



Short Communication

Effects of morphology and structure of titanate supports on the performance of ceria in selective catalytic reduction of NO

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ABSTRACT

The titanates with various morphologies and structures, e.g. nanoparticle (NP), nanotube (NT), nanowire (NW), nanorod (NR) and fragment (FR), were successfully synthesized in this paper, which were subsequently utilized as supports for CeO₂ in selective catalytic reduction of NO. Experimental results revealed that Ce/NP, Ce/NT and Ce/FR samples were highly active, whilst Ce/NW and Ce/NR samples showed very poor performance. We proposed that the difference in their performances was mainly originated from the resulting chemical states of CeO₂, which were induced by the nature of titanate supports, i.e. special surface properties and unique structures and morphologies.

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1. Introduction

The control of NO_x emission from flue gasses was a continuing challenge due to the increasing impact on environment from urban smog, acid rain, ozone depletion, and greenhouse effect [1]. Selective catalytic reduction (SCR) process with ammonia has been commonly recognized as one of the most desirable and attractive ways for NO_x removal. Although V₂O₅/TiO₂-based catalysts have been extensively employed in commercial SCR processes [1–3], the drawbacks associated with toxicity of vanadium pentoxide to environment, over-oxidation of NH₃ and formation of N₂O in high temperature range still remain [4].

Ceria supported on titanate nanoparticle (Ce/TiO₂) were reported to be environment-friendly deNO_x catalysts with good activity and N₂ selectivity in the temperature range of 275–400 °C [5–7]. However, researchers have been still seeking to further improve the SCR performance of Ce/TiO₂. For example, Chen et al. found that the addition of tungsten to Ce/TiO₂ catalyst could bring more adsorption species for NO_x and NH₃, and simultaneously enhanced the catalytic activity for NH₃-SCR [8]; Bayleta et al. investigated the NO_x reduction activity over different ceria/sulphated TiO₂ catalysts, which indicated that the deNO_x activity increased with sulfate contents [9]. Besides these, another potential way to improve the performance of Ce/TiO₂ catalyst is changing the structure of titanate support [7].

Nowadays, a variety of one-dimensional (1D) titania/titanate nanostructures have been synthesized and widely used as catalyst

supports due to their unique electronic and optical properties [10–15]. For example, titanate nanotube have been proposed being able to facilitate the adsorption of reactants on their active surface sites and were widely used as photo-catalysts, due to the high surface-to-volume ratio [10,11,14]; titanate nanowire have been considered as superior structures for charge transport, beneficial to sensing applications [14,16,17]; titanate nanorod have numerous structure defects, which are an interesting factor in lithium rechargeable batteries [14,18–20]; etc.

Since less attention has been paid to the different titanate structures/morphologies influencing on the SCR activity of CeO₂, this paper dealt with the effects of various titanate supports, e.g. nanoparticle, nanotube, nanowire, nanorod and fragment on the performance of CeO₂ in SCR of NO.

2. Experimental section

2.1. Catalyst preparation

Titanate nanoparticle (NP) used in the present study were commercially available P25 (Degussa, Germany). Titanate nanotube (NT) and titanate nanowire (NW) were prepared by hydrothermal treatment of P25 TiO₂ with 10 N NaOH solution [15,21]. The introduction of cerium onto NP, NT and NW was conducted by wet-impregnation method. Ceria loaded titanate fragment (Ce/FR) was made via an in-situ method, where an appropriate amount of cerium nitrate solution was added to TiO₂/NaOH mixture for hydrothermal treatment. The Ce/NT, Ce/NW, Ce/NP and Ce/FR samples were all calcined at 450 °C for 3 h. Ceria loaded titanate nanorod (Ce/NR) were

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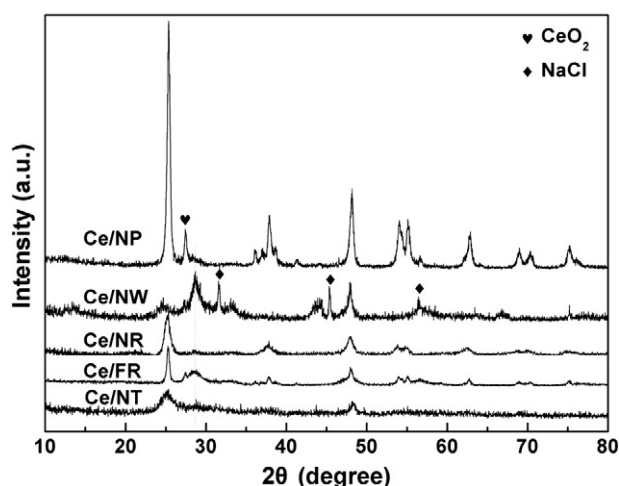


Fig. 1. XRD patterns of Ce/TiO₂ samples.

prepared by calcining the mixture of cerium nitrate solution and titanate nanotube (that was dried at 80 °C) at 550 °C for 2 h.

The loading amount of Ce was designed to be 1:19 (Ce/Ti molar ratio), which was an optimized loading by our preliminary experiments [7]. Catalyst preparation details were presented in Supplementary data S1.

2.2. Catalyst characterization

The crystal phases of samples were analyzed by using an X-ray diffractometer (XRD: model D/max RA, Rigaku Co., Japan; Cu K α radiation, 0.15418 nm). XPS (Thermo ESCALAB 250, USA) was used to investigate surface properties. The morphology, structure and grain size of samples were examined by transmission electron microscopy (TEM: JEM-2010; Tecnai G² F20). Brunauer–Emmett–Teller specific surface area (SBET) was determined by using a nitrogen adsorption apparatus (ASAP 2020, USA). All samples were degassed at 200 °C prior to measurements. H₂-TPR and NH₃-TPD were carried out on a custom-made TCD setup, details of which are present in Supplementary data S2.

2.3. SCR activity measurements

Selective catalytic reduction of NO with NH₃ was carried out in a fixed-bed reactor, in which 0.5 g of catalyst was filled. The typical reactant gas composition was as follows: 600 ppm NO, 600 ppm NH₃, 3.5% O₂ and balance N₂. Gas hourly space velocity (GHSV) was about 100 000 h⁻¹ for this system. NO, NO₂, N₂O and O₂ concentration were monitored by an infrared gas analyser with a O₂ sensor (Photon II, Madur Electronics, Austria).

3. Results and discussion

3.1. Morphology and structure investigations

XRD patterns of each sample are shown in Fig. 1. The peaks belonged to anatase (PDF-#21-1272) phase (at 2 θ = 25.28°, 37.80°, 48.05°, 53.89°, 55.06° and 62.69°) and rutile (PDF-#21-1276) phase (at 2 θ = 27.45°, 36.09° and 54.32°) were clearly observed in Ce/NP sample, which unsurprisingly given the characteristic XRD peaks of P25. For Ce/NT sample, the main crystal phase was an intermediate tunnel structure of H₂Ti₁₂O₂₅ [22,23], which transformed to anatase phase of Ce/NR sample (via a calcination at 550 °C for 2 h during the preparation). For Ce/NW sample, the peaks located at 2 θ = 24.7°, 44.1° and 47.9° could be indexed as the characteristic peaks of sodium titanate [16], probably in the form of Na₂Ti₃O₇ (PDF-#31-1329), whereas extra peaks centered

at 2 θ angles of 31.7, 45.4 and 56.5° could be corresponding to the characteristic peaks of NaCl (PDF-#05-0628), originated from the ion exchange of Na⁺ with H⁺ [16,17]. Another two distinct peaks at 2 θ = 28.5° and 33.1° belonged to CeO₂ (PDF-#43-1002) were also observed in Ce/NW sample. The main crystal phase of Ce/FR was anatase, together with some rutile phase and CeO₂. Amongst these samples, the Ce/NW revealed the most intense CeO₂ peaks, implying a better crystallization of CeO₂ on wire-like TiO₂ support.

From the HR-TEM images shown in Fig. 2, it is clearly seen that the expected morphologies of titanate supports had all been successfully obtained. A perfect tubular morphology of Ce/NT could be seen in Fig. 2(a), which was with an outer diameter of 8–10 nm, inner diameter of ca. 3 nm and length of several hundred nanometers. As being reported previously [7,24], the vast majority of ceria were present inside the channels of NT, maintaining Ce/NT as condensed layered titanate-H₂Ti₁₂O₂₅ structure.

The size of TiO₂ particles in Ce/NP sample was observed to be varied from 10 to 40 nm (Fig. 2(b)), whilst the average diameter of CeO₂ particles was measured at about 5.1 nm. For Ce/NR sample (Fig. 2(c)), due to the nanorod being severely aggregated, CeO₂ particles were covered up and hardly to be recognized. For Ce/NW sample, the length of nanowire could even reach ca. 3 μ m and the size of CeO₂ particles was at 15–30 nm. The particle size of ceria in Ce/NW sample was much larger than that in other samples, indicating that ceria crystallites could prefer to grow on nanowire support.

From Fig. 2(e), it can be seen that Ce/FR sample contained numerous titanate fragment with different shapes and sizes, which were originated from the delaminated TiO₂ crystallites during alkali treatment [21,25]. Ceria particles with 5–10 nm size were dispersed on the fragment. Curiously, a small amount of nanoribbons, single-layer sheets and nanotube was also found in this sample.

3.2. BET and XPS

BET surface areas were correlated well with the structure and morphology of titanate supports. Ce/NT sample had the largest surface area of 222.1 m²/g. High temperature annealed Ce/NR sample had a relatively low surface area at 82.2 m²/g. Ce/NW sample with solid wire structure showed an extremely low surface area of 16.1 m²/g, which was even much lower than that of Ce/NP (48.2 m²/g). Ce/FR sample had a complex morphology and structure, showing a surface area of 94.3 m²/g, which is larger than that of Ce/NP, but smaller than that of Ce/NT.

XPS was conducted to identify the surface nature and atomic concentration of various elements in the samples. It was observed that the surface concentration of Ce in Ce/NT sample was much lower than other samples. Our previous reports [24] had revealed that once CeO₂ particles entered into tubular channels, the XPS could only detect the outside Ce and part of inside Ce due to the thickness of NT wall (at 2–3 nm) that is very close to the penetration depth of XPS.

The photoelectron spectra of Ce 3d levels are displayed in Fig. 3. Peaks denoted as u, u2, u3, v, v2 and v3 were attributed to Ce⁴⁺ species, whilst u1 and v1 were assigned to Ce³⁺ species [26,27]. For Ce/NT, Ce/NP and Ce/FR samples, Ce³⁺ and Ce⁴⁺ were all coexisted. In comparison, Ce/NR sample had very weakened Ce³⁺ peaks, which were even nearly disappeared in Ce/NW sample. It is well known that Ce³⁺ mainly came from lattice defects and was accompanied by the formation of oxygen vacancies [28–30]. Furthermore, the lattice defects increased with the decrease of ceria particle size [29,30]. On the basis of XRD and TEM results, the CeO₂ particles in Ce/NW sample were very big and ceria in Ce/NR sample was covered up by aggregated nanorod. This was attributed to the disappearance of Ce³⁺ in this sample.

3.3. Reducibility of cerium species

Fig. 4 shows H₂-TPR profiles of each sample. It was extensively accepted that the reduction of CeO_x occurred first on surface at low

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