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Supporting Information

**The impacts of morphology and crystallite phases of titanium oxide on
the catalytic ozonation of phenol**

Shuang SONG*, Zhiwu LIU, Zhiqiao HE, Angliang ZHANG, Jianmeng CHEN*

*College of Biological and Environmental Engineering, Zhejiang University of
Technology, Hangzhou 310032, People's Republic of China*

Yueping YANG, Xinhua XU

*Department of Environmental Engineering, Zhejiang University, Hangzhou
310027, People's Republic of China*

Characterization of the Catalysts.

Crystal Structure. The crystalline structure of the catalyst samples was assessed on the basis of the XRD profiles, as shown in [Figure 1](#). The patterns show that the phase structure of TiO_2 compounds depended on the temperature of the hydrothermal synthesis and the calcination steps.

Samples NT-110-400, NR-160-400 and NW-200-400 were used to investigate the effect of hydrothermal temperature on the crystallite phases. The NT-110-400 and NR-160-400 catalysts exhibited clear diffraction peaks at 25.3° , 37.8° , 48.0° , 55.1° , 62.7° , 68.8° and 70.3° , which were assigned to the well crystallized anatase phase of (101), (004), (200), (211), (204), (116) and (220) crystal planes, respectively. Moreover, the peak intensities increased and the width at half height became narrower with increased hydrothermal temperature, indicating that the increase of hydrothermal temperature tended to improve crystallization of the anatase phase as well as the growth of anatase crystallites.

It is noteworthy that the anatase peaks could not be assigned to the NW-200-400 sample. Instead, some new peaks appeared at 14.17° , 24.88° , 28.57° , 33.20° , 43.57° , 48.42° and 57.93° , corresponding well to the (001), (110), (002), (111), (310), (003), (020) and (421) planes of $\text{TiO}_2\text{-B}$.

The calcination temperature plays an important role in the crystal structure of the catalysts. [Figure 1](#) shows the XRD patterns of the catalysts calcined at various temperatures. NT-110-400, NP-110-600, NP-110-750 and NP-110-800

had similar 2θ values of the diffraction peaks, suggesting that no additional phase was contained in the samples, except the anatase and rutile forms in the calcination temperature range 400 – 800 °C.

Variation of the peak of the (101) plane in anatase is related to the phase transformation of TiO_2 at different calcination temperatures (1). When the calcination temperature was increased from 400 °C to 600 °C, the intensity and width of the (101) peaks were enhanced and decreased, respectively, demonstrating that the crystal shape and the crystallite size became more integral and larger, respectively. Also, the diffraction peaks of rutile appeared at a calcination temperature of 600 °C, implying that the phase conversion temperature of TiO_2 from anatase to rutile was ~600 °C in our experiments. Furthermore, it is obvious that the intensity of the (110) plane of rutile increased and the (101) plane of anatase decreased, with increasing sintering temperature from 600 °C to 800 °C. Obviously, the higher temperature is helpful to the phase-transformation of TiO_2 from anatase to rutile. The phase contents of TiO_2 were calculated according to following formula (2):

$$W_R = 1/(1 + 0.8I_A/I_R) \quad (1)$$

$$W_A = 1 - W_R \quad (2)$$

where W_R and W_A are the rutile and anatase titania content, respectively; I_A and I_R represent the diffraction intensities of anatase (101) and rutile (110).

Table 1 shows that the volume fraction of the rutile phase was 4%, 50% and 90% at annealing temperatures of 600 °C, 750 °C and 800 °C, respectively.

Morphologies of Samples. The structure and morphology of the sample synthesized were affected substantially by both the hydrothermal temperature and the calcination temperature. As reflected in Figure 2a, the sample of NT-110-400 displays a clear-cut image of nanotube morphology, ~100 nm in length with an open end. Furthermore, the nanotube clearly exhibits two layers on both sides with finite wall thickness, and the outer and inner diameters of the tubes were estimated to be ~10 nm and ~7 nm, respectively. Upon hydrothermal treatment at 160 °C, the morphology of the products of NR-160-400 changed, forming short nanorods with a diameter of ~10 nm (Figure 2b). Increasing the hydrothermal temperature to 200 °C was accompanied by the formation of a wire-like structure with a diameter of ~60 nm (Figure 2c).

It is clear from these results that the hydrothermal treatment temperature has a marked effect on the morphological features of the resulting products, where it was found that the morphology of TiO₂ changes gradually from a nanotube to a short nanorod, followed by very long and wide nanowires with increasing hydrothermal temperature. Although the mechanism of TiO₂ nanotube formation is still the subject of debate, it is commonly accepted that nanotubes are formed by rolling up sheets exfoliated from bulk TiO₂ in order to saturate the dangling bonds from the surface and minimize the surface energy (3). Nian and Teng (4) suggested that transformation of the tube to a rod was due to the oriented attachment of adjacent nanotubes together with the local

shrinkage of the nanotubes by reducing the interlayer distance between the tube walls. Further increasing the hydrothermal temperature to 200 °C, besides initiating the nanocrystal growth process of oriented attachment involving spontaneous self-assembly of adjacent nanocrystals, the coarsening of the nanocrystals through the Ostwald ripening mechanism might take place as well, leading to the formation of the long nanowires (5, 6).

To investigate the effect of the calcination temperature on morphology, TiO₂ with the nanotube structure (synthesized at 110 °C hydrothermal treatment) was calcined at various temperatures, and the results of TEM analysis are presented in Figure 2. It was mentioned above that the tube structure could be maintained after calcining at 400 °C to produce the catalyst of NT-110-400 (Figure 2a). However, when the calcination temperature reached 600 °C, the tube-like structure vanished completely and it was transformed into nanopolyhedron-like structure. The transformation may originate from the decrease of the interlayer distance that followed dehydration of interlayer OH groups, leading to contraction and breakage of the tube structures (Figure 2d) (6, 7). Further increasing the calcination temperature to 800 °C resulted in larger catalyst nanocrystals, as shown in Figure 2e and 2f, owing to the agglomeration of smaller nanopolyhedra (8).

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