EFFECT OF AGING TIME ON THE FORMATION OF MESOPOROUS TITANIA NANOPARTICLES VIA SOL-GEL METHOD

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Abstract. This paper reports the effect of aging time (2, 4 and 6 days) on the formation of mesoporous mitania nanoparticles (MTN) prepared via sol-gel method. The structural properties of the prepared catalysts were investigated by X-ray diffraction (XRD), Field-emission scanning electron microscopy (FESEM) with EDX analysis and N_2 adsorption-desorption analysis (BET). The XRD analysis revealed that MTNs were successfully synthesized and possessed different crystallite size depending on the aging time. Morphology studies using FESEM-EDX witnessed the formation of agglomerated spherical nanoparticles in the range of 5-50 nm and uniform distribution of Ti and O on the surface of catalysts. N_2 adsorption-desorption analyses demonstrated MTN-2 possessed the largest surface area and pore volume compared to the MTN-4 and MTN-6, which due to blockage of the interparticle voids and excessive particles growth of MTN upon prolonged aging time. The MTN-2 achieved 88.35% of MB photodegradation within 210 min, followed by MTN-4 and MTN-6 with 78.87% and 66.38%, respectively. The superior performance of MTN-2 is aligned seamlessly to it low crystallite and particle size as well as high surface area, that promoted more active sites on the MTN surface, which in turn increased the photodegradation of MB. This study highlighted the promising potential of MTN-2 as a photocatalyst in MB photodegradation.

Keywords: Mesoporous titania nanoparticles, sol-gel, aging time, methylene blue, photodegradation

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1. INTRODUCTION

Titanium dioxide (TiO_2) is known as a promising photocatalyst as it promotes high physical and chemical stability, low toxicity and abundant, cheap and also environmental friendly [1]. At the moment, TiO_2 materials offer great potential in many applications such as photocatalysis, biomedicine, sensing instruments, energy storage and solar water splitting [2]. Recently, various TiO_2 nanomaterials with different structures have been fabricated and performed excellent performances in different areas. However, mesoporous TiO_2 materials have gained great attention owing to their uniqueness such as large surface areas, large pore volume and porous structure [3]. The large surface area material is desired as it can enhance the number of active sites that can boost the surface or interface-related processes such as catalysis, adsorption and energy storage. The large pore volume will allow to attain the high loading of guest species and also accommodate the structural changes. Meanwhile, the porous structure of material will facilitate the transportation of active species, which is advantageous for reaction kinetics [2].

Several methods have been performed to synthesize mesoporous TiO_2 materials such as templating approach, sol-gel, solvothermal, microwave-assisted and hydrothermal in which give different effect towards the properties of the materials [4]. All these approach methods have their own advantages, but sol-gel method which was first discovered in 1995 by Antonelli and Ying has gained tremendous interest as the most adaptable method since it utilizes low synthesize temperature and has a simple process [5]. Although this method undergoes a simple process, there are many factors influencing the quality of the prepared samples such as concentration, chelating agent, initial temperature, aging temperature and aging time. Among them, aging time is known to be the most significant factor as some properties of the samples can be modified during the aging process [6]. This finding is supported by a study from Kusumawardani et al. [7] which varies the aging time of Ti/zeolite at 14, 16 and 20 h. The results showed the least aged photocatalyst exhibited the largest surface area of 189.483 m^2g^{-1} and lowest band gap energy.

In other study, Rismawati et al. [8] also reported the effect of aging time (2, 3, 4, 5 and 6 h) in the preparation of amorphous phase nanosilica by sol-gel method towards crystallite size. Nevertheless, the reported studies dealing with the effect of aging time on the formation of mesoporous TiO_2 by sol-gel process are still insufficient among researchers. Therefore, the present study aimed to investigate the formation of Mesoporous Titania Nanoparticles (MTN) by varying the aging time via the sol-gel method.

In this study, MTN sols were aged at various aging time before being centrifuged and dried. Then, the samples were characterized using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM) with EDX analysis and N_2 adsorption-desorption analysis (BET) to analyze the changes in its physicochemical properties. The efficiency of the prepared MTN samples were elucidated through the photocatalytic dye degradation in which Methylene Blue (MB) was used as a model dye.

2. MATERIALS AND METHODS

2.1 Materials

Hexadecyltrimethyl-ammonium bromide (CTAB) and Titanium (IV) isopropoxide (TTIP) were purchased from Sigma-Aldrich. Ammonium hydroxide (NH_4OH) was purchased from Systerm and *n*-propanol was purchased from Bendosen. MB powder was purchased from Tunchem. All chemicals used in this research work were analytical grade and did not require any further purification.

2.2 Preparation of Catalysts

The MTN catalysts were synthesized using sol-gel method. 4.68 g of hexadecyltrimethyl-ammonium bromide (CTAB) surfactant was added into 720 mL distilled water, 120 ml *n*-propanol and 29 mL of 28% ammonia solution. Then, the mixture was magnetically stirred for 30 min at 50 °C in a water bath. After 30 min, the temperature of water bath was increased to 80 °C before 5.7 mL of titanium (IV) isopropoxide (TTIP) was added into the mixture. The solution was continued stirred for another 2 h in water bath to allow the mixture dissolved completely. After 2 hours of stirring, the observed white solution was transferred into a container and placed in the refrigerator (5 °C) for x = 2, 4 and 6 days. After reaching the desired days, the as-synthesized MTN solution was centrifuged at 4000 rpm to collect the gel product and dried overnight in oven at 100 °C. Finally, the product was calcined at 550 °C for 3 hours to remove the impurities. The aging time of MTN with x = 2, 4 and 6 days were denoted as MTN-2, MTN-4 and MTN-6, respectively.

2.3 Characterization of Mesoporous Titania Nanoparticles (MTN)

The prepared catalysts were then characterized by X-ray diffraction (XRD) analysis (Model: Rigaku MiniFlex) with Cu Kα radiation (λ = 1.5418 Å) at 2θ angle ranging from 20° to 80°. The phases were identified with aid of the Joint Committee on Powder Diffraction Standards (JCPDS) library. The crystallite sizes of the synthesized catalyst were determined based on the major peak at $2\theta = 25.37^{\circ}$ using the Debye-Scherrer equation.

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where d is the crystallite size, k is the shape factor ($k = 0.94$), λ is the wavelength of the X-ray radiation (Cu K_α = 0.1542 nm), β is the line width at half-maximum height and θ is the diffraction angle at the peak maximum. The morphological properties and element present of the catalysts were examined by Field-Emission scanning electron microscopy (FESEM) with Energy dispersive x-ray (EDX) analysis (Model: Hitachi, SU 8020, UHR). The N_2 adsorption-desorption analysis (Model: SA 3100 Surface Analyzer Beckman Coulter) was performed by using the brunauer-emmett teller (BET) method which could estimate the surface area, isotherm and pore size distribution of the catalysts. Before measurement, all samples were degassed at 300 °C and 0.1 Pa.

2.4 Photodegradation of Methylene Blue (MB)

The photodegradation was performed when 0.6 gL^{-1} of catalyst was added into 50 mL of MB solution and constantly stirred in a 100 ml glass vessel. Before illumination, the solution was magnetically stirred for 60 min in the dark to achieve adsorption-desorption equilibrium. Then, the reaction was continued for another 210 min with irradiation of 400W LED UV lamp (395 nm) under continuous stirring. During the reaction, 2 ml of aliquots were sampled every 30 min and centrifuged using a micro centrifuge at 13000 rpm for 30 min to separate the liquid phase from solid catalyst before being analyzed by UV-Visible (UV-Vis) spectroscopy (Model: Jasco V-570) at λ_{max} = 664 nm. The degradation percentage was calculated using the following equation;

$$\text{Degradation (\%)} = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \quad (2)$$

where C_o is the initial concentration of MB before being exposed to irradiation and C_t is the concentration of MB at a specific time.

3. RESULTS AND DISCUSSION

3.1 Physichochemical Properties of the Prepared MTN

The XRD pattern of MTN catalysts are presented in Figure 1. A series of XRD peaks referring to the common peaks of TiO_2 anatase phase (JCPDS card No. 00-021-1272) were detected at 25.37°, 36.97°, 37.94°, 38.66°, 48.04°, 53.89°, 55.06°, 62.69°, 68.76°, 70.29° and 75.05° for all catalysts, which corresponded to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes, respectively [9]. Then, the peaks attributed to TiO_2 rutile phase (JCPDS card No. 00-021-1276) were detected at 27.23° and 56.45° for all catalysts, which corresponded to (110) and (220) planes, respectively [10]. From the results, it can be observed that the peaks for all catalysts appeared in a similar pattern. It is important to note that the intensity for all peaks were decreased upon increasing aging time, which may be contributed from distortion of structural arrangement in the MTN, signifying the decrease of crystalline quality of nanoparticles. A similar finding was reported by Li et al. [11] that found a larger ZnO formed at a longer aging time resulted in structure distortion due to poor dispersion and crystallinity.

The calculated crystallite sizes of MTN-2, 4 and 6 were 0.26, 0.32 and 0.37 nm, respectively. The obtained results proved that the average crystallite sizes of the catalysts tend to increase upon the aging time and MTN-2 showed the smallest size compared to other catalysts. Yazici et al. [6] reported that prolonging aging time will cause the sol to continue react chemically and agglomerated to form larger sol particles. Other than that, the crystal seed had more available time to grow with the increasing of aging time. Another study reported by Jannane et al. [12] also showed the increment of ZnO thin film crystallite size from 16.55 to 21.30, 29.82 and 37.17 nm after the deposition solution was aged for 0, 24, 48 and 72 hours, respectively. The increase of crystallite size was due to the condensation and aggregation reactions of zinc species that can occur during the deposition solution being aged. From those findings, it is important to note that crystallite size was closely related to the aging time in sol-gel process.

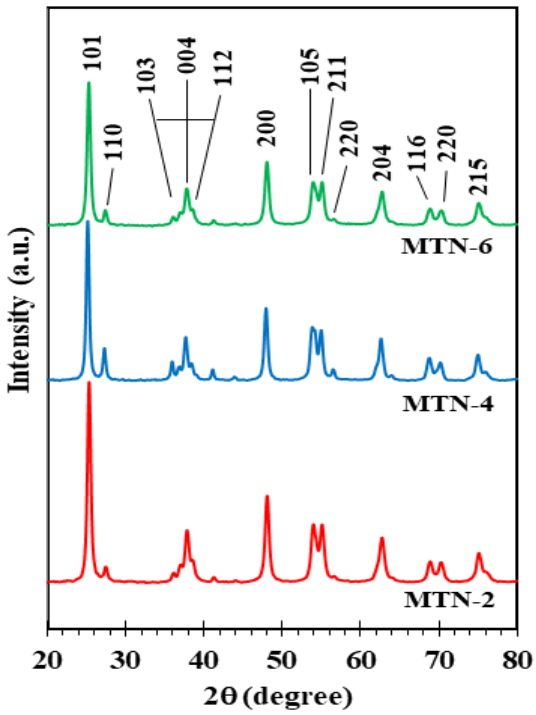

Figure 1: XRD patterns of MTN-2, MTN-4 and MTN-6

The FESEM images of the catalysts are presented in Figure 2. From the low magnification images at (a) 2k and (b) 6k, it can be seen that MTNs were in porous arrangement and formed abundance of narrow slits. At a higher magnification of 30k (c), it was observed that MTNs demonstrated disordered spherical particles that interconnect with each other forming mesoporous network structure [13]. The FESEM images at 200k magnifications (Figure (d) to (f)) revealed the effect of aging time on the particles size of the catalysts. The MTN-2 has the smallest particles distributed around 5.95 nm to 22.8 nm, followed by the MTN-4 around 7.94 nm to 28.8 nm.

The largest particles distribution was demonstrated by the MTN-6 with particles distribution around 10.9 nm to 43.7 nm. Based on the particles size measured, the calculated average particles size was in the following order: MTN-2 (11.4 nm) < MTN-4 (17.4 nm) < MTN-6 (24.9 nm). This result showed that increasing aging time in the preparation of MTN led to further hydrolysis and condensation of titanium precursors, which were then slowly aggregated to one another [11]. This finding aligns with a previous study by Lukong et al. [14] that has synthesized TiO_2 thin film with varying the aging time of TiO_2 sol to 24, 48 and 72 hours. The obtained results showed the 72 hours of sol aging exhibited more agglomerated flakes scattered over the substrate with larger shapes.

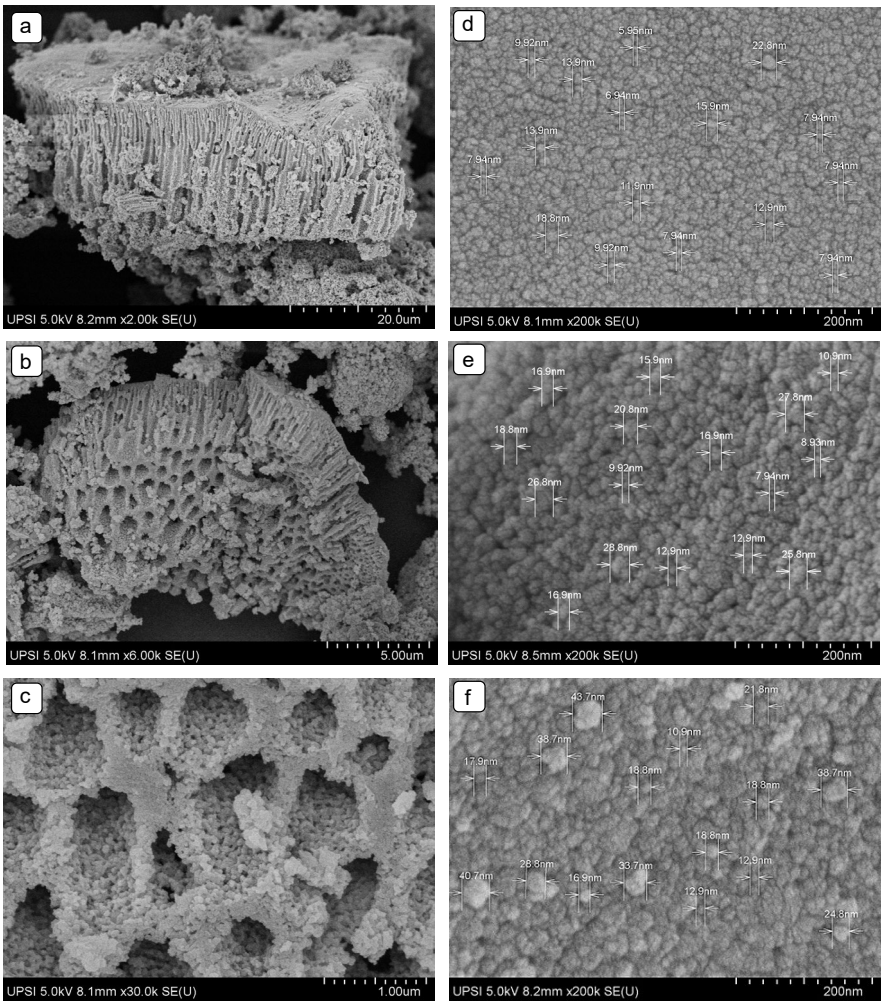

Figure 2: FESEM images of MTNs at (a) 2k, (b) 6k, and (c) 30k magnifications and FESEM images of (d) MTN-2, (e) MTN-4 and (f) MTN-6 at 200k magnification

Further analysis on the elemental distribution using EDX elemental mapping showed only Ti and O elements (as shown in Figure 3) were uniformly distributed on the surface of MTN structure.

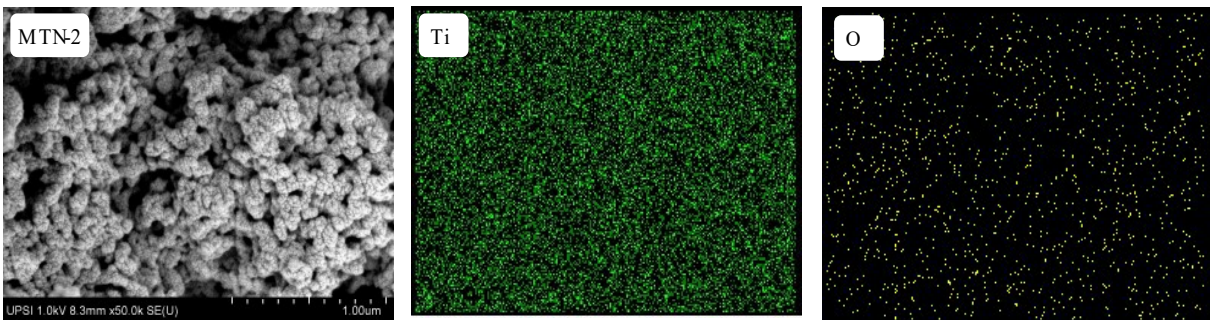

Figure 3: Elemental mapping images of MTN-2 for Ti and O elements

Figure 4 presents the N_2 adsorption-desorption isotherm and pore size distribution of the MTN catalysts. It was observed that all MTNs exhibited a Type IV isotherm with a H3 hysteresis loop, confirming the existence of mesoporous materials with slit-shaped pores that have non-uniform in size or shape in the synthesized catalysts [15]. The hysteresis loop at P/P_o = 0.9-1.0 observed in the isotherm was assigned to N_2 condensation within mesopores and smaller macropores, that was due to interparticle voids contributed by textural porosity between particles [15]. By increasing the aging time, it caused the isotherm curves and hysteresis loop to be gradually flattered which in accordance to the decreasing in surface area and porosity because of the particle's growth and interparticle voids drop [16]. It is suggested that the formation of bigger agglomeration of MTN in the MTN-4 and MTN-6 occupied more empty space between the particles, thus reducing the size particles voids. This is in line with distribution of pore in MTNs (Figure 4(b)), which showed that a bigger pore at 25-45, 50-62 and 70-90 nm were eliminated.

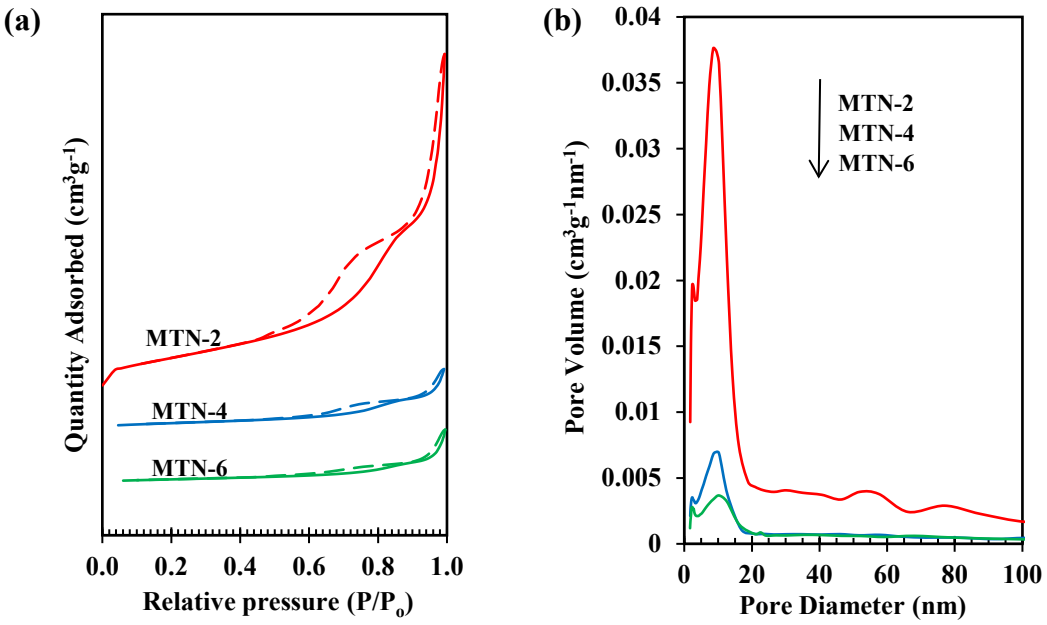

Figure 4: (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of MTN-2, MTN-4 and MTN-6

Based on the summarized pore structural informations in Table 1, the increasing of aging time to 4 and 6 days has decreased the surface area of MTN from 232.53 to 42.63, 28.69 m^2g^{-1}, respectively. A remarkable loss of pore volume were also observed from 0.8079 to 0.1442, 0.1239 cm^3g^{-1}. Upon the aging time, the changes in interparticle voids of all the catalysts were noticed to be decreased, indicating the major pore blockage has occurred due

Table 1: Pore structural information of MTN-2, MTN-4 and MTN-6 catalysts

Catalyst	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore size (nm)
MTN-2	232.53	0.8079	23.34
MTN-4	42.63	0.1442	16.30
MTN-6	28.69	0.1239	13.14

to the excessive grain growth. It can be seen in Figure 2(d) to (f), increasing aging time caused an increased in the particle sizes and smaller interparticles voids. Besides, the formation of a larger particles on the top surface might block some of the pores between the particles. The results indicated that the rudimentary pore formation favourably occurred in MTN-2, which showed that the mesoporosity of the nanoparticles can be influenced by the aging time [15].

3.2 Catalytic Testing on Degradation of Methylene Blue (MB)

The photoactivity of MTN samples were investigated on the degradation of MB under UV light irradiation, and the results were shown in Figure 5(a). All the catalysts were tested under dark condition to achieve adsorption-desorption equilibrium before being exposed to light irradiation. However, no significant change was observed after 60 min of dark test, which indicated that all samples have low ability in MB physical adsorption in dark conditions [17].

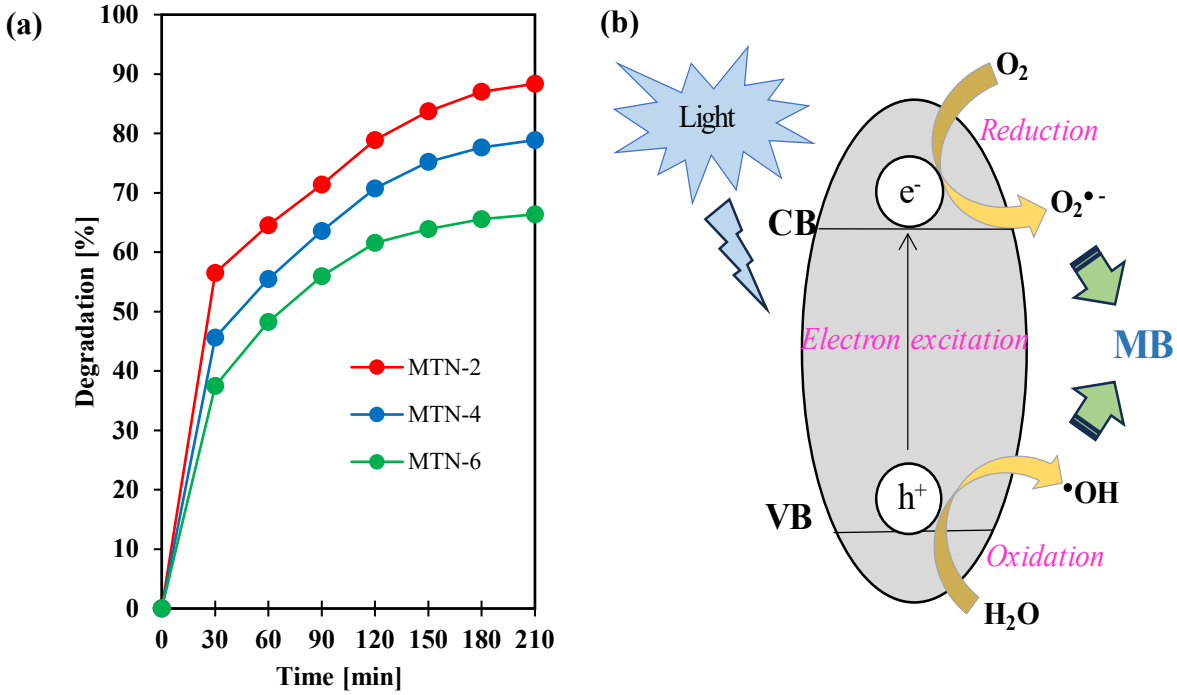

Figure 5: (a) Degradation percentage of MB using MTN-2, MTN-4 and MTN-6 and (b) Schematic illustration of MB photodegradation by MTN

From the results illustrated in Figure 5(a), MTN-2 exhibited the highest degradation with 88.35%, followed by MTN-4 and MTN-6 with 78.87% and 66.38% within 210 min of irradiation time, respectively. It is well known that in photodegradation (as illustrated in Figure 5(b)), the reaction starts with the photogenerations of ions (e^-) and holes (h^+) on the surface of the catalysts when electrons were excited from the valence band (VB) to the conduction band (CB) upon light exposure. Then, this active species will react with O_2 and H_2O to produce superoxide ($O_2^{\bullet -}$) and hydroxy (•OH) radicals. These highly oxidizing radicals will undergo a series of oxidation process when in contact with the MB to form water and CO_2 [18]. Based on the characterization results, MTN-2 was found to possess the smallest crystallite and particle sizes. Decreasing the crystallite and particle sizes seemed to promote a higher specific surface area for active sites generation and photodegradation. Besides, the presence of larger surface area and pore volume helps to improve the accessibility of active sites on the MTN surface to

react with the MB pollutants, which in turn will increase the degradation rates [19]. Reddy et al. [20] reported the improvement of degradation was achieved from 15% to 30% when the particle size decreased from 615 nm to 190 nm. Zhang et al. [2] reported that high surface area can generate abundant of active sites for adsorption and reaction of reactants, thus enhancing the photocatalytic activity. This statement was in accordance to the MB degradation results for MTN-2 but inconsistent to MTN-4 and MTN-6. Eventhough Table 1 showed huge differences in surface area and pore volume between the MTN-4/MTN-6 and MTN-2, the degradation percentage showed a little difference. Meanwhile, the degradation pattern was most likely closed to the pattern of crystallite and particle sizes. Considering all findings, it can be concluded that under the reaction parameters studied, the MB photodegradation was influenced by the crystallite and particles size to a greater extent compared to the surface area and pore volume.

4. CONCLUSIONS

In conclusion, MTN with various aging time were successfully prepared via sol-gel method and the efficiency of the catalysts were tested on the photodegradation of MB. The structural properties of the catalysts were examined via XRD, FESEM-EDX and N_2 adsorption-desorption analysis (BET). The obtained results clearly showed that prolonging the aging time will cause the crystallite and particle sizes of MTN to be increased due to the excessive hydrolysis and condensation of Ti precursors. Apart from that, the surface area and pore volume were significantly decreased upon the aging time due to the formation of larger agglomerates and major blockage of interparticle voids. The MTN-2 achieved the highest MB degradation with 88.35% compared to MTN-4 and MTN-6 that only achieved 78.87% and 66.38%, respectively. The greater degradation percentage could be due to its lowest crystallite and particle size as well as highest surface area, that promoted more active sites on the MTN surface, which in turn increased the degradation of MB. It can be seen that the aging time in the sol-gel process of MTN gives a significant effect on the crystallite size, particles size and the surface area of a catalyst. However, each structure's properties have a certain degree of impact toward the reaction based on the parameters studied.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards.

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