Properties and Photocatalytic Behaviour of Vanadia Loaded Titania Supported on MCM-41 Synthesized using Different Surfactants for Degradation of Methylene Blue

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Abstract

An attempt has been carried out to prepare vanadia loaded TiO\textsubscript{2} supported on MCM-41(V-TiO\textsubscript{2}/MCM-41) nanostructured photocatalysts using different surfactants. The surfactants used in the photocatalysts synthesis were dodecyl-trimethyl-ammonium bromide (DTAB), hexadecyl-trimethyl-ammonium bromide (CTAB) and octadecyl-trimethyl-ammonium bromide (STAB) which have varied carbon chains. The effect of crystallinity, surface area and porosity of the MCM-41 support on the physical-chemical properties of synthesized photocatalysts of vanadia loaded TiO\textsubscript{2}/MCM-41 and their photocatalytic performance were investigated. X-ray diffraction (XRD) patterns showed that the crystallinity of vanadia-TiO\textsubscript{2}/MCM-41 decreased with increasing of carbon-chain number of the surfactant used. Both surface area and pore volume of V-TiO\textsubscript{2} increased significantly from 16.2 m\textsuperscript{2}/g and 0.034 cm\textsuperscript{3}/g to 864.3 m\textsuperscript{2}/g and 0.618 cm\textsuperscript{3}/g, respectively, after being loaded on MCM-41 support which was prepared using CTAB. It was demonstrated that all the V loaded TiO\textsubscript{2}/MCM-41 materials exhibited remarkable improvement in photocatalytic degradation of methylene blue (MB) under the irradiation of visible light as compared to that of bare TiO\textsubscript{2} and V-TiO\textsubscript{2}. Among these materials, V-TiO\textsubscript{2}/MCM-41 which was synthesized using CTAB appeared to be the best photocatalyst with 57% of MB removal under visible light irradiation.

Keywords: Methylene blue, MCM-41, Photocatalyst, Surfactant, Titania, Vanadia

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Introduction

In the past century, dyes have been widely used as colouring materials in textile industries [1]. Among the popular dyes that have been used in the textile industries are basic dyes such as methylene blue, rhodamine B, malachite green, and acid dyes such as acid blue 9, acid orange 10 and acid orange 51 [2]. However, it was reported that the improper waste management of dyes had caused serious environment pollution. [3]. In addition, the effluents have been handled with several chemical and physical procedures such as adsorption [4], flocculation, and reverse osmosis [5,6] precipitation [7]. However, these approaches are considered non-destructive techniques as their applications always lead to another environmental issue [8–10]. Since the last decades, photocatalysis has been recognized as a promising green technology to fully degrade the trace elements of organic substances in contaminated wastewater [11]. Among all the reported photocatalysts, titania (TiO$_2$) and titania-based photocatalysts which utilize advanced oxidation processes (AOPs) have been recognised to have high efficiency in the degradation of organic pollutants [12]. The TiO$_2$-based photocatalysts are capable of degrading harmful organic chemicals into harmless compounds such as CO$_2$, H$_2$O and simple acids that interest in the total elimination of organic contaminants through the generation of hydroxyl radicals, •OH which is an effective and non-selective oxidant species [12–14].

TiO$_2$ has two thermodynamically stable crystalline polymorph forms which are anatase and rutile with a bandgap energy of ca. 3.2 and 3.0 eV, respectively [15]. Unfortunately, TiO$_2$ is suffering from several drawbacks and limitations due to its wide bandgap energy that only allows operation within the ultraviolet range [15,16]. Besides, its high electron-hole recombination rate has retained a limited amount of hydroxyl species on its surface which depicts a significant role as scavengers in the recombination process [15,17]. In addition, its low surface area (ca. 70 m$^2$/g) has become the main disadvantage that affects its performance [12,14,15–17]. In order to overcome the limitations and drawbacks of TiO$_2$ photocatalyst, many affords have been made to improve the photocatalytic efficiency of TiO$_2$ [12,14,16,17]. There are various reported methods and techniques in improving the performance efficiency of TiO$_2$. Amongst, metal ion doping on TiO$_2$ has appeared as a promising approach to improve the photocatalytic performance of TiO$_2$ [18,19]. The doped metal has a vast positive reduction potential that assists to suppress the recombination of photogenerated electron-holes and subsequently to increase the charge separation, thus leading to the increment of the wavelength response range. It has been documented that vanadium doped TiO$_2$ (V-TiO$_2$) showed a significantly higher photocatalytic activity than that of unmodified TiO$_2$ especially under visible light irradiation [20–22]. Although the modification of TiO$_2$ with vanadia has improved the photocatalytic performance of TiO$_2$, both surface area and porosity remained low in these metal oxide modified titania photocatalysts [21,22]. As the large surface area has become one of the important properties for high adsorption and degradation process owing to availability of more reaction sites [14–20,23], therefore, an attempt to increase both surface area and porosity of the photocatalyst is highly recommended.

MCM-41 or mobile composite matter 41 is one of the common catalysts supports owing to its excellent thermal stability, extremely high surface area and large porosity [24]. However, the effect of properties changing in MCM-41 supported photocatalyst caused by different surfactants used in the preparation of MCM-41 on the photocatalytic behavior of the modified metal doped titania photocatalysts remains unclear. Therefore, in this study, a series of photocatalysts supported on MCM-41 prepared with different surfactants were synthesized in order to explore the effect of surfactants on the preparation of MCM-41 support in the photocatalytic performance of modified V-TiO$_2$. Three different surfactants which are dodecyltrimethyl-ammonium bromide (DTAB), hexadecyltrimethyl-ammonium bromide (CTAB) and octadecyltrimethyl-ammonium bromide (STAB) were used in this work. Herein, we report the physical-chemical properties and photocatalytic activity of V-TiO$_2$ supported on MCM-41 for photocatalytic degradation of methylene blue (MB).

Experimental Section

Preparation of unmodified TiO$_2$

The unmodified TiO$_2$ photocatalyst was prepared via a sol-gel method similar as reported in the literature [25,26]. In the preparation of TiO$_2$, titanium tetraisopropoxide (TTIP, Ti(OCH(CH$_3$)$_3$)$_4$) was added with absolute ethanol as solvent and acetylacetone as chelating agent according to the molar ratio of 1: 100: 2. The mixture was stirred for 1h at room temperature and dried at 353 K overnight,
followed by calcination process at 773 K for 5 h. For the preparation of V-TiO$_2$, TiO$_2$ was prepared first prepared with similar procedure aforementioned above except for the addition of dopant. A 10 ml of titanium tetraisopropoxide (TTIP, Ti(OCH(CH$_3$)$_2$)$_4$), was added to 199.226 mL of absolute ethanol solvent, C$_2$H$_5$OH and 6.972 mL of acetylacetone, C$_3$H$_4$O$_2$ as chelating agent according to the molar ratio 1: 100: 2 respectively. The solution was then stirred for 1h at room temperature and denoted as solution A.

Preparation of vanadia loaded titanium dioxide (V-TiO$_2$)

Meanwhile, the vanadium oxide (V$_2$O$_5$) was prepared by dissolving 0.0933 g of vanadyl(V) acetylacetonate, C$_{12}$H$_{14}$O$_7$V which act as the precursor in acetylacetone, C$_3$H$_4$O$_2$. The mixture was then added dropwise to solution A to form a yellowish orange solution. The mixture was then stirred for 1 hour at room temperature and dried at 353 K overnight for evaporation of alcohol followed by calcination at 773 K for 5 hours. The molar ratio of the metal oxides to TiO$_2$ was fixed to 1 wt%.

Preparation of MCM-41 with different surfactants

The purely siliceous MCM-41 was prepared using sodium silicate solution (Na$_2$SiO$_3$) as silica source. The synthesis of MCM-41 was carried out according to molar composition as follow:

6 SiO$_2$: 1.5 Na$_2$O: CTABr: 0.15 (NH$_4$)$_2$O: 250 H$_2$O

Na$_2$SiO$_3$ solution was prepared through the mixing of 42.516 mL of tetraethylorthosilicate (TEOS), SiC$_2$H$_4$O$_2$ with 4.0404 g of sodium hydroxide, NaOH in 50 mL double distilled water. The mixture was then denoted as solution 1. For the preparation of surfactant, 12.305 mL of CTABr ((C$_{14}$H$_{31}$)N(CH$_3$)$_2$Br) and 0.68 mL of ammonium hydroxide (NH$_4$OH) were dissolved in 100 mL of double distilled water following by continuous stirring and heating at 353 K for 1 hour. The solution was then denoted as solution 2. Both solutions 1 and 2 were mixed simultaneously and was vigorously shaken for about 15 minutes followed by overnight drying at 370 K. The pH of the solution was adjusted to 10.2 using few drops of acetic acid (30 wt%) followed by overnight drying at 370 K. The final step involved the calcinations of the as-synthesized sample at 823 K to remove the organic template. The experiment was repeated using different surfactants which were DTAB, C$_{16}$H$_{31}$(CH$_3$)$_2$NBr, and C$_{18}$H$_{37}$(CH$_3$)$_2$NBr as different templates, respectively.

Preparation of V-TiO$_2$/MCM-41

In the preparation of V-TiO$_2$/MCM-41, the as-synthesized MCM-41 was added to the solution containing V-TiO$_2$. The mixture was stirred for 1 hour followed by drying process at 353 K. The mole ratio between V-TiO$_2$ and MCM-41 (Ti : Si) was set to 1 : 20. The solution was stirred, dried at 353 K and heated at 383 K for 24 hours followed by calcination at 773 K for 5 hours.

Characterization

The physical and chemical properties of the prepared photocatalysts were characterized using X-ray (XRD) diffractometer (Bruker Advance D8 diffractometer), diffuse reflectance ultra-violet (DR UV-Vis) spectrophotometer (Perkin Elmer Lambda 900 DRUV/VIS/NIR Spectrometer), Fourier transform infra-red (FTIR) spectrophotometer (Shimadzu Fourier-Transform Infrared FTIR-8300 Spectrometer), nitrogen (N$_2$) adsorption-desorption isotherm surface area analyzer (NOVA 1200 Quantachrome Autosorb), field emission scanning electron microscope (FESEM) (JEOL JSM-6701F) attached with energy dispersive X-ray (EDX).

Photocatalytic testing

Photocatalytic degradation of MB was carried out at room temperature under the irradiation of visible light. A 0.1 g of prepared photocatalyst was suspended in the 50 mL of MB solution. Before the photocatalytic reaction, the solution was kept in the dark condition for 3 hours to achieve equilibrium. The photocatalytic degradation was carried out under visible light irradiation (550 W tungsten halogen lamp) under constant stirring for 5 hours. The initial and final concentration of MB was measured using UV-Vis spectrophotometer at a wavelength of 464.0 nm and the photocatalytic activity was measured using equation (1)

$$\text{Activity (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where $C_0$ is initial concentration and C is final concentration.
Results and Discussion

As shown in Figure 1, the as-prepared white solid powder TiO\textsubscript{2} showed a formation of anatase and rutile phases after calcined at 773 K for 5 hours. The presence of anatase phase of TiO\textsubscript{2} can be observed at ca. 2\(\theta\) of 25.5° while the formation of rutile phase of TiO\textsubscript{2} can be observed at ca. 2\(\theta\) of 27.5°. These two diffraction peaks were found to be consistent with the typical anatase-rutile of TiO\textsubscript{2} as widely reported in the literature [12–14,17]. In addition, both anatase and rutile peaks were completely matched according to the JCPDS 21-1272 and JCPDS 21-1276 library.

![Figure 1](image)

**Figure 1.** XRD patterns of (a) TiO\textsubscript{2} and (b) V-TiO\textsubscript{2}.

The addition of 1 wt.% of V resulted the composition of anatase phase decreased from 66.8 to 56.6%. However, the composition of rutile phase was increased to 33.3 to 43.4%. The significant changes in the anatase-rutile composition were due to the cationic vacancies generated by V\textsuperscript{5+} ions, thus leading to an increase in crystallite size of the samples from 19.85 to 20.24 nm. Meanwhile, the crystallite size of rutile phase decreased from 24.40 nm to 22.73 nm. This finding was also similar to the one that has been reported in the literature [26].

As can be seen in Figure 2, the intense peaks at ca. 2\(\theta\) of 2.5° (101), 4.5° (110) and 5.2° (200) were corresponded to the diffraction peaks of MCM-41 with different surfactants which were DTAB with a carbon number of 15 (Figure 2(a)), CTAB with a carbon number of 18 (Figure 2(b)) and STAB with a carbon number 21 (Figure 2(c)) [27–29]. Based on the XRD patterns, the degree of crystallinity of MCM-41 decreased from 76.3 to 32.8% with an increasing number of the carbon chain. The increase in peaks intensities was owing to the destruction of the pore wall and the collapse of lattice structure that related to the presence of excess colloidal silica in MCM-41 framework [30]. In addition, the greater the carbon number would obstruct the removal of templates during calcination process [31].

Based on FTIR spectra as shown in Figure 3, the substitution of isomorphous V atoms into the tetrahedral site was confirmed when the presence of V caused the increased in mean Ti-O distance in the wall, thus, shifting the peak to lower wavenumber [26]. On the other hand, the additional peaks observed at around 967.35 to 1086.77 cm\textsuperscript{-1} were corresponded to asymmetric stretching of Si-O-Ti and Si-O-Si, suggesting the successful formation of MCM-41 as catalyst support to V-TiO\textsubscript{2} regardless of different surfactant used in the preparation of MCM-41 [27–29].

![Figure 2](image)

**Figure 2.** XRD patterns of (a) V-TiO\textsubscript{2}/MCM-41(DTAB), (b) V-TiO\textsubscript{2}/MCM-41(CTAB), and (c) V TiO\textsubscript{2}/MCM-41(STAB).

The N\textsubscript{2} adsorption-desorption isotherms of prepared TiO\textsubscript{2} and V-TiO\textsubscript{2}/MCM with different surfactants used were depicted in the Figure 4(a–e). From the isotherm, both TiO\textsubscript{2} and V-TiO\textsubscript{2} showed a type III isotherm with hysteresis type H3 [25-26, 32] while others showed a type IV isotherm with uniform mesopores [27–29,32]. The presence of hysteresis loop in both TiO\textsubscript{2} and V-TiO\textsubscript{2} isotherm in relative pressure (P/P\textsubscript{0}) between 0.5 and 0.9 was due to interparticle porosity [33]. Meanwhile, the isotherm pattern for all V-TiO\textsubscript{2} prepared with MCM-41 catalyst support were similar to the typical isotherm of MCM-41 as reported in literature [27–29].
Based on Table 1, it was observed that the addition of V into TiO$_2$ did not give significant change in the surface area of TiO$_2$. This result was also similar to previously reported V doped TiO$_2$ [26]. However, upon addition of catalyst support MCM-41...
Interestingly, the sample prepared using CTAB has a peak at around 240 nm which attributed to tetrahedral Ti species while peak at around 280 nm which attributed to octahedral Ti species [25,26]. The current findings strongly suggested that it is crucial to optimize the uses of surfactant in order to achieve MCM-41 with high surface area. Although the reason is still unclear, it was believed that the high carbon number might cause the excess and unreacted carbon content thus affect the surface area value [34]. As observed, the pore diameter of both TiO$_2$ and V-TiO$_2$ were higher than that of V-TiO$_2$/MCM-41 materials. However, their pore volume was relatively small hence influencing the values of surface area.

The DR UV-Vis spectroscopy analysis as shown in Figure 5 demonstrated a red-shift after the addition of V into TiO$_2$. The shifting to longer wavelength was due to several factors such as the decrease in band gap energy as more rutile phase of TiO$_2$ was formed [25,26]. It was reported that rutile phase has low band gap energy compared to anatase phase [15]. In addition, the increase in crystallite size due to the insertion of V$^{5+}$ ions in the lattice structure was also reported to cause the adsorption in longer wavelength [26]. These results and findings were in agreement with the XRD results that have been discussed aforementioned above. The wide peak at around 240-260 nm corresponded to tetrahedral Ti species while peak at ca. 300 corresponded to octahedral Ti species [25,26].

Table 1. Surface area, pore diameter and pore volume values of synthesized photocatalysts.

| Sample          | Surface Area (m$^2$/g) | Pore Diameter (Å) | Pore Volume (cm$^3$/g) |
|-----------------|------------------------|-------------------|------------------------|
| TiO$_2$         | 12.80                  | 88.56             | 0.028                  |
| V-TiO$_2$       | 16.20                  | 83.00             | 0.034                  |
| V-TiO$_2$/MCM-41(CTAB) | 864.30             | 29.46             | 0.637                  |
| V-TiO$_2$/MCM-41(STAB) | 795.80             | 31.06             | 0.618                  |
| V-TiO$_2$/MCM-41(DTAB) | 812.40             | 30.79             | 0.625                  |

Similarly, the pore volume of V-TiO$_2$ increased remarkably after loading onto MCM-41. Amongst, MCM-41 prepared using CTAB (864.30 m$^2$/g) showed a higher surface area compared to those prepared using STAB (795.80 m$^2$/g) and DTAB (812.40 m$^2$/g). The band gap energy of the prepared samples was determined via Tauc plot and the values are summarized in Table 2. As can be seen in Figure 2, the loading of V into TiO$_2$ has resulted in a decrease in band gap energy. However, the band gap energy increased upon supporting on MCM-41. Since the amount of V-TiO$_2$ was too low to be observed as shown in the respective DR UV-Vis spectra (Figure 6), band gap energy of the samples was determined based on the MCM-41 peak. It is expected that modification of V-TiO$_2$ with MCM-41 would have the band gap energy around ca. 2.7 eV as reported in the literature [26]. It has been reported that the modification with transition metal created an occupied level in the band gap that enabled the highest amount of the tetrahedral Ti species as compared to those prepared using DTAB and STAB. On the other hand, the peak of V$^{5+}$ could not be observed as its concentration was too low.

Figure 5. DR UV-Vis spectra of (a) TiO$_2$ and (b) V-TiO$_2$.

Figure 6. DR UV-Vis DRS spectra of (a) V-TiO$_2$/MCM-41 (DTAB), (b) V-TiO$_2$/MCM-41 (CTAB), and (c) V-TiO$_2$/MCM-41 (STAB).

As can be seen in Figure 6, all the MCM-41 supported samples only showed one intense peak at 260 nm which attributed to tetrahedral Ti species. Interestingly, the sample prepared using CTAB has the highest amount of the tetrahedral Ti species as compared to those prepared using DTAB and STAB. On the other hand, the peak of V$^{5+}$ could not be observed as its concentration was too low.

The band gap energy of the prepared samples was determined via Tauc plot and the values are summarized in Table 2. As can be seen in Figure 2, the loading of V into TiO$_2$ has resulted in a decrease in band gap energy. However, the band gap energy increased upon supporting on MCM-41. Since the amount of V-TiO$_2$ was too low to be observed as shown in the respective DR UV-Vis spectra (Figure 6), band gap energy of the samples was determined based on the MCM-41 peak. It is expected that modification of V-TiO$_2$ with MCM-41 would have the band gap energy around ca. 2.7 eV as reported in the literature [26]. It has been reported that the modification with transition metal created an occupied level in the band gap that enabled the...
photocatalyst to function under visible light as well as to reduce the recombination rate of electron-holes [12,14,19,20].

Table 2. Bandgap energy of TiO$_2$, V-TiO$_2$ and V-TiO$_2$/MCM-41 samples.

| Samples               | Band Edge (nm) | Band gap Energy (eV) |
|-----------------------|----------------|----------------------|
| TiO$_2$               | 417            | 2.97                 |
| V-TiO$_2$             | 500            | 2.47                 |
| V-TiO$_2$/MCM-41(DTAB)| 368            | 3.40                 |
| V-TiO$_2$/MCM-41(CTAB)| 368            | 3.40                 |
| V-TiO$_2$/MCM-41(STAB)| 368            | 3.40                 |

The FESEM images of prepared photocatalysts are shown in Figure 7. Based on the micrographs, it was observed that all the samples showed an irregular shape of aggregates containing the non-uniform shape of fine particles with diameter ranges of 80 – 100 nm. It can be concluded that the addition of V and catalyst support MCM-41 did not give significant changes to the structure of TiO$_2$.

![FESEM images](image)

Figure 7. FESEM images of (a) TiO$_2$, (b) V-TiO$_2$, (c) V-TiO$_2$/MCM-41 (DTAB), (d) V-TiO$_2$/MCM-41 (CTAB), and (e) V-TiO$_2$/MCM-41 (STAB).

The photocatalytic performance of all the prepared photocatalysts was evaluated through the photodegradation of MB at room temperature under irradiation of visible light for 5 hours. The experiments conducted under dark conditions showed that low adsorption (2-3 %) of MB was obtained using all the prepared samples. Based on Table 3, both TiO$_2$ and V-TiO$_2$ demonstrated a low photocatalytic activity as only 2 and 8% of activity, respectively was obtained. The results were also similar to the one that reported in the literature [26] as the addition of V did not give a significant contribution to the photocatalytic activity of TiO$_2$ as V was believed to be formed as bulk on the TiO$_2$ surface since the hydrolysis of TiO$_2$ took place 1 hour prior to addition of V. However, the slight increase in the photocatalytic activity was due to the presence of more rutile phase in V-TiO$_2$. Since rutile phase possesses slightly narrow band gap energy (3.00 eV) [15], therefore, it might work in a low region of the visible light region thus contributing to the better activity. The addition of catalyst support MCM-41 to V-TiO$_2$ had significantly increased the photocatalytic activity up to 57 and 55% for MCM-41 prepared using CTAB and STAB, respectively.

Table 3. Photocatalytic activity of the prepared V-TiO$_2$/MCM-41 with different surfactants.

| Photocatalysts               | Activity (%) |
|-----------------------------|--------------|
| TiO$_2$                     | 2            |
| V-TiO$_2$                   | 8            |
| V-TiO$_2$/MCM-41(DTAB)      | 19           |
| V-TiO$_2$/MCM-41(CTAB)      | 57           |
| V-TiO$_2$/MCM-41(STAB)      | 55           |

Although all the V-TiO$_2$/MCM-41 samples did not show absorption in the visible light region, it was proposed that the high photocatalytic activity achieved by the MCM-41 supported photocatalysts was due to the large surface area and high pore volume. These properties led to more MB molecules being adsorbed to the surface of photocatalyst. As a result, the more adsorbed MB molecules would be accumulated and concentrated close to the V-TiO$_2$ particles which believed to be inside the MCM-41 support. The loaded V into TiO$_2$ particles are suggested to reduce the recombination rate of TiO$_2$, thus leading to higher photocatalytic activity [26,35]. However, the addition of MCM-41 prepared using DTAB showed a slight increase in activity as only 19% was observed. Although the reason is unclear, it was suggested that the low photocatalytic activity was due to the less synergetic interaction for DTAB.
and low efficiency of adsorption with MB. As a result, less phenol molecules could be adsorbed onto the surface [36].

Conclusions

V-TiO₂/MCM-41 photocatalysts were successfully synthesized using different surfactants which were DTAB, CTAB and STAB. The addition of 1 wt% of V into TiO₂ had induced the rutile phase and extended the absorption wavelength in the visible light region thus narrowed the band gap size. Preparation of MCM-41 catalyst support using all three surfactants showed a remarkable increase in the surface area. The high photocatalytic activity was achieved on sample V-TiO₂/MCM-41 (CTAB) as up to 57% of MB was successfully degraded within 5 hours of reaction under visible light irradiation. It was suggested that the high surface area (864 m²/g) and pore volume (0.618 cm³/g) were among the main factors in achieving high activity as more MB could be adsorbed and concentrated directly to V-TiO₂ particles. Besides, usage of CTAB had also contributed to higher crystallinity and higher amount of tetrahedral Ti species, leading to enhanced catalytic activity in the MB degradation. It has been demonstrated that C number of the surfactant used in MCM-41 has a great effect on the properties and catalytic performance of the resulting photocatalysts.

Conflict of Interest

The authors declare that there is no conflict of interest.

Reference

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