TNT catalyst at low-temperatures. The reduction potential of titania nanotube encapsulated manganese oxide has been significantly improved. This indicates a strong interaction between Mn and Ti, which could be originated from the confinement effect of titania nanotubes, leading to the enrichment in Mn/TNT redox potential. Our high resolution-TEM studies illustrate that the 100% pure anatase phase titania precursor (TiO_2 Hombikat) generated the hierarchical two curled layers nanotubes, whereas rutile titania precursor (TiO_2 Sigma Aldrich, 95% rutile 5% anatase) produced well-defined tubular structures. Our HR-TEM results are in good agreement with Raman spectroscopy analysis where the formation of Ti—O—Ti bonding and creation of oxygen vacancies have been established. For the layered tubular structures, existence of abundant surface active components and increased surface area contribute to the remarkable low-temperature SCR activity.

2. Experimental

2.1. Synthesis of materials

2.1.1. Titania nanotubes synthesis

The synthesis of the titania nanotubes was achieved by dissolving 2 g of TiO_2 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 ground in mortar and sieved in a mesh with 300 μm openings. The resulting titania nanotubes are denoted as TNT or TNT-X where X indicates the TiO_2 precursor used for the preparation.

2.1.2. Synthesis of M/TNT (M = Mn, Co, Cr, Ce, Fe, V and Cu) catalytic formulations

A series of metal oxide (Mn, Co, Cr, Ce, Fe, V, Cu) confined titania nanotubes with constant loading of 15 wt% of metal on the support were prepared by adopting the wet impregnation method. The as-synthesized nanotubes (TNT) were used as the support of the catalytic formulations, using manganese(II) nitrate hydrate ($MnN_2O_6{\cdot}xH_2O$ 99.99% trace metal basis from Sigma-Aldrich), cerium(III) nitrate hexahydrate ($CeN_3O_9{\cdot}6H_2O \geq 99.0\%$ from Fluka Analytical), chromium(III) nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$, 99% from Sigma Aldrich), iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$ 98+% from Sigma Aldrich), copper(III) nitrate hemipentahydrate ($Cu(NO_3)_2{\cdot}2.5H_2O$ 99.99% from Aldrich), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$ 98% from Sigma Aldrich) and ammonium metavanadate ($H_3NO_3V \geq 99.0\%$ from Sigma Aldrich) as the metal oxide precursors. The required amount of the precursor was added to a 200 mL beaker containing 2 g of the support along with 100 mL of deionized water. The excess water was slowly evaporated in a water bath with continuous stirring at 70 °C. The resulting materials were oven dried at 80 °C for 18 h. Finally, the powders were ground in mortar and sieved in mesh with 300 μm openings in order to obtain homogeneous powder. Prior to the catalytic activity evaluation experiments, the materials were calcined in a tubular oven at 400 °C for 2 h with 5 °C temperature increments per minute in open-air. The resulting catalytic formulations are denoted as M/TNT where M denotes the active metal component (Mn, Co, Cr, Ce, Fe, V, Cu) and summarized along with the specific surface area, pore volume and pore diameter in Table 1.

2.1.3. Synthesis of Mn–Ce(x)/TNT catalysts

After the evaluation of a series of metal oxide confined titania nanotube catalysts, we have synthesized Ce-promoted Mn/TNT formulations by altering the Mn/Ce atomic ratios. The as-synthesized titania nanotubes prepared from TiO_2 (Hombikat) were used as the support and manganese oxide along with cerium oxide were loaded by adopting the wet impregnation method. Manganese (II) nitrate hydrate ($MnN_2O_6{\cdot}xH_2O$ 99.99% trace metal basis from Sigma-Aldrich) and cerium (III) nitrate hexahydrate ($CeN_3O_9{\cdot}6H_2O \geq 99.0\%$ from Fluka Analytical) were used as the metal oxide precursors. In order to prepare the catalytic formulations the required amount of metal precursors were added to a 200 mL beaker containing 2 g of TNT and 100 mL of deionized water. The excess water was slowly evaporated in a water bath with continuous stirring at 70 °C. The resulting materials were oven dried at 80 °C for 18 h, and then were ground in a mortar