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Photocatalytic activity of modified g-C_3N_4/TiO_2 nanocomposites for NOx removal

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ABSTRACT

The oxidation of gaseous nitric oxide (NO) towards solid nitrate (NO_3^-) involves several intermediate steps, including reactions that lead to the formation of even more toxic nitrogen dioxide (NO_2). In this work, novel graphitic carbon nitride/titania (g-C_3N_4/TiO_2) composites coupled with calcium carbonate ($CaCO_3$) were synthesized by annealing mixtures of melamine, commercial TiO_2 (P25) and calcium acetate ($Ca(CH_3COO)_2$) at 550 °C for 3 h. The structural, morphological and chemical analyses revealed that $CaCO_3$ was formed and homogeneously incorporated in g-C_3N_4/TiO_2 photocatalysts. The composite materials exhibited significantly increased photocatalytic NO oxidation under visible light in comparison to pure g-C_3N_4 and TiO_2 with the presence of $CaCO_3$ to greatly inhibit NO_2 release thus improving the overall air quality. The results were related to the influence of both visible light-active g-C_3N_4 photocatalyst and the basic character of $CaCO_3$ component.

1. Introduction

Atmospheric pollution caused by the presence of nitrogen oxides (NOx) in the air, has been recognized as one of the most serious environmental problems [1]. The term NOx usually refers to NO and NO_2 which are the two most common compounds of the nitric oxides group. Although their formation is sometimes found in natural processes, the majority of NOx emissions are based on human activity, e.g. internal combustion engines, industrial furnaces and oil-fired heating [2]. The NOx content in urban atmosphere constitutes a major environmental and health concern due to their toxicity, negative effect on the ozone layer and formation of acid rain [3,4]. Therefore, the development of efficient methods to promote the NOx removal from the atmosphere is becoming increasingly important. At present, various non-catalytic methods like selective non-catalytic reduction, solid and liquid absorption, as well as numerous catalytic processes such as plasma assisted catalytic reduction, direct decomposition, selective catalytic reduction and photocatalytic oxidation are employed. Most of these methods though require specific equipment, tuning, high temperatures or suffer from system contamination and plugging. Among them, photocatalytic NOx oxidation is considered advantageous due to the mild reaction conditions, large scale implementation, utilization of solar light and low cost.

The use of photocatalytic processes for the oxidation of inorganic toxic gases has gained much attention and numerous semiconductors have been proposed as photocatalysts.

To date, TiO_2 has been renowned as one of the most promising photocatalysts due to its unique properties such as strong oxidation ability, thermal and chemical stability, and low cost [5,6]. However, its photocatalytic efficiency is limited by the fast recombination of the photo-induced electron-hole pairs and the large band gap energy (~3.2 eV). Enormous efforts have been made to enhance the photocatalytic performance of TiO_2 [7]. Metal or metal oxide deposition [8,9], nonmetal elements doping [10,11], coupling of composite semiconductor [12] and surface sensitization [13] have been effective on promoting the photocatalytic activity of TiO_2. g-C_3N_4/TiO_2 composites have been intensively investigated for the photocatalytic oxidation of pollutants and the addition of g-C_3N_4 was found to effectively enhance the photocatalytic activity [14–16]. Recent reports indicate that the unique electronic band structure of g-C_3N_4 is responsible for the enhanced photocatalytic performance of the composites [17,18]. Furthermore, the indirect semiconductor g-C_3N_4 with a medium band gap (~2.7 eV) is highly

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stable under intense thermal and chemical conditions because of its tri-s-triazine based building blocks [19].

Despite the fact that g-C_3N_4/TiO_2 composites have been regarded as efficient photocatalysts for NO removal, there has been little progress in eliminating the released NO_2. While the direct NO_2 oxidation generates harmless nitrates (NO_3^-) [20], the oxidation of NO to NO_3^- involves several intermediate steps before it is fully oxidized, with the most important of them involving the formation of NO_2 [21]. As NO_2 is more toxic than NO, its release heavily counteracts the overall photocatalytic efficiency [22,23]. An improvement in the air quality can only be guaranteed by a selective photocatalyst which suppresses the formation and the release of undesired intermediates. As a result, the selectivity has recently attracted more attention [24,25]. Recent studies indicate that calcium based substances, such as calcium aluminates or $CaCO_3$, enhance the adsorption of NO_2 and potentially improve the conversion performance of the photocatalysts, resulting in more efficient NOx removal [26,27].

In this work, novel $CaCO_3$ containing g-C_3N_4/TiO_2 composites were synthesized using $Ca(CH_3COO)_2$ as a $CaCO_3$ precursor. A specific g-C_3N_4/TiO_2 ratio was used and the influence of different $CaCO_3$ concentrations was examined. The photocatalysts were characterized and examined for NO oxidation under UV and visible light irradiation and a toxicity assessment was performed.

2. Experimental

2.1. Sample preparation

All chemicals used were of analytical grade and were used without any further purification. Commercial titanium dioxide (Aeroxide TiO_2 P25) was purchased from Evonik Industries. Melamine powder was purchased from Alfa Aesar and calcium acetate from Merck.

The g-C_3N_4/TiO_2 photocatalysts were prepared by annealing a mixture of melamine and TiO_2 in weight ratio 1/3 with a given amount of $Ca(CH_3COO)_2$. Specifically, appropriate amounts of melamine and TiO_2 were dispersed in 30 mL distilled water and then $Ca(CH_3COO)_2$ was added in 0, 5 and 10 wt% towards the total amount of 4 g. The suspension was stirred for 15 min and dried at 60 °C. Then, the mixture was put into an open alumina crucible and heated in a tube furnace at 550 °C for 3 h with a heating rate of 20 °C/min. Argon flow was used in order achieve inert atmosphere. Finally, the product was collected and ground into fine powder. The obtained samples were named MTi*x*, where *x* represents the percentage of $Ca(CH_3COO)_2$. Pure g-C_3N_4 and TiO_2 photocatalysts were similarly modified with $Ca(CH_3COO)_2$ for comparison and the samples were named M*x* and Ti*x* respectively.

2.2. Characterization

A Siemens D500 X-Ray diffractometer was used for the XRD measurements. SEM characterization was performed using a FEI Inspect Microscope equipped with tungsten filament operating at 25 kV. The N_2 adsorption-desorption isotherms were obtained with a Quantachrome Autosorb-iQ instrument. The FT-IR transmittance spectra of the materials embedded in KBr pellets were measured on a Bruker Equinox-55/S instrument. X-Ray photoelectron spectroscopy was investigated with ultrahigh vacuum VG EXCALAB 210 electron spectrometer using Mg Kα (1253.6 eV) as radiation source. The chemical composition of the samples was determined by ICP analysis using a Perkin-Elmer Optima 3000 instrument. The UV–vis diffuse reflectance spectra were recorded by a Shimadzu UV-2100 spectrophotometer using $BaSO_4$ as reference.

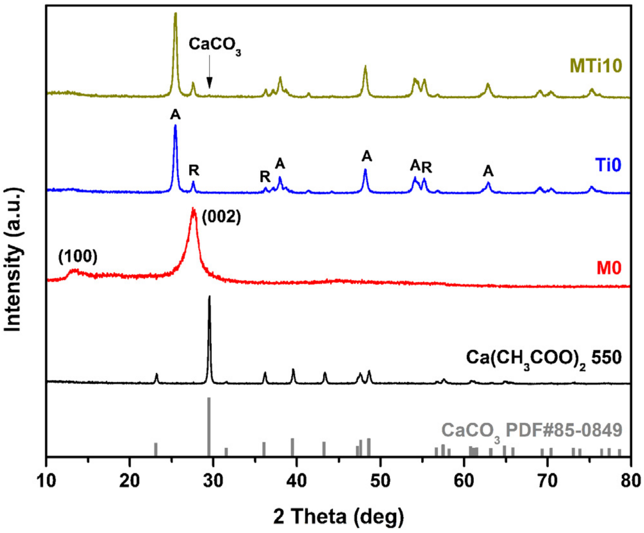

Fig. 1. XRD patterns of the MTi10, Ti0 and M0 samples, as well as $Ca(CH_3COO)_2$ after treatment at 550 °C and the corresponding PDF card of $CaCO_3$.

2.3. Photocatalytic activity evaluation

The photocatalytic activity of the materials was evaluated by NO oxidation, using a standard procedure based on ISO/DIS 22197-1 [28]. According to the standard, NO gas is adsorbed on the surface of the photocatalysts and oxidized to NO_2 gas followed by oxidation to nonvolatile NO_3^- under illumination. The samples were prepared by pressing the photocatalytic materials in flat holders with surface area of 20 cm^2, which were then placed in a continuous flow reactor with dimensions 30 cm x 5 cm. The NO gas concentration in the reactor was set to 1 ppm, supplied from a compressed (50 ppm) gas cylinder Linde Hellas Ltd. The total flow rate was adjusted at 3 L/min by mass flow controllers (equivalent to a velocity of approximately 0.2 m/s), using a mix of dry and wet air for keeping the relative humidity at 50%. The gas stream ran over each sample in the dark for a period of 10 min, to reach equilibrium between the sample and the gas phase at 1 ppm. The photocatalytic activity of the materials was measured under UV-A irradiation (Philips Cleo Compact 15 W lamps) with intensity 10 W/m^2, as well as under visible light irradiation (Nordex T5-8W–4000 K lamps) with intensity 7000 lx for 30 min at ambient temperature. The concentrations of NO, NO_2 and NOx (where NOx represents the sum of NO and NO_2) were monitored by a Horiba APNA-370 chemiluminescence-based NOx analyzer (with lower detectable limit of 0.0005 ppm) equipped with an O_3 lamp and a silicon photodiode sensor. The materials showed reproducible photocatalytic activity, which was tested using three samples of each material. A schematic illustration of the experimental setup is presented in Supporting Information (Fig. S1). Also, an example of experimental concentration curve of the monitored gases with indicated characteristic parts is given (Fig. S2).

3. Results and discussion

3.1. Crystalline structure

The XRD patterns of selected pure and composite materials are shown in Fig. 1. The pattern of the $Ca(CH_3COO)_2$ after heating at 550 °C ($Ca(CH_3COO)_2$ 550) is also presented. The peaks are clearly corresponding to the calcite polymorph of $CaCO_3$ (JCPDS85-0849) [29]. For pure g-C_3N_4 (M0), two characteristic peaks are observed. The strong peak at 27.6° corresponds to the (002) plane, which is attributed to the interlayer stacking of aromatic rings with a dis-

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