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Effect of washing pH on the properties of titanate nanotubes and its activity for photocatalytic oxidation of NO and NO_2

Nhat Huy Nguyen, Hsunling Bai*

Institute of Environmental Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 300, Taiwan

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ABSTRACT

This study reports for the first time on the role of contaminant sodium to neutralize the acidic reaction products during the NOx photocatalytic reaction and prevent surface deactivation of TNTs (titanate nanotubes and their derived materials). TNTs were synthesized by the hydrothermal method and washed under different pH values. The materials were then characterized by SEM, TEM, BET, ICP, TPD, and XRD analyses. The photocatalytic oxidations of NO and NO_2 were tested under the ambient condition to evaluate the activity of the materials. The results showed that the value of washing pH was an effective control factor for achieving TNTs with desired microstructure and physical–chemical properties. In the photocatalytic removals of NO and NO_2, it revealed that both of the Na content and the structure of TNTs materials play important roles on the NOx removal pathway, initial efficiency and decay rate. The highest efficiencies were achieved by TNTs washed at pH 3–5 (T-3∼5), which may be due to their high amount of crystalline anatase for photocatalytic reaction and high sodium content for neutralization of acidic products. The mechanism based on the neutralization of the HNO_3 resultant from the NOx photo-oxidation was also proposed.

1. Introduction

Nitrogen oxides ($NOx = NO + NO_2$), which are linked to many environmental and health issues, are considered as criteria pollutants in many countries. Therefore, the photocatalytic removal of NOx using TiO_2-based materials has been studied extensively [1,2]. It has been reported that properties of TiO_2 photocatalyst including crystal phase, crystal size, crystallinity and surface area would affect the NO removal efficiency [3–6]. The photocatalytic removal of NO_2 was also found to be increased by adding K^+ into TiO_2 photocatalyst [7] or by using tubular TiO_2 with high surface area and anatase crystallinity [6]. However, there is still limited information on the effect of chemical properties such as Na content and crystalline composition of TiO_2 material on both NO and NO_2 removals by photocatalysis.

On the other hand, TNTs have attracted considerable attention due to their special tubular structure with high surface area and high activity [8–11]. The post-treatment of acid washing has been proven to have a significant effect on the TNTs properties such as morphology, surface area, microstructure, sodium content and activity [12–24]. Since the surface area of TNTs was reported to reach the highest value at washing pH of 1.6 [21], most of the studies on TNTs were performed with TNTs washed at pH 1.6. The literature studies also showed that TNTs washed at the intermediate acid concentration of 0.01 M had the highest photocatalytic activity for the removals of basic violet 10 dye [14,16] or phenol [24]. Because the washing pH value is a more practical controlling parameter than the washing acid concentration, it may be worthwhile studying the effect of washing pH on the properties of the TNTs photocatalysts. However, there still remains some questions of whether pH 1.6 could make the best TNTs material simply because it has the highest surface area? In addition, TNTs have been applied for NOx abatement and the results showed that the high activity of TNTs photocatalyst was strongly depended on its anatase nanorod and surface area [6,24]. However, only pure TNTs were used in the literature and the effect of remnant sodium content of TNTs on the photocatalytic activity for NOx removal has not been addressed.

In this study, TNTs washed at different pH values were prepared for the photocatalytic oxidations of NO and NO_2. The effects of washing pH on the physical and chemical properties of TNTs were identified. Furthermore, the key properties of TNTs affecting the photocatalytic activity for NOx removal were revealed.

2. Experimental

The TNTs photocatalysts were synthesized by hydrothermal treatment of 12 g TiO_2 (P25, Degussa) with 180 ml of 10 N NaOH solution under 135 °C for 24 h [6,25]. The produced slurry was

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* Corresponding author.
E-mail address: hlbai@mail.nctu.edu.tw (H. Bai).

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filtrated and dispersed in 1 L of DI water, which resulted in a solution at pH of ca. 13. Nitric acid solution was then slowly added into the solution until the desired pH values were reached. These solutions, with the final pH values of 0.5, 1, 1.6, 2, 3, 4, 5, 6, and 7, were subsequently sonicated for 30 min and followed by filtration. After that, the materials were washed with 1 L of DI water and filtrated. The washing and filtration process was repeated several times until the pH value of the filtrate reached ca. 7, at which the excessive acid content was totally removed. The TNTs materials were named as T-*x*, where *x* indicated the washing pH value. Another sample from hydrothermal treatment was washed and filtrated with only DI water for around 15 times, with which the non-acid washed solution reached pH 9 (named as T-9). All materials were then dried at 120 °C overnight and finally calcined at 500 °C for 2 h in air [6]. Among the TNTs materials, the one washed at pH of 0.5 was totally dissolved in the acid solution and no solid material was obtained on the filter after filtration.

The SEM, TEM, and BET analyses were applied for understanding the properties of as-synthesized and calcined TNTs. In addition, the calcined materials were further subjected to the ICP, TPD, and XRD analyses. The NH_3-TPD and CO_2-TPD were performed by using a chemisorption analyzer (AutoChem II, Micromeritics). For that purpose, 0.11 g sample was pretreated under He gas at 400 °C for 4 h. The sample was then cooled down to 50 °C, followed by adsorption with CO_2–He or NH_3–He gas, respectively, for CO_2-TPD or NH_3-TPD analyses for 1 h. It was then purged with He gas for 1 h, and finally analyzed under the temperature range of 50–800 °C [26,27]. The amount of acid or basic site was calculated based on the amount of CO_2 or NH_3 desorbed.

The separated photocatalytic oxidation tests of NO and NO_2 were conducted to evaluate the activity of the TNTs materials. A schematic of the photocatalytic testing system can be found in Fig. S1 of the Supplementary Material. The NO and NO_2 concentrations were analyzed by a chemiluminescence NOx analyzer (SIR, S-5012). The mixed gas flow was controlled at the following condition: flow rate of 400 cm^3/min, relative humidity of $55 \pm 5\%$, temperature of 25 ± 2 °C. The amount of photocatalyst for each experiment was 0.11 ± 0.01 g, it was coated on three glass substrates with the total size of $L \times W = 30\,cm \times 5\,cm$. The inlet concentration of NO (balanced in N_2) or NO_2 (balanced in Ar) was controlled to be at 9.75 ± 0.25 ppmv (balanced in clean and humidified air to reach RH of $55 \pm 5\%$). The reaction tests were performed under UV-A irradiation (highest intensity at 365 nm) of 1.25 mW/cm^2.

The conversion efficiency and selectivity in NO reaction are defined as followings [6] (the calculation in NO_2 reaction is similar to that in NO reaction):

$$\text{NO conversion efficiency} = \left(1 - \frac{NO_{out}}{NO_{in}}\right) \times 100\% \qquad (1)$$

$$NO_2 \text{ selectivity} = \frac{NO_{2,out} - NO_{2,in}}{NO_{in} - NO_{out}} \times 100\% \qquad (2)$$

$$\text{NOx removal efficiency} = \left(1 - \frac{(NO + NO_2)_{out}}{(NO + NO_2)_{in}}\right) \times 100\% \qquad (3)$$

3. Results and discussion

3.1. TNTs synthesis and characterization

The TEM images of as-synthesized TNTs are displayed in Fig. 1 (SEM results can be seen in Fig. S2 of Supplementary Material). It is observed that Degussa P25 was in particle shape while TNTs showed different geometries depending on their washing pH values. Except for T-9, which had curled sheet or wood shavings shape, the nanotubular structure appeared in all samples washed at pH 1–7, with better tube appearance and more tubular amount being observed for TNTs washed at pH 1.6–4. Curled sheet or wood shavings shape was also found in TNTs washed at pH 7 and 5. Hence, it is likely that the acid washing process has an effect the morphology of as-synthesized TNTs, which appeared differently in three pH ranges of pH > 7, pH 7–5, and pH 4–1. The non-tubular structure of T-9 (as seen more clearly from the HR-TEM in Fig. S3 of Supplementary Material) is different from the literature, which widely reported that the formation of nanotubes is in the hydrothermal step [28–31]. There may be two possible reasons for non-nanotubes observed in this study at pH 9. The first reason could be that the washing process was not completed, and there was excessive sodium content in the materials. The second reason could be that the hydrothermal condition in this study was not sufficient for the formation of nanotubes. Thus the acid washing step could be served as an assisted condition for the nanotubes formation. This is similar to the results reported by Papa et al. [32], where their acid treatment could help to transform the nanoribbons to nanotubes after hydrothermal process.

Fig. 2 plots the variations of surface area, pore volume, and pore size with washing pH for as-synthesized TNTs (detailed pore size distribution is provided in Fig. S4 of Supplementary Material). The surface areas of all TNTs were much higher than that of P25. The T-9, which had the lowest surface area, still showed three times higher than P25. The specific surface area of TNTs increased from 158 to 395 m^2/g when pH decreased from 9 to 2. Possible reasons for the increase in the specific surface area could be the formation of more nanotubes under higher acidic condition, the decrease in the wall thickness, the lower mass of the material due to the exchange of Na by H, and the removal of more intercalated water [13]. And the decrease in surface area when pH further decreased from 2 to 1 could also be explained by the lower nanotubes yield, the appearance of nanosheets, the spontaneous formation of anatase particles under low washing pH [21] or high acid concentration [24,33] as well as the increase in density of the solid [34]. Among TNTs materials, T-2 showed the highest surface area, pore volume, and pore size of 395.1 m^2/g, 1.31 cm^3/g, and 13.3 nm, respectively. This differs slightly from previous studies which reported that the highest surface area was achieved at pH 1.6 [20–22]. This is due to that washing condition at pH 2 has never been tested. In terms of microstructure, the washing process conducted under acid condition (i.e. pH from 5 to 1) seems to be the best choice of washing method, whereby the TNTs materials possessed little differences in surface area, pore size, and pore volume.

The TEM images of calcined TNTs are exhibited in Fig. 3 (SEM results can be seen in Fig. S5 of Supplementary Material). Obviously, all the materials calcined at 500 °C were either partially (T-4∼7) or totally (T-1∼3) lost their tubular structure. Four types of morphology could be found, which included: (i) irregular porous clusters (T-5∼9), (ii) tubular structure (T-4∼7), (iii) rod shape (T-1∼4), and (iv) particle shape (P25 and T-1∼4). In this study, washing at higher pH values (e.g. pH 4–7) retained a part of the tubular structure of TNTs while washing at lower pH values (e.g. pH 1–3) led to the corruption of tubular structure at high calcination temperature. These results are also in agreement with those reported in the literature that washing at less acidic condition has a positive effect on the thermal stability of the TNTs materials [13,14,35–37]. Among the TNTs, T-4 possessed tube, rod, and particle morphologies and it had more tubular shape retained after calcination. This can lead to a conclusion that pH 4 is an optimum condition for obtaining a good nanotubular structure of calcined TNTs.

The variations in BET surface area, pore volume, and pore size with washing pH for calcined TNTs are depicted in Fig. 4 (detailed pore size distribution is provided in Fig. S6 of Supplementary Material). The surface area of TNTs decreased significantly after calcination, as compared to the values shown in Fig. 2. However, all TNTs still showed higher surface areas of 1.5 times (T-5∼9) to