Influence of the sol–gel preparation method on the photocatalytic NO oxidation performance of TiO_2/Al_2O_3 binary oxides

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A B S T R A C T

In the current work, TiO_2/Al_2O_3 binary oxide photocatalysts were synthesized via two different sol–gel protocols (P1 and P2), where various TiO_2 to Al_2O_3 mole ratios (0.5 and 1.0) and calcination temperatures (150–1000 °C) were utilized in the synthesis. Structural characterization of the synthesized binary oxide photocatalysts was also performed via BET surface area analysis, X-ray diffraction (XRD) and Raman spectroscopy. The photocatalytic NO(g) oxidation performances of these binary oxides were measured under UVA irradiation in a comparative fashion to that of a Degussa P25 industrial benchmark. TiO_2/Al_2O_3 binary oxide photocatalysts demonstrate a novel approach which is essentially a fusion of NSR (NO$_x$ storage reduction) and PCO (photocatalytic oxidation) technologies. In this approach, rather than attempting to perform complete NO$_x$ reduction, NO(g) is oxidized on a photocatalyst surface and stored in the solid state. Current results suggest that alumina domains can be utilized as active NO$_x$ capturing sites that can significantly eliminate the release of toxic NO_2(g) into the atmosphere. Using either (P1) or (P2) protocols, structurally different binary oxide systems can be synthesized enabling much superior photocatalytic total NO$_x$ removal (i.e. up to 176% higher) than Degussa P25. Furthermore, such binary oxides can also simultaneously decrease the toxic NO_2(g) emission to the atmosphere by 75% with respect to that of Degussa P25. There is a complex interplay between calcination temperature, crystal structure, composition and specific surface area, which dictate the ultimate photocatalytic activity in a coordinative manner. Two structurally different photocatalysts prepared via different preparation protocols reveal comparably high photocatalytic activities implying that the active sites responsible for the photocatalytic NO(g) oxidation and storage have a non-trivial nature.

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1. Introduction

Air pollution in the urban settings leads to significantly detrimental implications on human health. Some of the main air borne contaminants in the atmosphere are nitrogen oxides (NO$_x$), sulfur oxides (SO$_x$), volatile organic compounds (VOCs) and particulate matter (PM) [1]. NO$_x$-based contaminants are emitted to the atmosphere through various anthropological, industrial or natural combustion processes [1–3]. Under atmospheric conditions, NO(g) can be homogeneously oxidized to NO_2(g) via thermal (non-catalytic) chemical pathways. NO_2(g) is considered to be even more toxic than NO(g), as it can cause asthma and many other respiratory illnesses [4]. In the last few decades, various technologies have

been developed in order to reduce airborne toxic NO$_x$ species which include selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), NO$_x$ Storage and Reduction (NSR) (also called Lean NO$_x$ Traps, LNT) and Three Way Catalysis (TWC) technologies [4–13]. However, almost without exception, these technologies are effective only at elevated temperatures (i.e. $T \geq 250 °C$).

Heterogeneous photocatalytic oxidation (PCO) is an alternative approach that can be utilized under ambient conditions (i.e. room temperature and atmospheric pressures) for air and water purification [14–18]. A large variety of photocatalytic materials that can provide air purification under UV or visible light excitation have been reported in the literature [15,19–28]. TiO_2-based materials are among the most effective photocatalysts operating under ambient conditions for air purification applications [15,22,25,26,29]. However, TiO_2 is also known to have some drawbacks, such as poor mechanical properties and low specific surface area (SSA), which limit its catalytic performance [30–32].

In a recent study, we have reported a TiO_2/Al_2O_3 binary oxide system demonstrating a promising gas-phase photocatalytic $DeNO_x$ performance, which was found to be superior to a commercial TiO_2 (Degussa P25) benchmark photocatalyst [33,34]. This material was designed to demonstrate a novel approach which is essentially a fusion of NSR and PCO technologies. In this approach, rather than attempting to perform complete NO_x reduction, NO_x is oxidized on a photocatalyst surface and stored in the solid state in the form of nitrates and nitrites on a storage component. Unlike the photocatalytic metal-oxide surface, which is not water-soluble, stored nitrates and nitrites (or their protonated surface derivatives) can be readily washed off the photocatalyst surface (e.g. via rain or wet scrubbing), restoring the photocatalytic activity of the surface and regenerating the photocatalyst.

Chemical and structural properties of the binary oxide systems strongly influence the NO_x oxidation and storage capacity [16,18]. Along these lines, in the current work, we focus on TiO_2/Al_2O_3 binary oxide photocatalysts which are synthesized using two different sol–gel routes (i.e. P1 and P2) and thermally treated at various temperatures. The first family of TiO_2/Al_2O_3 binary oxide materials prepared via P1 manifests itself as inhomogeneously dispersed TiO_2 crystallites deposited on alumina, while the second one prepared via P2 is a mostly amorphous sponge-like $Al_xTi_yO_z$ mixed oxide with a more homogenous morphology [35]. Thus, in the current contribution, the influence of the photocatalyst binary oxide structure on the photocatalytic performance and NO_x storage capability are investigated. Photocatalytic performances of these two different families of TiO_2/Al_2O_3 binary oxides are also compared to a commercial benchmark photocatalyst (i.e. Degussa P25) in order to show that photocatalytic $NO_x(g)$ abatement can be significantly improved by utilizing TiO_2/Al_2O_3 binary oxide systems.

2. Experimental

2.1. Preparation and structural characterization of TiO_2/Al_2O_3 binary oxides

TiO_2/Al_2O_3 binary oxide materials were prepared by two different sol–gel synthesis protocols denoted as P1 and P2 which were described in detail in our earlier reports [11,12,33,35]. Briefly, in the first synthetic protocol (P1), γ-Al_2O_3 (PURALOXS Ba200, 200 m^2/g, SASOL GmbH, Germany) and $TiCl_4$ (Fluka, titanium (IV) chloride solution) were used as starting materials. In order to form a gel, 25 vol% NH_3 was added to the aqueous γ-Al_2O_3 and $TiCl_4$ mixture under constant stirring. In the second protocol (P2), titanium (IV) isopropoxide (TIP, 97%, Sigma–Aldrich) and aluminum tri-sec-butoxide (ASB, 97%, Sigma–Aldrich) were used as precursors. Synthesized P1 and P2 materials were subsequently calcined in air for 2 h at temperatures ranging between 150 and 1000 °C. In the synthesized materials, TiO_2 to Al_2O_3 mole ratios were adjusted to be either 0.5 or 1.0. These ratios were chosen based on our previous studies, which indicated that for (P2) Ti/Al materials, TiO_2 to Al_2O_3 mole ratios of 0.5 and 1.0 yielded some of the best performing photocatalysts [33]. Currently synthesized samples are labeled as "(P#) n Ti/Al-T", where P# denotes the utilized synthesis protocol (i.e. P1 or P2), n stands for the TiO_2 to Al_2O_3 mole ratio (i.e. 0.5 or 1.0) and T corresponds to the calcination temperature in Celsius scale. A commercially obtained TiO_2 photocatalyst (Degussa P25, 99.5%, Sigma–Aldrich) comprised of approximately 80–85% anatase and 15–20% rutile by mass; was also used as a benchmark sample in order to compare photocatalytic activities of different samples under identical photocatalytic conditions [36].

BET specific surface area measurements were performed using a Micromeritics Tristar 3000 surface area and pore size analyzer via low-temperature isothermal adsorption–desorption of N_2. Before the surface area measurements, materials were outgassed in vacuum at 350 °C for 4 h. The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku powder diffractometer, equipped with a Miniflex goniometer and an X-ray source with CuK_α radiation, λ = 1.5418 Å, 30 kV, and 15 mA. The XRD patterns were recorded in the 2θ range of 10–60° with a scan rate of 0.02° s^{-1}. Diffraction patterns were assigned using Joint Committee on Powder Diffraction Standards (JCPDS) cards supplied by the International Centre for Diffraction Database (ICDD). Raman spectra were recorded using a HORIBA Jobin Yvon LabRam HR 800 spectrometer, equipped with a confocal Raman BX41 microscope and a CCD detector. The Raman spectrometer was also equipped with a Nd:YAG laser (λ = 532.1 nm); the laser power was adjusted to 20 mW for data acquisition.

2.2. Gas phase photocatalytic activity measurements

A custom-design photocatalytic flow reactor system was used in the photocatalytic activity measurements [33,37]. The flow reactor system consisted of a gas manifold system, mass flow controllers (MKS 1479A), a capacitance pressure gauge (MKS Baratron 622B), a custom-made photocatalytic reactor and a chemiluminescence NO_x analyzer (Horiba APNA 370). The gas manifold system was connected to gas cylinders containing $N_2(g)$ (99.998%, Linde GmbH), $O_2(g)$ (99.998%, Linde GmbH), and 100 ppm NO diluted in $N_2(g)$ (Linde GmbH). Mass flow controllers (MFC) calibrated for N_2 and O_2 gases were used to control the volumetric flow rates of the gases. Flow rate of the gases were adjusted to 0.750 standard liters per minute (SLM) for $N_2(g)$, 0.250 SLM for $O_2(g)$ and 0.010 SLM for the mixture of 100 ppm NO(g) diluted in $N_2(g)$. The mixed gases were bubbled through a thermostatic humidifier filled with deionized water which was kept at 25 °C. The relative humidity of the total gas mixture was 70% which was measured at the sample position in the flow reactor with a Hanna HI 9565 humidity analyzer. For a typical photocatalytic performance measurement, 950 mg of a powder sample was placed on a 2 mm × 40 mm × 40 mm polymethyl methacrylate (PMMA) planar sample holder and the gas mixture was allowed to sweep over the photocatalyst powder which was packed into the sample holder. Before the photocatalytic performance measurements, the embedded TiO_2/Al_2O_3 samples were irradiated with UVA light (F8W/T5/BL368, Sylvania or F8W/T5/BL350, Sylvania) under atmospheric conditions for 18 h in order to remove the surface contaminations and to activate the photocatalysts. After this initial ex situ pretreatment step, activated photocatalyst powders were placed in the flow reactor which was equipped with an 8 W UVA lamp. During the performance analysis experiments, (P1) Ti/Al samples were irradiated with a 368 nm wavelength light source (F8W/T5/BL368, Sylvania, Germany) and (P2) Ti/Al samples were irradiated with a 350 nm wavelength light source (F8W/T5/BL350, Sylvania, Germany). For both cases, photocatalytic performances of the Ti/Al photocatalysts were normalized using the photocatalytic performance values of the Degussa P25 benchmark samples, which were measured under the identical photocatalytic conditions using the corresponding UVA light source utilized in the Ti/Al sample measurements.

For the determination of the relative photocatalytic performances, per cent photonic efficiencies (ζ%) were utilized which are described in Eqs. (1) and (2).

$$\zeta\% = \left(\frac{n_{NO_x}}{n_{photon}} \right) \times 100 \tag{1}$$

where, n_{NO_x} represents either the decrease in the total number of moles of all gaseous NO_x species or the number of moles of $NO_2(g)$ generated in a 60 min photocatalytic activity test. Furthermore, n_{photon} corresponds to the total number of moles of incident UVA