The effects of TiO$_2$ morphology and crystal on the catalytic degradation of ammonia nitrogen with ozone

Zhiwu Liu*, Daxiang Huang, JingTang, Chaocan Zheng, Yuan Meng
JinHua Polytechnic, JinHua 321000, Zhejiang, China

*Corresponding author e-mail: nec10@163.com

Abstract. TiO$_2$ nanostructures with various morphologies and crystal structures have been synthesized by hydrothermal method using Degussa P25 as a precursor and subsequent calcination at different temperature. The zonation catalytic activities of the as-prepared samples were investigated by degradation of ammonia nitrogen aqueous solution with ozone. The effects of the phase composition, surface area and shape of the nanostructures on degradation of ammonia nitrogen were evaluated. The initial degradation rate of ammonia nitrogen had been correlated with the morphology, and crystal structure examinations done with the help of transmission electron microscopy (TEM) and X-ray diffraction (XRD). The research done demonstrated that more rutile phase and the vast surface area are favourable for the zonation catalysis. The dependence of the zonation catalytic activity on the shape of catalyst surface is not significant as usually expected.

1. Introduction
Heterogeneous catalytic zonation, a novel alternative to traditional Advanced oxidation processes (AOPs), has been drawing a great deal of attention as a promising technology, owing to its potentially higher effectiveness in the mineralization of dissolved organics and its lower negative effect on water quality. The transition metals oxides, viz. MnO$_2$, TiO$_2$, Al$_2$O$_3$, CeO$_2$ and Zeon [1-3] are the most commonly used catalysts for the zonation processes. Among them, Titanium oxide (TiO$_2$) is chemically stable, stable toward zonation process, comparatively inexpensive to product and absence of toxicity.

The role of TiO$_2$ in promoting zonation reactions has been already documented. Water molecule adsorbed on the vacant surface site would undergo the dissociation into OH$^-$ and H$, yielding surface-OH groups with the surface metal and oxygen sites, respectively. Subsequently, the dissolved ozone react with surface-OH groups, forming unstable oxidizing species, which plays vital role in producing hydroxyl radicals [4].

The influence of surface morphology on the catalytic activity has been demonstrated in many fields. One-dimensional (1D) nanostructured TiO$_2$ with various morphologies and shapes, including Nano rods, nanotubes, nanowires and Nano spheres, have been extensively studies as a result of their unique electronic, optical properties and their potential applications in modern technology [5]. Nanotubes have been proposed to facilitate the adsorption of reactants on the active surface sites, due to a high specific surface area and an open mesoporous morphology [6]. Nanowires is regarded as a superior structure for charge transport, which makes it an interest factor in sensing applications [7]. Nano rods
have higher reversibility and insertion ratios with respect to compact materials in lithium rechargeable batteries, ascribing to their large surface area and the numerous structure defects. Hence, care is needed in drawing morphology on the decisive factor of activity in catalytic zonation reaction system [8].

In addition, the crystal phase have been suggested as one of major factor for catalytic activity of TiO2. Based on the structure, there are mainly four polymorphs of TiO2 involved, Rutile (tetragonal), Anastasia (tetragonal), Brookside (orthorhombic), and TiO2- B (probably monoclinic) 9. It is commonly believed that anatine is the active phase in the photo catalytic reaction, while pure rutile normally shows no activity at all in this case. TiO2-B polymorph has demonstrated to be a more excellent candidate for hosting lithium, due to its structure is more open than other polymorphs. Moreover, it is worth note that Yang et al. suggested that rutile are more beneficial in enhancing zonation catalytic activity than anatine in the degradation of nitrobenzene. However, no systematic investigations was carried out with regard to the dependence of crystal phase of TiO2 on catalytic zonation [10].

Herein, the effect of the morphology and crystal structure of TiO2 on the initial degradation rate of the catalytic zonation of ammonia nitrogen was investigated. To further search for the cause, the surface-OH groups were determined to establish the relationship between the number of surface-OH and surface areas, as well as the number of surface-OH and crystal phase composition.

2. Experimental

2.1. Materials and preparation

All chemicals used in this study were analytical grade and were used without further purification. Deionized water was used in all experiment. The fabrication of different morphology TiO2 samples referred to literatures and can be briefly described as follows: 4 g of TiO2 powder (P25, Degussa) was dispersed in an aqueous of 10M Noah and charged into 200 mL Teflon-lined autoclave container. The autoclave was maintained at 110-150 and 200 °C under autogenous pressure for 24 h. After cooling to room temperature, the precipitated powders were filtrated and washed with 0.1 N aqueous Hall solutions and distilled water, until the pH of the rinse solution was 7.0. The products were dried at 80 in an oven and finally claimed in a chamber furnace (CWF 1100, CARBOLITE) at 400 co. with a heating rate of 5 co. min-1 for 2 h. The respective powder samples hydrothermally treated at 110-150 and 200 °C were collected and denoted as samples NT-110-400, NR-150-400, and NB-200-400, respectively. Furthermore, the sample, which hydrothermally treated at 110, were claimed at 600, 700, 750 and 800 co. in air for 2 h to in vestigate the effect of annealing temperature, hereafter named as NT-110-600, NT-110-700, NT-110-750 and NT-800 respectively.

2.2. Characterization of catalyst

Transmission electron microscopy (TEM) analyses were conducted to investigate the morphologies and microstructures of the titan ate samples with a Tacna G2 F30 S-Twin microscope operated at an accelerating voltage of 300 kV with 0.20 nm point resolution. X-ray powder diffraction (XRD) measurements were performed using a thermal ARL X-ray diffract meter (Thermo, France) with Cu Kα radiation to evaluate the identity of any crystalline phase or structures in the TiO2 samples. The accelerating voltage and the applied current were 45 kV and 40 mA, respectively.

The crystallite size was calculated from X-ray line broadening by the Scherer equation $D = \frac{0.89 \lambda}{\beta \cos \theta}$. Where D is the average crystallite size in nm, $\lambda$ is the Cu Kα wavelength (0.15406 nm), $\beta$ is the full-width at half-maximum, and $\theta$ is diffraction angle.

The porous structure characteristics, including specific surface area, pore volume, and pore size distribution, were obtained from the conventional analysis of nitrogen desorption–desorption isotherms measured at –196 co. with Micrometrics ASAP 2010 apparatus. The specific surface area...
was determined by using the BET method and the pore volume was determined by means of the Barrett-Joyner-Helena (BJH) desorption isotherm.

2.3. Procedures and Analysis

The catalytic degradation experiments of ammonia nitrogen in the presence of ozone were performed in a semi-continuous flow mode at 20 °C, which consists of a CHYF-3A ozone generator (Hangzhou Ronin Electronic Equipment Co., China), a 1000 mL reactor (diameter 80 mm, height 260 mm). In a typical catalytic degradation procedure, a volume of 800 ml of simulative waste water (the initial concentration of ammonia nitrogen was 100 mg L⁻¹) and All the activity tests were made with the same total amount of catalyst (0.8g) The solution was continuously magnetically stirred and a mixture of O2 and O3 was fed into the reactor through the porous plastic diffuser located at the bottom of the reactor to produce fine bubbles at a 50 mL min⁻¹ flow rate. The initial pH was 6.35 without any adjustment. To absorb the residual ozone, off-gas was introduced into a glass bottle containing 2% (w/v) KI solution. The control experiments of single zonation (without catalyst) were also carried out under the same procedures. Before reaction, the suspension was stirred in the dark for 60 min to reach adsorption–desorption quasi-equilibrium. For degradation experiments, aliquots suspension were withdrawn at regular time intervals to determine the residual ammonia nitrogen. The oxidation reaction was quenched by the addition of a small amount of sodium thiosulfate immediately. Before measurement, suspension was filtered through 0.45 mm PVDF syringe filters to remove TiO2 particles. The temperature of the ammonia nitrogen solution (22 ± 1 °C) and the filter solution (55 ±1 °C) were controlled by a thermostat (THD-2015, Teaching Instrument Factory, Ningbo, China). Concentration of ozone dissolved in the aqueous phase was measured by the audiometric method [11]. Experiments were repeated three times, and all of the data are the average of triplicate determinations.

3. Results and Discussion

3.1. Crystal structure

The crystalline structure of catalyst samples can be assessed on the basis of XRD profiles displayed in Figure 1. The patterns show that the phase structure of TiO2 compounds would depend on the temperature, referring to the hydrothermal synthesis and calcination, respectively.

As far as the effect of hydrothermal temperature is concerned singly, both of the NT-110-400 and NR-150-400 catalysts exhibited the clear diffraction peaks at 25.3°, 37.8°, 48.0°, 55.1° and 62.7°, assigned to the well crystallized anatine phase of (101), (004), (200), (211) and (204) crystal planes (JCPDS 21-1272), respectively. Moreover, the peak intensities increase and the width at half height become narrower in accompany with the increase of hydrothermal temperature. This result indicates that the increase of hydrothermal temperature tend to improving the crystallization of anatine phase as well as the growth of anatine crystallites.

It is worth to notice that the anatine peaks attributed to the sample of NB-200-400 nearly disappeared, but some new peaks occurred simultaneously at 14.12°, 24.86°, 28.64° and 48.64°, well corresponding to the (001), (110), (002) and (020) planes of TiO2-B (a metastable and synthetic crystal form).

The calcination temperature also play an important role on the crystal structure of catalysts. As can be seen from Figure 1, the XRD patterns of the NT-110-400, NR-110-600, NR-110-700, NR-110-750 and NR-110-800 had similar 2θ values of diffraction peaks, suggesting that no additional phase contained in the samples, except the anatine and rutile in the calcination temperature range of 400 °C to 800 °C. Table 1 listed the phase contents of TiO2 calculated according to following formula [12]

\[
WR = 1/(1 + 0.8IA/IR)
\]
Where WR and WA are the content of rutile and anatine titanic, respectively, IA and IR represent the diffraction intensities of anatine (101) and rutile (110).

![XRD patterns of TiO2 catalysts](image)

**Figure 1.** The XRD patterns of TiO2 catalysts

3.2. **BET surface area of samples**

The properties of catalysts of prepared samples, including the surface area (SBET), average pore diameter, and pore volume, are compiled in Table 1. The observation of Table 1 gives the information that significant changes in SBET and pore volume were observed and the values fall from 280 m2/g to 28 m2/g, as the reaction temperature and annealing temperature increased respectively. The observed highest surface area of the NT-400 is attributed to the smaller size of the particle and the presence of Nano-tube in the NT-110-400 sample. The pore size distribution based on Barrette–Joyner–Helena (BJH) model of samples is shown inset of Fig. As can be seen from figure, the distributions are relatively wide, ranging between 2 and 100 nm, and the peak shifted from 16 nm up to 62 nm. Beside the peak pore size is larger for NT-110-400 than other samples. According the classification of IUPAC, the isotherms of the samples showed in Figure 2 belong to the type IV with a H3 hysteresis loop except NT-800, indicating the presence of mesopores materials. As shown in Figure, the incomplete monolayer adsorption of samples shifts toward a higher relative pressure value as the hydrothermal temperature and the annealing temperature increased, reaffirming NT-110-400 exhibits a smallest pore size.
Table 1. Physicochemical parameters and the initial degradation rate of ammonia nitrogen for the catalysts.

| Sample   | $S_{BET}$ (m$^2$ g$^{-1}$) | Crystallite phase | Concentration of surface-OH (%) | Density of surface-OH (mmol g$^{-1}$) | Initial degradation rate (IDR) (mg L$^{-1}$ min$^{-1}$) | IDR/S (mg L$^{-1}$ min$^{-1}$ m$^{-2}$) |
|----------|-----------------------------|-------------------|---------------------------------|----------------------------------------|--------------------------------------------------------|----------------------------------------|
| NT-110-400 | 287                          | A                  | 100                             | 0.551±0.048                           | 6.14±1.23                                               | 0.027±0.005                            |
| NR-160-400 | 110                          | A                  | 100                             | 0.200±0.015                           | 2.13±0.29                                               | 0.024±0.003                            |
| NW-200-400 | 38                           | TiO$_2$-B          | 100                             | 0.063±0.008                           | 0.79±0.23                                               | 0.026±0.008                            |
| P25       | 51                           | A 80 R 20          |                                 | 0.136±0.014                           | 2.30±0.71                                               | 0.056±0.018                            |
| NR-110-600 | 62.4                         | A 96 R 4           |                                 | 0.138±0.013                           | 1.50±0.92                                               | 0.030±0.019                            |
| NR-110-750 | 23                           | A 50 R 50          |                                 | 0.190±0.016                           | 2.49±1.11                                               | 0.135±0.060                            |
| NR-110-800 | 6.2                          | A 10 R 90          |                                 | 0.097±0.012                           | 1.04±0.43                                               | 0.210±0.086                            |

3.3. Morphology of samples

The structure and morphology features of the sample synthesized were substantially affected by both the hydrothermal and calcination temperature. As reflected in Figure 2, the sample of NT-110-400 displays the clear-cut image of nanotube morphology, ~100 nm in length with an open end. Furthermore, the nanotube clearly exhibits two-layer on both sides with finite wall thickness, and the outer and inner diameters of the tubes were estimated to be 10 nm and 6 nm, respectively. Upon hydrothermal treatment at higher temperature of 160°C, the surface morphology of the products NR-150-400 changed, forming short Nano rod with a diameter of ~10 nm. Accompanying with the hydrothermal temperature rising to 200 ocean kind of wire-like structure come to occupy the Fig 3. The lengths and the diameters of the TiO$_2$ nanowires are ~20 and ~200 nm, respectively.

It is clear from these results that the hydrothermal treatment temperature has a strong effect on the morphological features of the resulting products, where it was found that the morphology of TiO$_2$ changes gradually from pure dense nanotubes to short Nano rod, followed by transferring to bundles of very long and wide nanowires with increasing the hydrothermal temperature. Although the formation mechanism of titanate nanotube are still disputed, it was commonly accepted that nanotubes are formed by rolling up of sheet exfoliated from bulk TiO$_2$. The transformation of the tube-to-rod structure is ascribed to the possibility that the crystal growth experience an imperfect oriented attachment of adjacent nanotubes, involving together with the local shrinkage of the nanotubes via reducing the interlayer distance between the tube walls at a high hydrothermal temperature. Further increasing the hydrothermal temperature as high as 200 °C, the crystal growth would proceed toward self-assembly of the Nano rods with the high affinity, leading to the formation of the long nanowires.

To investigate the effect of calcination temperature, the TiO$_2$ powers with the nanotube structure (synthesized at 110 °C hydrothermal treatment) were claimed at various temperatures, and the results of TEM analysis are presented in Figure 3. It had been validated above that the tube-structure could be maintained after claiming at 400 °C for the catalyst of NT-110-400. However, when the calcination temperature reached 600 °C, the tube-like structure has completely vanished, transforming into the short Nano rod-like structure. The transformation originate from the decrease of interlayer distance due to dehydration of interlayered OH groups, leading to the contraction and breaking of the tubes.
structures. Further increasing the calcinations temperature to 800 °C, the catalyst Nano crystals become larger as shown in Figure 3, owing to the agglomeration of smaller Nano rods.

3.4. Effect of surface morphology
The catalytic zonation may depend on the surface morphology of catalysts. To investigate the effect of the surface morphology of TiO2 on the catalytic degradation of ammonia nitrogen in the presence of ozone, NT-400, NR-400 and NB-400 catalysts are selected to eliminate the influence of rutile phase, representing nanotube-like, Nano rod-like, and Nano belt-like, respectively. As can be seen from Table 1, a higher hydrothermal temperature led to a slower degradation rate, i.e. 6.14, 2.13, and 0.79 mgL⁻¹min⁻¹ initial degradation rate when hydrothermal temperature was 110, 150 and 200 °C, respectively.

The surface-OH groups on the heterogeneous catalytic surface are believed to have important function for catalytic zonation. The quantities of the surface-OH groups were determined to get more detailed information on their relationship with morphology of catalysts, and the results are given in Table 1. From Fig. 4 and Table 1, it can be seen that the TiO2 catalysts with larger surface areas, corresponding to greater surface-OH groups, shows more efficient ozone catalytic reactivity for the decomposition of ammonia nitrogen, implying that the surface area is the one of the main factors prerequisite to achieve high catalytic reactivity of ozone.

As shown from the inset of Fig. 5, a good linear correlation between the initial rates of ammonia nitrogen degradation and the relative intensity of surface-OH in the process of ammonia nitrogen catalytic zonation, regardless of different morphology of TiO2 involving nanotube, TiO2 Nano rod,
and TiO2 Nano belt, indicating that the removal efficiency of ammonia nitrogen is determined by intensity of surface-OH, which is certainly proportional to surface area as discussed below, under the present experimental conditions. Thus, the difference in surface-OH numbers per surface area unit of these samples is not marked enough to correlate the catalytic activity with the type of morphology of catalysts. From the results above we conclude that the catalytic coronation of ammonia nitrogen with TiO2 as catalysts is independent of surface morphology.

![Figure 4. Relationship between IDR/S of catalysts and the surface morphology of TiO2](image)

**Figure 4.** Relationship between IDR/S of catalysts and the surface morphology of TiO2

![Figure 5. Relationship between the density of surface HO groups on catalysts and the surface morphology of TiO2](image)

**Figure 5.** Relationship between the density of surface HO groups on catalysts and the surface morphology of TiO2

3.5. Effect of crystal phase

Various crystal phase own different amount of oxygen vacancies site, which is considered to be an important parameter contributing to the performance of the catalytic zonation process. We can, therefore, deduced that the different crystal phase component might affect the degradation of ammonia nitrogen during catalytic zonation. To investigate whether crystal phase of samples correlated with the degradation of ammonia nitrogen, the samples of different crystal phase combinations were extracted to compare the degradation rate below.
Table 1. Compiles that the amount of the rutile phase increased in accordance with increasing sintering temperature. The volume fraction of the rutile phase of 20%, 80% were obtained at annealing temperatures of 400, 600, 750 and 800°C, respectively. Values of the initial degradation rate per unit area of catalyst were calculated to avoid the influence of surface area, the results were also list in Table1.

Figure 6 shows that a robust correlation ($r^2=0.95$) was found between the amount of rutile phase contents of samples NT-400, NT-600, NT-700, NT-750 and NT-800 and the corresponding initial reaction rates of ammonia nitrogen degradation in a unit area of the TiO$_2$ surface. This is because the yield of surface-OH per unit area linearly increased with the amount of rutile phase content as shown in Fig. 7. As a result, the rutile phase exhibit superior catalytic activity in zonation in comparison to anatines phase.

The following elucidation is put forward to explain the probable reason for the high catalytic activity of rutile phase for zonation reactions. It is well know that oxygen vacancies with Ti$^{3+}$ atoms in the lattice present on anatine TiO$_2$ as well as rutile phase. Ozone and water molecules fills the oxygen vacancies on the TiO$_2$ surface to undergo distortion until becoming unstable, and then dissociating to form a surface oxygen atom. The oxygen atom could react with the next ozone molecule and water molecule, leading to the generation of HO species reacting with no chemisorbed organic molecule [13] As reported, the surface of anatine exhibits less propitious to form oxygen vacancies with respect to rutile, because the removal of a bridging oxygen result in the formation of a five-fold coordinated Ti site on rutile, which is more stable than a four-fold coordinated Ti site generated at oxygen vacancies on anatine [14]. Furthermore, the number of Ti$^{3+}$ site located in the rutile component are greater as compared to anatine phase, Combined above, crystal phase was responsible for catalytic coronation and the rutile phase is more appropriate for the system.

![Graph](image-url)

**Figure 6.** Correlation between the IDR/S and he content of the rutile phase
4. Conclusion

In summary, the catalytic activities of TiO2 depend mainly on their specific surfaces and crystallite phases in the process of zonation of ammonia nitrogen, whereas the morphology has very little influence on the process. A superior catalyst should maximize the surface area and the content of the rutile form of TiO2. Therefore, development of methods for the synthesis of TiO2 with a large surface area and a high content of rutile is worthy of further study.

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Figure 7. Correlation between the density of surface OH groups on catalysts and the content of the rutile phase
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