

Article

Synthesis of Mesoporous TiO₂ with a Template Free One Step Reaction of Acid-Catalyzed TiC

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Abstract. Mesoporous titania (TiO₂) having high specific surface areas of 163 to 306 m²/g was prepared by a template-free one step reaction between TiC precursor and aqueous nitric acid (HNO₃) solution. The effects of reaction parameters including acid concentration, reaction time and temperature were investigated. The properties of the prepared TiO₂ induced by those parameters were characterized by various techniques such as thermal gravimetric/differential thermal analysis (TG/DTA) and X-ray diffraction (XRD). It was found that the TiC was completely oxidized to TiO₂ at reaction time of 8 h, 70 °C with 5 M HNO₃. At this condition, the obtained TiO₂ composed a mixed phase of 45% anatase and 55% rutile and showed the highest pore volume of 0.239 cm³/g with specific surface area of 306 m²/g. Moreover, all the anatase was transformed into the rutile when the reaction time reached 48 h. The rates of the rutile transformation increased with increasing the acid concentrations but decreased with increasing the reaction temperatures. The pore volumes and the specific surface areas were reduced by increasing the acid concentrations or the reaction temperatures. It is possibly because at the conditions of the high acid concentrations or the high temperatures, the mesoporous framework of TiO₂ was collapsed. Based on the acid conditions, a peptization process was adopted to describe the effects of all investigated parameters.

Keywords: Mesoporous titania, titanium carbide, nitric acid, acid-catalyzed, peptization.

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1. Introduction

Mesoporous TiO₂ has attracted much attention, because of its high specific surface area, high porosity, and good chemical and thermal stability. It is extensively used in the photocatalysis fields, catalytic supports and solar cells. Since Antonelli and Ying [1] reported a modified sol-gel synthesis of hexagonally packed mesoporous TiO₂ by using alkyl phosphate surfactants and titanium isopropoxidebisacetylacetonate in 1995, many researchers have performed broadly on synthesis of mesoporous TiO₂ by several methods.

Currently, the most frequently used technique to synthesize TiO₂ is a template method including a hard-template or a soft-template [2]. A template such as Silica (SiO₂), carbon, and (natural and/or synthetic) polymers were used in the hard-template method to possess well-confined void in the form of channels, pores, or connected hollow spaces while surfactants were used in the soft-template method to form micelles (direct or inverse) [3]. Wang et al. [4] used dodecylamine (a neutral amine surfactant) as a template and tetrabutyltitanate (TBT, a neutral inorganic material) as a precursor to synthesize amorphous TiO₂ with wormhole-like framework mesostructure by aging at the ambient temperature for 24 h and at 100 °C for 48 h in an autoclave. Li et al. [5] also prepared mesoporous TiO₂ by using P123 and F127, commercial surfactants, as templates and Ti-solution as a precursor, and then the templates were removed by calcination at 350°C. Furthermore, Wang et al. [6] prepared mesoporous TiO₂ powder by hydrolysis condensation process using Triton X-100 (TX-100, a non-ionic surfactant) as a template and tetrabutylorthotitanate (TBOT) as a precursor in ethanol as a solvent. TiO₂ synthesis by different polymers such as poly(styrene-block-butadiene) copolymer as a template and TBT as a precursor with the final step of templates removal by calcination at 550°C was also studied by Xionge et al. [7] Moreover, Hamaloğlu et al. [8] synthesized TiO₂ microbeads by using -SO₃Na attached-poly(HPMA-Cl-co-EDMA) microbeads as a template and TiCl₄ precursor in an aqueous medium (60 mL, 0.1 M) and then calcined at different temperatures (450 °C, 500 °C, 550 °C, and 600 °C) for 4 h with a heating ramp of 2 °C/min under air atmosphere to remove the polymeric template.

It can be observed that by the template method, a thermal treatment at high temperatures is needed to remove templates for the final step. As a result, the mesoporous framework could be collapsed by the thermal treatment that leads to surface area and pore volume reduction. Moreover, the additional step to remove the template which causes an environmental impact must be concerned. Therefore, a template-free sol-gel which can solve these problems was first demonstrated by Liu et al. [9]. In that study, nitric acid was used as a catalyst and TiO₂ with a high surface area of 106 m²/g was then produced without a structure-directing template. Raveendran et al. [10] have also revealed a template-free method to prepare spherical anatase mesoporous TiO₂ which has nanometer/submicron size by using hydrolytic condensation of titanium butoxide (TiOB) dispersed in ethyl acetate at room temperature. It was found that the obtained TiO₂ exhibits high surface area (388 m²/g) while the mesoporous organization was attributed to the self-assembly of TiOB molecules through site-specific intermolecular interactions. The ethyl acetate played a role in dispersing the bulk TiOB associated into thermodynamically stable spherical assemblies, retaining their meso-scale order. Huang et al. [11] also prepared the high surface area mesoporous TiO₂ by a sol-gel process at ambient temperature using TBT as a precursor, inorganic acid i.e. hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), or phosphoric acid (HPO₃) as a catalyst, in the absence of any templates.

A novel reaction between TiC and aqueous HNO₃ to produce anatase TiO₂ with a narrow diameter distribution of mesopores was presented by Shieh et al. [12]. The reaction was performed in one step condition (70 °C) with a short reaction time (1 h) without any surfactants or polymers as templates. This method is useful for fabrication of the high surface mesoporous TiO₂ through one-step oxidation with only TiC as a starting material.

To develop better understanding in this latest template-free sol-gel method, the variation of parameters influencing the reaction should be determined. Therefore, in this work the mesoporous TiO₂ was prepared with HNO₃ as an acid oxidizing agent and TiC as a precursor with variation in reaction parameters including acid concentration, reaction time and reaction temperature. The prepared TiO₂ and the TiC precursor were investigated for their properties such as thermal properties and morphologies to describe the oxidation event in the process and the effect of reaction parameters on the oxidation.

2. Experimental

2.1. Preparation of TiO₂

TiC (1.4 g) in black powder form (Aldrich, nominally less than 4 μm in particle size) was added to 16 ml of aqueous HNO₃ solution (5 M) at 70 °C with a vigorous stirring. At reaction times of 4, 8, 24, 48, and 72 h, fine grey powder was collected, centrifuged, and washed with ethanol and de-ionized water for several times, respectively. Thereafter, it was dried at 70 °C overnight in an oven to remove the water. The dried samples were subsequently calcined in a tube furnace with air (95 ml/min) at 200 °C with a heating rate of 10 °C/min and held for 30 min. The as-prepared samples were cooled down to room temperature in N₂ flow (75 ml/min). To investigate the effects of acid concentration and reaction temperature, the above procedure was repeated by changing the acid concentration to 9 M or the reaction temperature to 80 °C with the reaction time of 24 h.

2.2. Characterization of TiO₂ and Precursor

The obtained TiO₂ and also the TiC precursor were characterized for their crystal structure by X-ray diffraction (XRD) analysis using a SIEMENS D-5000 diffractometer with Cu-K_α radiation and Ni filter. The scanning patterns were recorded in the 2θ range of 20-80° using a step size of 0.04 degree, which the average crystallite size of prepared-TiO₂ was estimated by using the Debye-Scherrer equation. Surface properties of the samples were measured by N₂ physisorption with micromeritics chemisorb 2750 series. Moreover, thermal properties were analyzed by thermogravimetric/differential thermal analyses (TG/DTA) using SDT Analyzer Model Q600 from TA Instruments, USA) with heating rate of 10 °C/min in flowing air (100 ml/min). CHNS/O analyzer (Perkin Elmer with PE2400 Series II model) with thermal conductivity detector (TCD) was used to determine carbon content (%w/w). Additionally, morphologies were investigated by JEOL model JSM-5800LV scanning electron microscope (SEM) and transmission electron microscope (TEM, JEOL JEM-2010 with an LqB6 filament) operated at 200 kV.

3. Nomenclature

Nomenclature of sample is given as follows TiO₂_A_B_C

where A is concentration of HNO₃ in M

B is reaction temperature in °C

C is reaction time in h

For instance, the TiO₂_5M_70C_8h refers to TiO₂ obtained by using 5 M HNO₃, at 70 °C for 8 h.

4. Results and Discussion

4.1. Crystal Structure

An X-ray diffractometer was used to characterize crystal structures of the prepared TiO₂ by comparing with the TiC precursor, and to identify the TiO₂ phases as anatase, rutile, or mixed phase. Changes in crystal structure with times were investigated by varying the reaction times from 4 h to 72 h at 70°C and at acid concentration of 5 M HNO₃. The XRD patterns of the TiO₂ and the TiC precursor are shown in Fig. 1. It was found that all TiO₂ samples exhibited the TiC characteristic peaks suggesting that the TiC precursor still remained in the samples until the reaction time of 72 h. At the reaction time of 4 h, the high intensity of the peaks assigned to TiC was shown. The intensity of TiC characteristic peak decreased with increasing the reaction time to 8 h and did not change significantly after the reaction time was longer than 8 h. This indicates that at the short reaction time (4h), a high amount of TiC was present in the TiO₂ sample due to low degree of TiC oxidation into TiO₂. At the longer reaction time (8 h), the amount of TiC decreased and was apparently constant after 8 h. This suggests that the TiC oxidation was almost complete at 8 h and leaving nearly the same amount of non-oxidized TiC inside the TiO₂ after 8 h.

Phase transformation of the samples can be observed by the XRD measurement as shown in Fig. 1. It can be seen that at 4 h and 8 h, only the characteristic peaks of anatase TiO₂ were observed. At 24 h, the

characteristic peaks of rutile TiO_2 also appeared along with the anatase peaks suggesting the presence of mixed phase TiO_2 . At 48 and 72 h, only the rutile peaks appeared. This implies that the phase transformation had been finished at 48 h.

Shieh et al. [12] proposed that the formation of TiO_2 through the reaction of TiC with aqueous nitric acid (5 M) at 70°C is unique. No TiO_2 was generated with the reactions of TiC using other oxidizing agents, i.e. HCl , H_2SO_4 , H_3PO_4 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{S}_2\text{O}_7$, and Na_2CrO_4 at the same condition. The formation of the TiO_2 mesoporous structure does not seem to be the result of mesopore-etching of TiC particles and transformation of TiC pore walls into TiO_2 by HNO_3 . Instead, TiC is probably transformed into Ti_mX_n species which are intermediate phases such as oxycarbide ($\text{TiC}_x\text{O}_{1-x}$) and unstable oxide (Ti_mO_n). The formation of intermediate phases during the initial stages of oxidation remains to be elucidated [13]. The intermediate phases are further hydrolyzed and condensed to form the amorphous TiO_2 and then the crystalline TiO_2 through peptization as shown in Eq. (1).

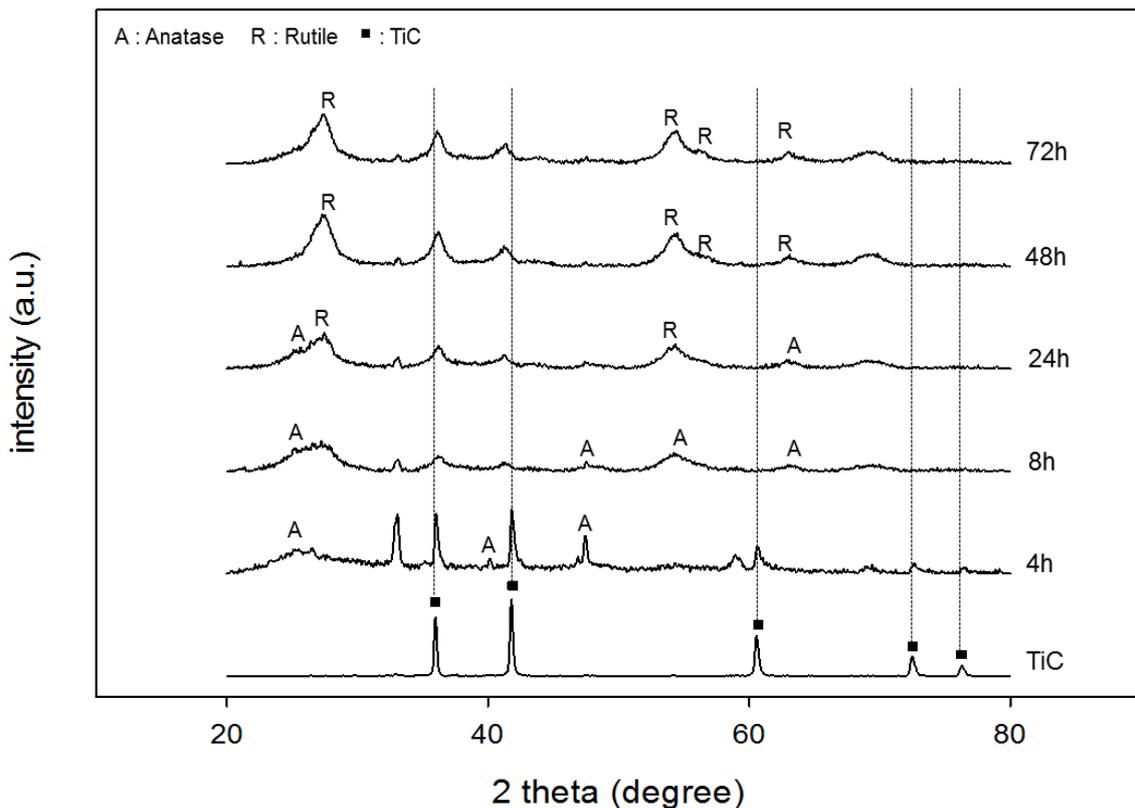
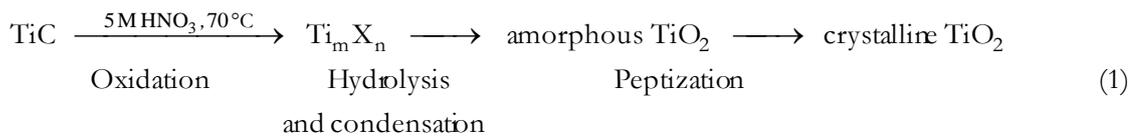


Fig. 1. XRD patterns of TiC and the prepared TiO_2 at various reaction times (5 M HNO_3 and 70°C).

4.2. Thermal Properties

The samples of the prepared- TiO_2 at various conditions were characterized by TGA/DTA technique. In addition, the pure TiC precursor was also characterized by this technique to represent the oxidation pattern under a normal atmosphere without the acid oxidizing agent (HNO_3). The TGA/DTA curves of TiC precursor are shown in Fig. 2 indicating that the TiC weight increased about 28% after complete oxidation, which was in a good agreement with the theoretical value ($\approx 33\%$), corresponding with the TiC oxidation equation (Eq. (2)).

opposite result occurred when the acid oxidizing agent (HNO_3) was presence in the system since the TiO_2 could be formed at the relatively low temperature (70°C).

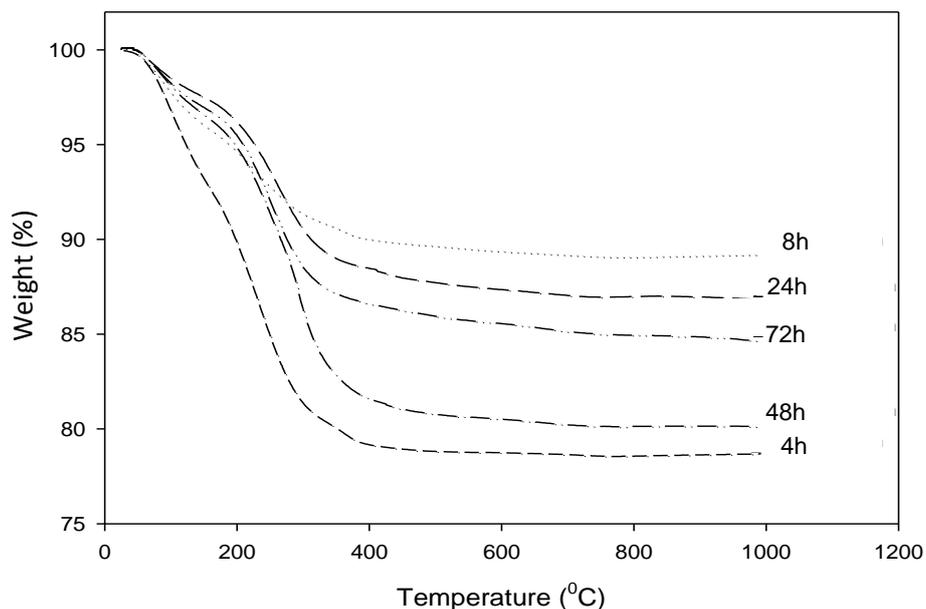


Fig. 3. TGA curves of the TiO_2 prepared at various reaction times (5 M HNO_3 and 70°C).

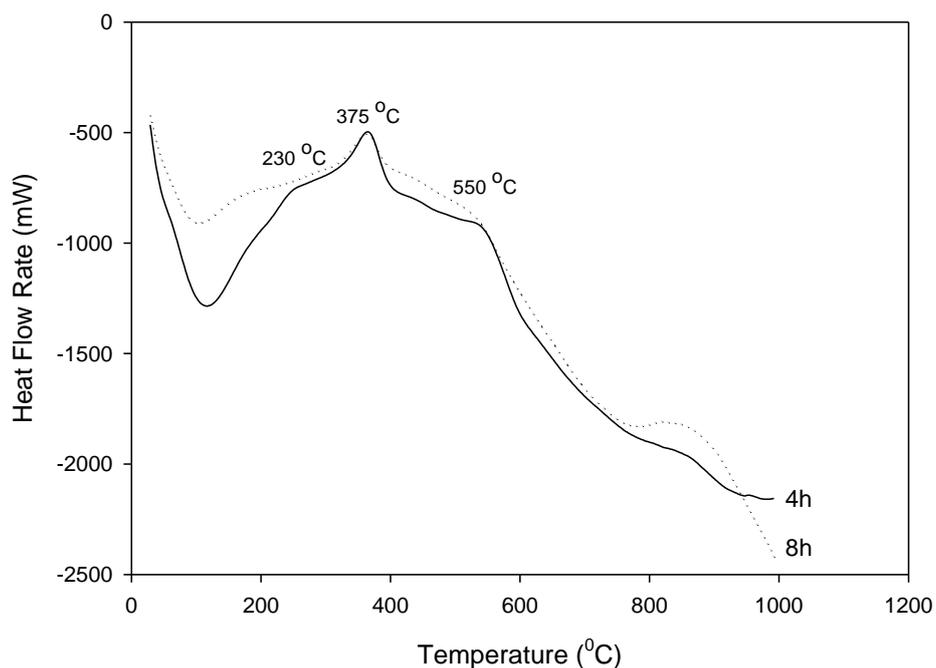


Fig. 4. DTA curves of the TiO_2 prepared at various reaction times (5 M HNO_3 and 70°C).

4.3. Surface Properties and Adsorption Isotherms

Surface properties of the prepared TiO_2 and the TiC precursor were investigated by N_2 adsorption analyzer to obtain their pore sizes, pore volumes and BET surface areas as shown in Table 1. Based on Debye-Scherrer equation, the crystallite sizes and the contents of anatase phase can be calculated and also shown in Table 1. The average crystallite size of the prepared TiO_2 was approximately 3.7 nm. It can be seen that the highest surface area and pore volume were reached in *sample 3* at the reaction time of 8 h, which the prepared TiO_2

containing the mixed phase of anatase (45%) and rutile (55%). Moreover, it was found that the decrease of the anatase phase with longer reaction times led to the lower surface areas as shown in *sample 3-5*.

Table 1. Phase compositions, crystalline sizes and surface properties of TiC and TiO₂ prepared at various conditions.

Sample	Type	%Anatase	d_{xrd}^a (nm)	surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
1	TiC	n.a.	200.0	4	17.22	0.006
2	TiO ₂ _5M_70C_4h	n.a.	n.a.	181	3.82	0.120
3	TiO ₂ _5M_70C_8h	45	3.5	306	3.78	0.239
4	TiO ₂ _5M_70C_24h	34	3.9	248	3.55	0.194
5	TiO ₂ _5M_70C_48h	0	3.9	163	5.33	0.129
6	TiO ₂ _5M_70C_72h	0	3.6	205	4.46	0.151
7	TiO ₂ _5M_80C_24h	40	4.0	185	3.82	0.138
8	TiO ₂ _9M_70C_24h	0	3.1	131	4.25	0.086

^a calculated by Debye-Scherrer equation.

The effects of acid concentrations and reaction temperatures on the phase transformation which induces the changes in surface properties are also noticed in Table 1. It was found that when the acid concentrations were increased from 5 M (*sample 4*) to 9 M (*sample 8*), phase transformation from anatase to rutile was accelerated. For the effect of the reaction temperatures, it was found that the phase transformation to rutile was decreased by raising the temperatures from 70 °C to 80 °C (*sample 6 and 7*). The crystallite sizes and pore sizes of the samples were slightly different by changing reaction parameters. With the stronger acidity, the mesoporous structure of the samples was accelerated to collapse during oxidation process. As a result, pore volume and BET surface area were decreased as seen in *sample 8* comparing with *samples 2-6*. The reaction temperature also affected the mesoporous structure particularly the surface area with the values of 248 and 185 m²/g for the reaction temperatures of 70 and 80 °C, respectively.

The N₂ adsorption/desorption isotherms of TiO₂ samples are shown in Fig. 5. It was found that the reference TiO₂ (Degussa P-25) exhibited type-III isotherm (nonporous or macroporous materials). The isotherm of the TiO₂ prepared at 4 h was altered from type-III to type-IV (mesoporous materials) with a hysteresis loop. The isotherms of TiO₂ prepared at 8 h and 24 h were also similar with that at 4 h. The isotherms gradually changed back to nonporous type-II isotherm at 48 and 72 h reaction times with 100% of rutile phase.

The pore size distribution of the TiO₂ samples are shown in Fig. 6 and it was found that all samples which prepared at various times had similar average pore sizes (around 3-4 nm) within the mesoporous scale. Therefore, the reaction time did not affect the pore size distribution of the TiO₂ samples.

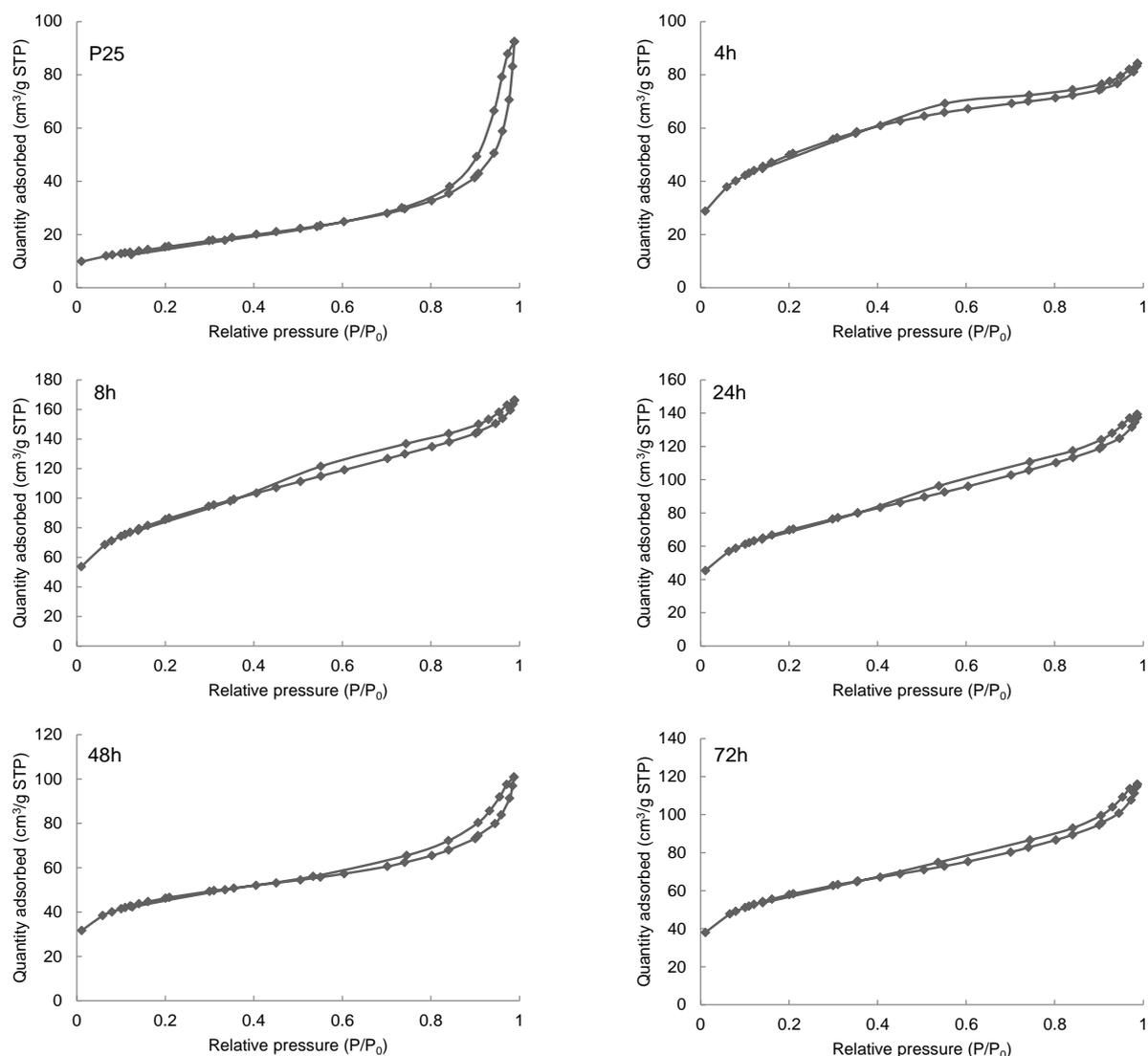


Fig. 5. N_2 adsorption/desorption isotherms of the commercial TiO_2 (P25) and the TiO_2 prepared at various reaction times (5 M HNO_3 and $70^\circ C$).

4.4. Morphology

SEM was used to investigate the morphology of the prepared TiO_2 comparing with the TiC precursor. Figure 7(a) shows the TiC particles which have particle sizes less than $10 \mu m$, smooth surface and sharp edges. The SEM images of the prepared TiO_2 particles are shown in Fig. 7(b). It can be observed that the primary particles with nanocrystallite size, agglomerated to form secondary particles with quite spherical shape and rough surface, without sharp edges.

To observe the phase development in the TiO_2 samples over reaction time, a TEM measurement was performed on the TiO_2 samples which were prepared at various reaction times. It can be seen that the TiO_2 prepared with 8 h reaction time exhibits clusters of very fine crystals with a quite spherical shape which is characteristic of the anatase phase. At 48 h reaction time, the TiO_2 particles developed a rod-like shape which is characteristic of the rutile phase, corresponding to the XRD results as mentioned earlier. When the reaction time reached 72 h, the tinier crystalline particles of the rutile were observed in the TiO_2 sample.

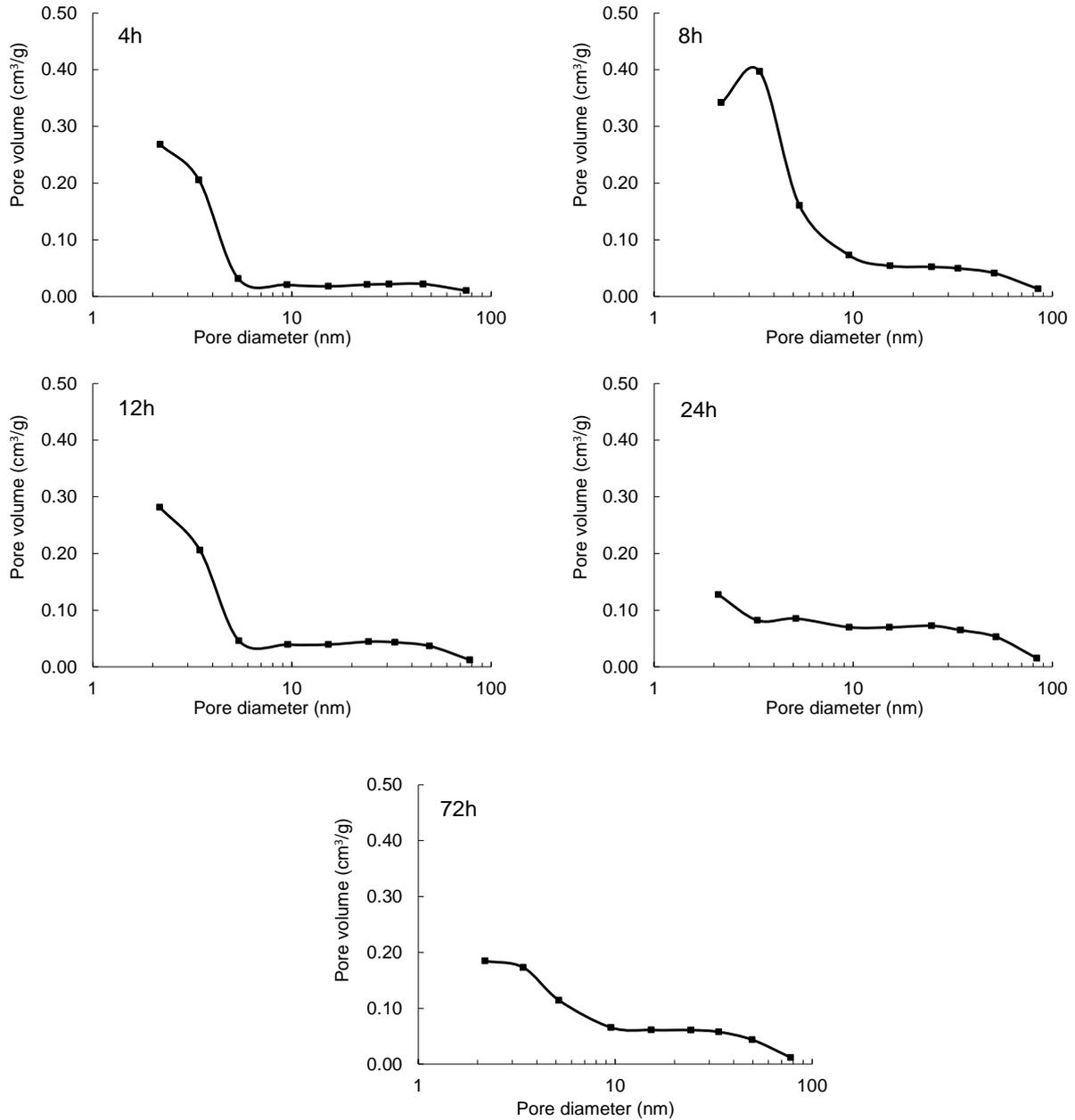


Fig. 6. Pore size distributions of the TiO₂ prepared at various reaction times (5 M HNO₃ and 70°C).

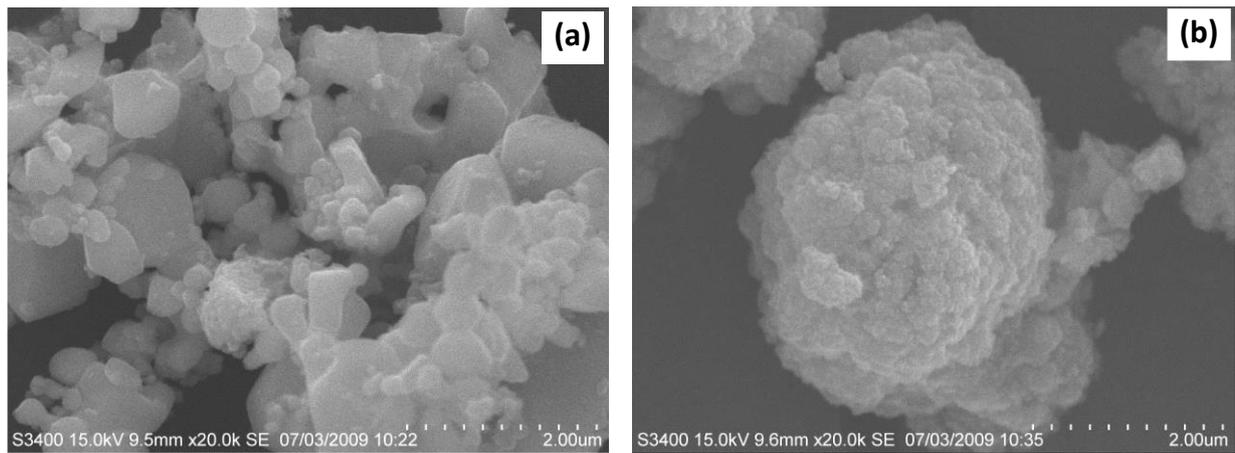


Fig. 7. SEM images of (a) TiC and (b) TiO₂_5M_70C_8h.

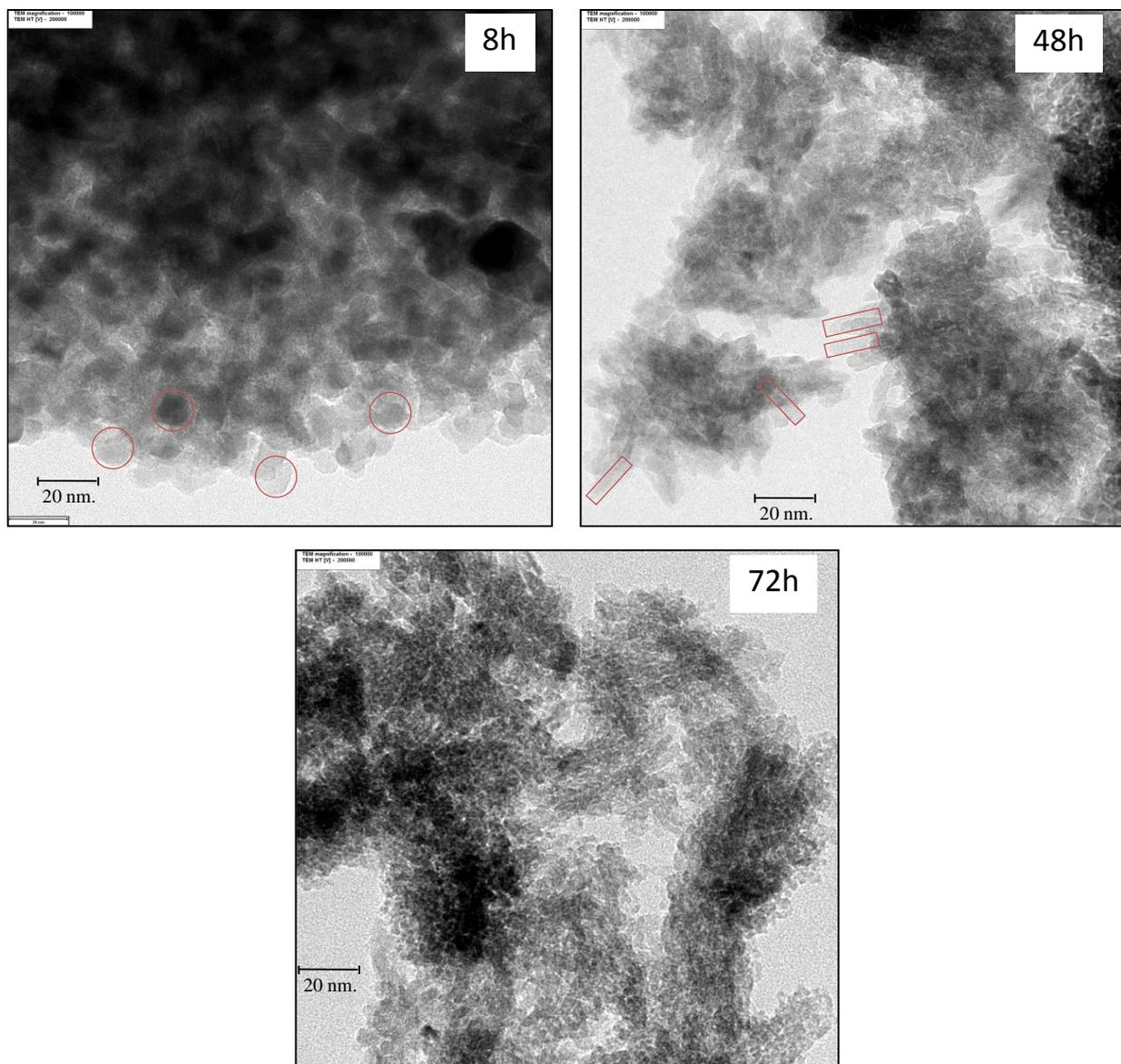


Fig. 8. TEM images of the TiO₂ prepared with various reaction times(5 M HNO₃ and 70°C).

4.5. Carbon Content

The percentages of carbon in the oxidized samples were evaluated with times as shown in Fig. 9. In the early period of 8 h reaction time, the carbon content dramatically decreased perhaps due to the extreme oxidation of the carbon with aqueous nitric solution. The produced gases from the oxidation can be detected in this stage. After 8 h, the amount of carbon gradually decreased due to the constant degree of oxidation. This agrees with the XRD results. In addition, the presence of the carbon in the oxidized samples is consistent with the TGA/DTA results which exhibit the lower weight loss than the theoretical value due to the incomplete oxidation of some TiC particles leaving the residual carbon in the samples.

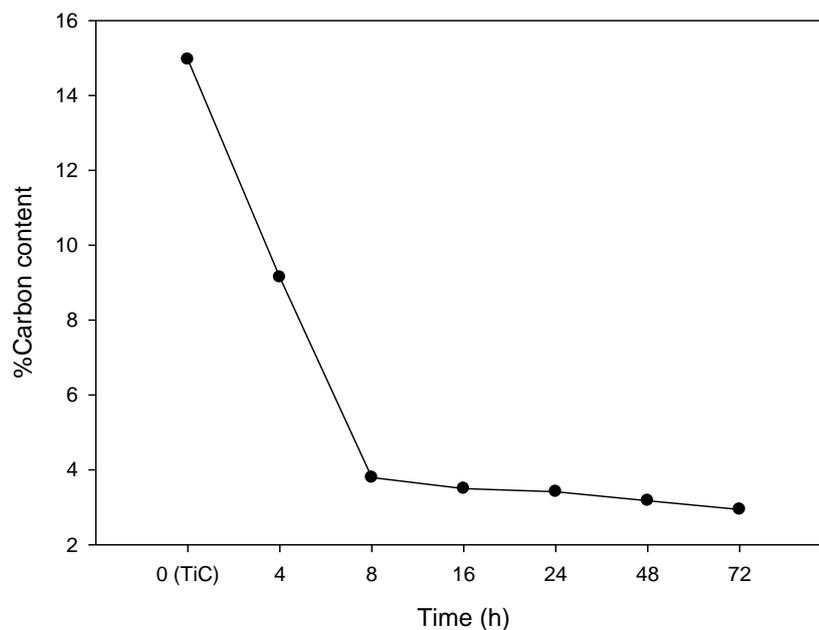


Fig. 9. % Carbon content of the oxidized TiC at various reaction times.

4.6. Peptization Process

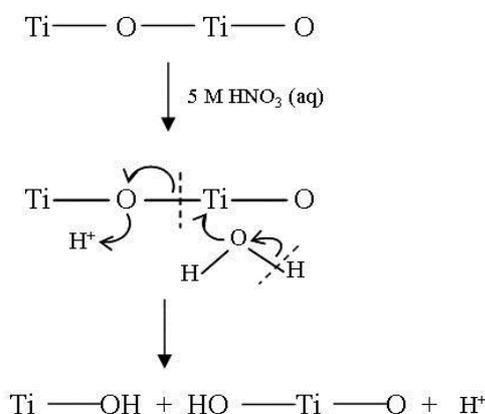
It can be observed in the results above that the reaction parameters including reaction time, temperature, and acid concentration significantly influence the phase transformation of TiO₂. Therefore, to understand these results, peptization process could be adopted to explain the effect of reaction parameters on TiO₂ phase transformation.

Peptization is a process to redisperse a coagulated colloid by electrostatic force in the presence of electrolyte (peptizing agent). This process can occur with HNO₃ acid as a peptizing agent. When the acid was present in TiO₂ precipitates which were continuously generated during TiC oxidation and still held in acid condition until the oxidation had been complete, the TiO₂ particles would be dissolved and recrystallized into anatase or rutile phase [18].

It was found in this study that the peptization process succeeded in transforming the anatase-TiO₂ into rutile-TiO₂. For the longer reaction times and the higher acid concentrations, the phase transformation to rutile increased. This corresponds to the work of Yang et al. [19, 20] who prepared rutile rod-like particles by hydrothermal method using HNO₃ peptization. They found that the TiO₂ particles obtained by this method exhibited the XRD peaks of the anatase. Furthermore, the rutile phase was also observed when increasing reaction time or acidity (H⁺ concentration). To explain this phenomenon, the peptization mechanism should be reviewed as follows.

The peptization begins when HNO₃ is present in the amorphous titania and deoxolation could possibly occur via Scheme 1. From Scheme 1, the electrophilic proton (H⁺) of HNO₃ would engage the oxygen atom between two titanium atoms. The titanium atom can attract the electron density from the O atom in H₂O. Subsequently, the oxolation bonds of TiO₂ ($\equiv\text{Ti-O-Ti}\equiv$) is broken to form hydroxyl groups of Ti-OH. Less number of oxolation bonds among titanium atoms reduces the agglomerate degree of the precipitated TiO₂. Therefore, the higher concentration of the acid peptizing agent with the longer reaction time enhances the

titanium species with fewer oxolation bonds. This could create conditions for the formation of rutile nuclei after structural rearrangements leading to the higher transformation of anatase-TiO₂ into rutile-TiO₂ as shown in the results.



Scheme 1. Deoxolation process of peptization of TiO₂.

Zhang and Gao [21] also found that at low concentrations of the peptizing agent (HCl), the structural arrangements favored the formation of anatase. At higher acid concentrations, the number of oxolation bonds of TiO₂ were reduced leading to structural rearrangements to form corner sharing octahedral chains that is a characteristic of the rutile phase. In addition, Khalil et al. [22] found that the peptization with sulfuric or acetic acids led to more stabilization of anatase phase than nitric acid. Therefore, the acid type could be a factor influences the phase transformation as

For the effect of the reaction temperatures, it was found that at the higher temperature (80 °C), the ratio of rutile phase decreased. Kumar et al. [23] suggested that the phase transformation rate can be affected by the coordination or the number of nearest neighbors in actual physical contact of the primary particles. The coordination can affect either the nucleation rate or the crystal growth rate. In the nucleation step, a higher coordination enhanced the presence of a rutile nucleus which was expected to be larger than an anatase nucleus. The higher temperature can accelerate the movement of the primary particles. Consequently, the aggregation of the particles occurred [24] (the high coordination) with the larger nuclei of the rutile. However, in the crystal growth step, the higher temperature caused a fast crystallization which yielded the less stable anatase form [25]. Hence, it can be concluded from the results in this study that the effect of the temperatures was more pronounced in the crystal growth step than the nucleation step.

5. Conclusion

The high specific surface area TiO₂ was prepared via template-free one step method using TiC as a precursor and nitric acid as oxidizing agent. The highest surface area was obtained with using 5 M HNO₃ at 70 °C for 8 h having 45% anatase. When the reaction times increased, an amount of the rutile phase continuously increased, and was completely transformed to pure rutile TiO₂ phase at the reaction time of 48 h. The increase in acid concentrations also increased the phase transformation from anatase to rutile. This is because increasing reaction time or acidity (H⁺ concentration) led to structural rearrangements towards the more formation of corner-shared octahedral chains which is characteristic of the rutile phase. However, at the higher temperature (80 °C), the ratio of rutile phase decreased. The peptization process was adopted to describe the effects of all reaction parameters.

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