**INTRODUCTION**

1. **The reason to choose the subject**

Recently, titanium dioxide was widely used as a photocatalyst. However, only ultraviolet radiation, accounting for about 4% of solar radiation, corresponds to photons with greater energies than the band gap energy of TiO2 is absorbed and produce photochemical efficiency. Therefore, a great number of researches have been done to improve photochemical activity of this catalyst in visible light region. In addition, it also attracted much attention about the coordination of titanium dioxide with nano carbon materials in order to take advantage of out standing properties of these materials such as high electrical conductivity, nano-sized diameter, high adsorption and absolute black level which create a synergistic effect with titanium dioxide, leading to the formation of a catalyst system with great photochemical activity on the surface. This could improve light absorption and reduce the recombination rate of e- and h +, creating separated redox sites.

The common method used to synthesis TiO2/nano carbon composite is sol-gel method withhigh cost titanium alkoxide precusors. This issue together with harsh heating treatment conditions to form anatas phase (the most active phase of TiO2) in the presence of carbon make the cost ofcatalyst increases significantly.

**2. Objectives**

This thesis is aim to synthesis micro nano composite photochemical catalyst based on TiO2 and nano carbon by simple and effective methods from available materials.

1. **Scientific and pratical meanings**

In this study, TiO2/nano carbon composite catalysts with high photochemical activity in visible light region were sucessfully sythesized. Especially, catalyst preparation conditions were systematically investigated. The study demonstrated TIP Growth mechanism of CNF and also showed that synergistic effect between CNT and TiO2 in TiO2 TM/TiO2 sol-gel/CNT catalyst contributed to the catalytic activity improvement of this catalyst compared to the activity of individual components.The thesis preliminarily explored the mechanism of sulfur compounds oxidation reactionoverTiO2/nanocarbon composite. Additionally, through photoluminescence technique, effect of reducing recombination between electrons and fiber optic holes thanks to the presence of CNT in catalystwas demonstrated, thus, mechanism of photochemical enhancement reaction of TiO2 and CNT composites was proposed. These results clearly indicated the scientific value of thisthesis.

The research results about photocatalytic process to handle persistent organic compounds in wastewater and photooxidation of sulfur compounds in fuel revealed the practical value of the thesis which are the premise of researches using photocatalysts in prevention and treatment of environmental pollution.

**4. Innovations and creativities**

**1. Catalyst support based on nano carbon fiber developed on carbon felt was successfully synthesized and development mechanism of nano carbon fiber was proven. This was the first time** TIP Growth mechanism of **CNF formation was successfully demonstrated by SEM technique.**

2. TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/TiO2 sol-gel/CNF catalysts were well synthesized by adhesion of commercial TiO2 and CNT or CNF/C using TiO2 sol-gel adhesive. TiO2TM/CNT-(alginat) was prepared by heterogeneous gelation of commercial TiO2­and CNT using sodium alginate as gelating agent. It was proven that synergistic effect between CNT and TiO2composition in TiO2 TM/TiO2 sol-gel/CNT catalyst contributed to the catalytic activity improvement of this catalyst compared to the activity of individual components.

**3. Effects of catalyst supports on catalytic activity were studied. The experimental results showed that catalyst based on CNF/C support has high activity and stability. After many regeneration times, this catalyst still remained high and stable activity. In contrast, catalyst based on active carbon had very low photochemical effectiveness and catalytic activity sharply decreased with reaction time.**

4. Photo oxidation reaction of DBT and 4,6-DMDBT over TiO2 TM/TiO2 sol-gel/CNT, TiO2 TM/CNT-(alginat), commercial TiO2 and TiO2 TM/TiO2 sol-gel/THTcatalysts the mechanism of oxidation reaction of sulfur compounds on TiO2/nanocarbon composite catalyst was studied. Furthermore, effect of reducing recombination between electrons and fiber optic holes thanks to the presence of CNT in catalystwas demonstrated by photoluminescence method.

**5. Thesis’s structure**

The thesis consits of 130 pages which is divided as following sections: Introduction (02 page), Literature review (38 pages), Experimental (22 pages), Results and discussion (52 pages), conclusion (02 pages), Innovations and creativites (01pages), List of publication (01 page) and References (12 pages). This thesis also icludes 15 tables and 76 figures.

**B – MAIN CONTENTS OF THE THESIS**

**Chapter 1 – LITERATURE REVIEW**

In this chapter, athour give a comprehensive reviewof titanium dioxide based- photochemical material, structure of nano carbon material and synergistic effects between nanocarbon and titanium dioxide as a catalyst for photochemical reactions.

**Chapter 2: EXPERIMENTAL**

Experiments were carried out at Keylaboratory for Petrol chemical and Refinery Technologies, Viet Nam Institue of Industrial Chemistry and University of Science and Technology – the University of Da Nang.

**2.1. Synthesis of catalysts**

**- Synthesis of (CNT) material:** CNT material was synthesized via chemical vapour deposition (CVD) method, using Liquefied Petroleum Gas (LPG) and hydrogen over Fe/γ-Al2O3 catalyst.

**- Synthesis of C - CNF:** C – CNF material was synthesized by CVD with C foil which was impregnated Ni and using LPG and H2 as precursors.

**- Preparation of TiO2 sol-gel as an adhesive:** TiO2 sol-gel was prepare by sol-gel method from titanium isopropoxide (Ti(OC3H7)4) precusor. Effects of molar ratio, hydrolysis time and temperature, pH, aging time and temperature, and post synthesis temperature treatment on TiO2 sol-gel preparation were also investigated.

- **Synthesis of TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/TiO2 sol-gel/CNF catalysts**: TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/TiO2 sol-gel/CNF catalysts were synthesized from a collage of the carbon nanostructures on a TiO2 surface through a TiO2 sol-gel thin layer with weight composition of TiO2 TM/ CNT (CNF)/TiO2 sol-gel are 0,8/0,2/0,05; 0,15/0,2/0,7 and 1/0,3, respectivly.

- **Synthesis of TiO2 TM/CNT-(alginate) catalyst:** TiO2 TM/CNT-(alginate)based- photochemical catalyst was synthesized as follow: TiO2 TMand CNT were dispersed by ultrasonic and then granulated by heterogeneous gelation method in CaCl2 solution with sodium alginate gel system.

- **Sythesis of TiO2 TM/TiO2 sol-gel/THT**: For comparison, TiO2 TM/TiO2 sol-gel/THT catalyst wassynthesized in the same way as the TiO2 TM/CNT-(alginate) catalystwith replacement of CNT by activated carbon and the weight ratio of TiO2 TM/TiO2 sol-gel/THT = 0.8/0.2/20. Norit Rox 0.8 activated carbon was purchased from Norit (USA) with specific surface area of 1195.8 m2/g, pore volume of 0.84 cm3/g and particle size of 10µm. TiO2 TM/TiO2 sol-gel/THT as-synthesized powder were granulated as cylinder shape with diameter of 3 mm and length of 5-7 mm.

**2.3. CHEMICAL PHYSICS CHARACTERIZATION**

Catalyst, material and product samples were characterized by morden techniques such asSEM, TEM, XRD, BET, TG/DTA and photoluminescence.

**2.2. CATALYTIC ACTIVIY STUDY**

**2.2.1. Evaluate photocatalytic activity via methylene blue degradability**

***Model sample:***Prepared methylene blue solution of 200 mg/l. pH of reaction mixture was adjusted by H2SO4and NaOH dilute solution.

***Light sources:*** High pressure mercury lamp and Sunlight.

***2.3.1.1. Evaluate catalytic activity of TiO2TM/TiO2 sol-gel/CNT catalyst***

0.2g of catalyst was added into a glass reactor and 100 ml of methylene blue solution (concentration of 200 mg/L) was poured into the reactor. This solution was then placed in the dark to establish an adsorption-desorption equilibrium. After that reaction mixture was irradiated by high pressure mercury vapor lamp or sunlight. Periodic sampling during the reaction to analyze the remaining concentration of MB and compare to the initial MB concentration, thereby calculating the amount of MB has reacted. Activity of TiO2TM/TiO2 sol-gel/CNT catalyst was also compared to TiO2 TM, TiO2 sol-gel and TiO2 sol-gel/CNT catalysts at the same conditions.

***2.3.1.2. Evaluate catalytic activtyof TiO2TM/TiO2 sol-gel/ CNF catalyst***

Evaluation photocatalytic activity of TiO2TM/TiO2 sol-gel/CNF was conducted in a reactor system using MB solution (200 mg/L) as reagent. MB solution with controlled flow rate was flowed through reactor tubes filled with catalyst. Photocatalytic activiy of TiO2TM/TiO2 sol-gel/ CNF catalyst was compared tocylindrical pellets ofTiO2TM/TiO2 sol-gel/THT catalysts at the same experimental conditons. Effects of retention time, irradiation intensity and catalytic activity durability were studied.

**2.3.2. Application of catalyst in photooxidation reaction of persistent organic compounds in waste water**

Waste water samples from production process of detergent and pesticide which contains much of persistent organic compounds and COD from 215 to 350 mgO/L were used to evaluate photoactivity of the catalysts. Efficiency of the process is determined by analyzing COD index of wastewater samples before and after treatment (ASTM D1252).

**2.3.3. Evaluate catalytic activity of catalysts via photo-oxidationreaction of DBT and 4,6-DMDBT in diesel**

Experiments to evaluate catalytic activity via photo-oxidation reaction of DBT, 4,6 DMDBTand commercial diesel were carried out in photo reactor system with solid catalyst in suspension form.

***2.3.4. Sample analytical methods***

*Sample analytical methods include:*

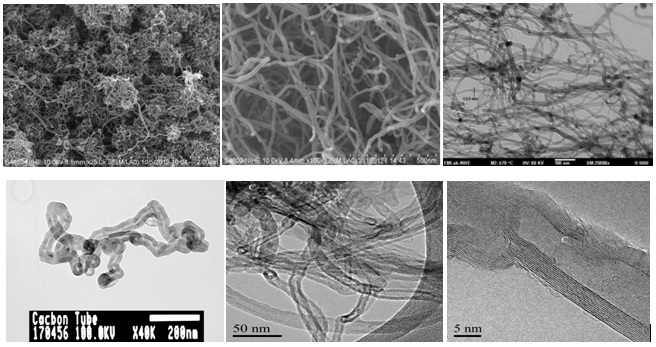
* UV-vis spectra were performed by UV-Vis (JENWAY 6305) spectrophotometerat wave length of 650 nm. This data was utilized to calculate the initial concentration of methylene blue and the concentration of methylene blue after photochemical process.
* COD index of sample before and after treatment were measured according to ASTM D1252, at Analysis Center, Viet Nam Institute of Industrial Chemistry (VIIC).
* HPLC Analyses were performed on an Agilent HPLC 1200 instrument at Key Laboratory for Petrolchemical and Refinery Technologies (Keylab PRT), VIIC.
* GC-MS analyses were carried out on Agilent GC-MS 6890N instrument at Keylab PRT, VIIC.
* Total sulfur content of samples before and after photo-oxidation and adsorption was determined on TS - 100V instrument according to ASTM D5453-06 Trace Sulfur Analyzer at Gasoline, oil and Gas testing laboratory–Quality Assurance and Testing Center 1- No. 8, Hoang Quoc Viet, Cau Giay, Ha Noi.

**Chapter 3: RESULTS AND DISCUSSION**

**3.1. SYNTHESIS OF NANO CARBON**

**3.1.1. Synthesis and characterization of CNTs material**

Microstructure characterization results of as-synthesized CNTs material are illustrated in Fig. 3.1.

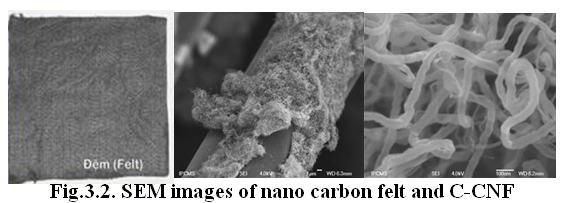


**Fig. 3.1. TEM images of CNTs**

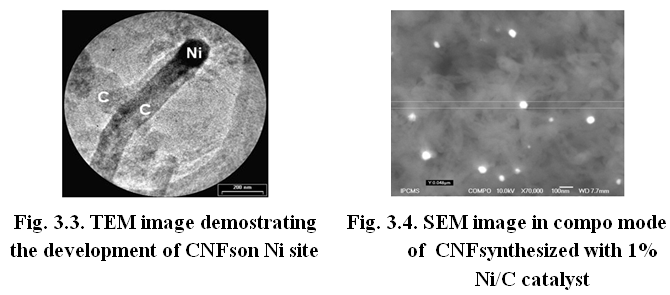
As shown in Fig. 3.1., the obtained CNTsare highly uniform with external diameter of 13 - 20 nm, internal diameter of approximately 10 nm and specific area of 172 m2/g. CNTs have a typical multi-wall structure with thicknessof about 5 nm.

**3.1.2. Synthesis of C-CNF material**

Figure 5 shows SEM micrographs of carbon-felt, CNF/carbon-felt and CNFs on the surface ofcarbon-felt. It was found that the diameter of the CNFs was approximately 50 nm. CNFs showed robust attachment to the carbon-felt surfaces.

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TEM image of CNFs (Fig. 3.3) shows that Ni catalyst sites were pushed off the surface of the support and located at the top of nano carbon fiber.



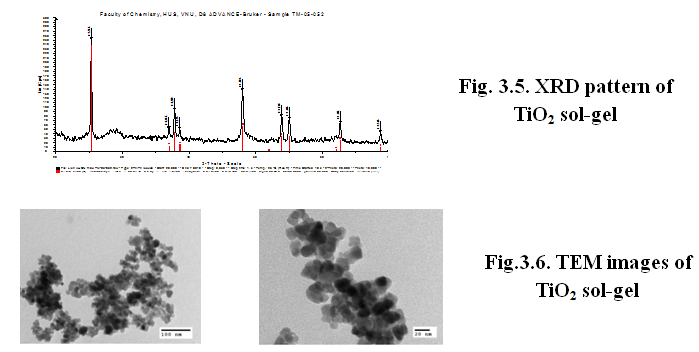
SEM image in compo mode of CNFs is illustrated in Fig. 3.4. which indicates the presence of Ni particles.The bright spots are Ni particles with high electron density and great electrical conductivity while the dark spots are CNFs

**3.2. SYNTHESIS OF PHOTOCATALYST BASED ON TiO2/NANO CARBON“COMPOSITE”**

**3.2.1. Synthesis of adhesive based on TiO2 sol-gel**

Effects of various parameters on synthesis of TiO2 sol-gelwere investigated. The suitable synthesis parameters are as follows:gel composition: Ti/EtOH/HNO3 = 1/17/0,1; pH of reaction mixture = 3; Hydrolysis temperature: ambient temperature; hydrolysis time: 5 hours; aging temperature: room temperature; aging time: 4 days; TiO2 sol-gel was dried at 80oC for3 h; calcinated sample at 350oC for 3h.

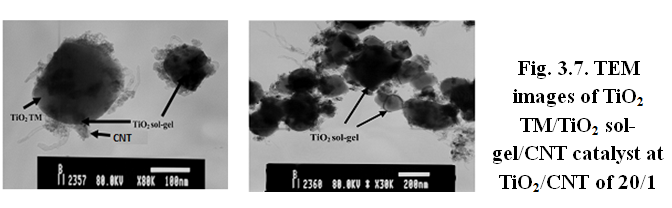
With these conditions, as-prepared TiO2 sol-gel has small particle size, SBET of99.2 m2/g, well-dispersed and could be use as a suitable adhesive for TiO2/nano carbon. In addition, this material also has some chemical physic characteristics as shown in Fig. 3.5. and Fig. 3.6.

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**3.2.2. Synthesis ofTiO2 TM/TiO2 sol-gel/CNT catalyst**

***3.2.2.1. Characterization of TiO2 TM/TiO2 sol-gel/CNT catalyst***

The TiO2/TiO2 sol-gel/CNTs composite was investigated by transmission electronic microscopy (TEM), and the results are given in Figure 3.7. We could identify from these images that the CNTs were ‘glued’ on the TiO2 surface due to the presence of a TiO2 sol–gel layer; moreover, these TEM images also revealed good mechanical stability for this complex composite. In fact, this composite resisted high-power microwave radiation for an extended period on the TEM sample preparation stage with no observable isolated carbon nanostructures.



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|  | **Fig. 3.8. Photocatalytic activity ofcommercial TiO2and TiO2/CNT catalysts** |

Catalytic activity of TiO2/CNT in comparison with that of commercial TiO2through MB degradation reaction was showed in Fig. 3.8. The experimental result revealed that TiO2 TM/TiO2 sol-gel/CNT catalyst had much higher photo catalytic activity than that of commercial TiO2.

***3.2.2.2. Evaluate catalytic activity of TiO2 TM/TiO2 sol-gel/CNT catalyst in Metylen Blue (MB) photochemical reaction under radiation of high pressure mercury lamp***

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|  | **Fig. 3.9: Activity of different catalysts in MB photochemical reaction** |

In case of TiO2 sol-gel/CNT 350 catalyst, in the first 20 minutes, MB conversion was quite high and higher than that of TiO2 TM and TiO2 sol-gel 600 catalysts. In the next reaction time, catalytic activity of TiO2 sol-gel/CNT 350 is lower than that of TiO2 TM and TiO2 sol-gel 600. Activity of TiO2 sol-gel/CNT 600 catalyst was fluctuated with reaction time which is similar to that of TiO2 sol-gel/CNT 350 catalyst but at a higher level of activity. Especially, among these catalysts, TiO2 TM/TiO2 sol-gel/CNT 350 had highest activity which was 10% higher than activity of TiO2 TM catalyst. This result indicated that composite catalyst with higher activity was successfully synthesized.

* + - 1. ***Catalytic activity ofTiO2 TM/TiO2 sol-gel/CNT catalyst in Metylen Blue (MB) photochemical reaction using sunlight radiation***

1. *Effect of sunlight intensity on MB conversion*

Experimental conditions were as follow: ratio of catalyst (g)/MB solution of 200 ppm (volume) was 0.2, reaction time was 30 minutes. MB degradation yield was determined by analyzing the obtained solution after the reaction time to time.Sunlight intensity was assessed through luminous flux density on a surface area of the reaction tube by illuminance measurements of solar light on catalytic surfaces, units Klux.

Effect of sunlight intensity on MB conversion at various times from 8 h to 18 h in sunny days was presented in Fig. 3.10.

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|  | **Fig.3.10. Effect of light intensity on MB conversion (form8 a.m to 18 pmin sunny days)** |

The results showed that, in the sunny days, there was a significant change in the sunlight intensity at different times of day, therefore, MB conversion also tend to change with the change of sunlight intensity and the stronger sunlight intensity was, the higher MB conversion was.

The study results about influence of sunlight intensity in cloudy days at time frame from 8h to 17 h 30 were showed in Fig.3.11.

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|  | **Fig. 3.11. Effect of light intensity on MB conversion (from 8 a.m to 17.30 pm in the cloudy days)** |

The rerulsts showed that in the cloudy days with low sunlight intensity, catalyst still exhibited activity but not high processing efficiency. To improve the efficiency and capacity of the process, it requires the support of the other artificial light sources which have a higher light intensity and more stable.

1. *Using lamps in cloudy days or night time*

Experiments were carried out in the early evening or night time (from 18h to 24h the day before and from 0h to 7h next day), when there was no sunlight or the light was very weak. Light source was used high pressure mercury lamp (Osram) with power of 500W and average light intensity at the surface reaction of 102 Klux.Investigated results about MB conversion versus lighting time were showed in Fig. 3.12.

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|  | **Fig. 3.12. MB conversion from 18p.m of the day before to 7 a.m of the next day (using high pressure mercury lamp)** |

As seen from Fig 3.1.2, when using high pressure mercury lamp, light intensity was stable so MB conversion is constant during reaction time from 18 p.m to 7 a.m and reached the equivalent value of MB conversion in sunny days. Hence, in the night time or the days with bad weather such as cloudy or rainy and so on, it is possible to use high pressure mercury lamp to replace the sunlight soure.

**3.2.3. Synthesis ofTiO2TM/CNT-(alginate) using sodium alginate as an adhesive**

Specific surface area of TiO2TM/CNT-(alginate) catalysts with different TiO2/CNTweightratio was showed in table 3.1.

**Table 3.1. Specific area (SBET) ofTiO2/CNT**

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| **Sample** | **TiO2/CNT weight ratio** | **SBET (m2/g)** |
| TiO2 | - | 8.4 |
| TiO2/CNT20/1 | 20/1 | 17.3 |
| TiO2/CNT10/1 | 10/1 | 34.2 |
| TiO2/CNT3/1 | 3/1 | 38.3 |

The results indicated that the specific surface area of TiO2TM/CNT (alginate) increased sigfinicantly witht the raise of CNT content in the sampleThis can be explained that because CNT has a high specific surface area so the combination of CNT with commercial TiO2 increases the specific surface area of TiO2 TM / CNT (alginate) compared with commercial TiO2 (8.4 m2/g).

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|  |  | **Fig.3.13. SEM images ofTiO2TM/CNT (alginate) samples with TiO2/CNT weight ratio of (a) TiO2 (b) 20/1, (c) 10*/*1 and (d) 3/1** |
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Figure 3.13illustrated SEM images of TiO2TM/CNT (alginate)with various weight ratio of TiO2/CNT. As seen in Fig. 3.13 b, at TiO2/CNTweight ratio of 20/1, few CNTs were interwoven among the TiO2 particles.. At a 10/1weight ratio, the CNTs were in contact with each other and interwoven among the TiO2 particles (Fig. 3.13 c). At a 3/1 weight ratio (Fig. 3.13d) CNTs are well dispersed, draping over and nearly covering some of the TiO2 particles. It was found that the CNTs are uniformly distributed and are mixed well with TiO2, forming uniform microstructures in the TiO2TM/CNT (alginate) composite.

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|  |  | **Fig. 3.14. TEM images of TiO2TM/CNT (alginate) samples with TiO2/CNT weight ratio of (a) TiO2, (b) 20/1, (c) 10/1 and (d) 3/1** |
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Fig. 3.14. showed TEM micrographs of TiO2/CNTs composites with different TiO2/CNTs weight ratios. It was found that few CNTscover the TiO2 particles in TiO2/CNTs composites with weight ratio of TiO2/CNTs of 20/1 (as shown in Fig. 3.14 (b)). When the content of CNTs in the CNTs/TiO2composites increased and the weight ratios became 10/1 and 3/1, the CNTs came in contact with each other and embedded the TiO2 particles (as shown inFig.3.1.4 (c) and (d), respectively). When the TiO2/CNTs composites had weight ratio of 3/1, the CNTs were uniformly dispersed and covered all the TiO2 particles. This indicates again that CNTs were well dispersed on the surface of the TiO2particles and that the CNTs and TiO2 particles were in close contact with each other.

XRD patterns of CNT, TiO2andTiO2TM/CNT (alginate)(TiO2/CNT = 20/1) after calcination at 400oC for5h were exhibited in Fig. 3.15.

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|  | **Fig. 3.15. XRD patterns of (a) CNT, (b) TiO2 TM and (c) (20/1) TiO2TM/CNT (alginate)** |

A characteristic peak of the CNTs corresponding to the reflection planes was identified (shown in Fig. 3.15a). In this sample, only the anatase phase appeared in the TiO2 and CNTs/TiO2 composite. The reflection at around2 θ = 48.18º was attributed to the crystalloid form of anatase TiO2,where there was no interference from CNTs. From the comparison of spectra between Fig. 3(b) and (c), the structure of TiO2 in the CNTs/TiO2 catalyst is almost the same. This indicatedthat there was no difference in the microstructure of TiO2before and after combination with MWNTs.

Results of photocatalytic activity test in MB degradation reaction were illustrated in Fig. 3.16.

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|  | **Fig. 3.16. Catalytic activity of (20/1) TiO2 TM/CNT-(alginate) catalyst** |

The obtained results showed that similar to TiO2 TM/TiO2 sol-gel/CNT catalyst, combination between TiO2and CNT using heterogeneous gelation methodhad also resulted in the formation of catalyst with much higher activity in comparison with that of TiO2.

Photoluminescence is usuallyemployed to investigate surface structure and excited states andto follow surface processes involving the electron/hole fate of TiO2. Fig. 3.17presented the photoluminescence spectra of the TiO2 TM/CNT-(alginate) composite with various CNTs/TiO2weight ratios. The photoluminescence spectrum for anatase TiO2 showed a characteristic by a broad peak at around 475 nm, whereas no luminescence of MWNTs is observedin the range of 450–650 nm. The photoluminescence intensities of TiO2 TM/CNT-(alginate)composites with various mass ratios were lower than that of TiO2 indicating reduced charge recombination of TiO2 TM/CNT-(alginate)composites in comparison to TiO2 anatase alone. In other words, the combination of CNTs and TiO2 contributed to improving photocatalytic activity of TiO2.

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| Description: huynh quang  (a)  (b)  (c)  (d)  (e) | **Fig. 3.17. Photo luminescence spectra of TiO2 TM/CNT-(alginat) with CNT/TiO2weight ratio of: (a) TiO2, (b) 1/20, (c) 1/10, (d) 1/3 and (e) CNT** |

**3.2.4. Study on synthesis of TiO2 TM/TiO2 sol-gel/CNFcomposite**

***3.2.4.1. Characterization of TiO2 TM/TiO2 sol-gel/CNFcomposite***

Effects of weight ratioofTiO2 TM/TiO2 sol-gel/CNF was indicated in Fig. 3.18.

Results showed that with weight ratio of TiO2 TM / TiO2 sol-gel / CNF of 0.8 / 0.2/0.7, the obtained material had the most uniform TiO2 TM distribution on CNF surface and most of CNF surface was covered by TiO2 TM. With other weight ratio of TiO2 TM/TiO2 sol-gel/CNF, TiO2 TM has not been distributed unifromly on CNF surface. At lower ratio, There was presence of some positions without TiO2 (Fig 3.18a) and at higher ratio, CNF surface was covered with a thich layer of TiO2 TM (Fig 3.18 c, d).

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| Description: D:\PTNTD LHD\De tai nghi dinh thu\Tài liệu TiO2-NDT-Lien\TEM\TiO2-CNF-01-001\TiO2-CNF-01-001_q126.tif  **(a)** |  | **Fig.3.18.SEM images of TiO2 TM/TiO2 sol-gel/CNFsamples with the ratio of**  **(a) 0.8/0.2/1.0**  **(b) 0.8/0.2/0.7**  **(c) 0.8/0.2/0.6**  **(d) 0.8/0.2/0.5** |
| **(c)** | Description: D:\PTNTD LHD\De tai nghi dinh thu\Tài liệu TiO2-NDT-Lien\TEM\TiO2-CNF-01-001\TiO2-CNF-01-001_q136.tif  **(d)** |

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|  | **Fig.3.19. SEM image of TiO2 TM/TiO2 sol-gel/CNFcatalyst with TiO2 TM/TiO2 sol-gel/CNFof 0.8/0.2/0.7** |

***3.2.4.2. Evaluate catalytic activity of TiO2 TM/TiO2 sol-gel/CNF catalyst in photooxidation MB reaction***

Catalytic activity of TiO2 TM/TiO2 sol-gel/CNF catalyst and TiO2 TM/TiO2 sol-gel/THT reference catalyst in MB photo oxidation reactionwas presented in Fig. 3.20. The experimental results revealed that TiO2 TM/TiO2 sol-gel/CNF had a very high andstable activity, however, TiO2 TM/TiO2 sol-gel/THT catalyst showed a low photochemical efficiency and catalytic activity decreases dramatically with reaction time.

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|  | **Fig. 3.20: Activityof TiO2 TM/TiO2 sol-gel/CNFandTiO2 TM/TiO2 sol-gel/THT catalysts** |

***3.2.4.3. Preliminary study of stability of TiO2 TM/TiO2 sol-gel/CNF catalyst***

The change of MB conversion over reaction time and regenration was shown in Fig. 3.21.

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|  | **Fig. 3.21: Catalytic activity stablity of TiO2 TM/TiO2 sol-gel/CNF** |

It was found that in the first time, catalytic activity was highly stable and MB conversion reaches 100% within 80 hours. After the first regenaration, MB conversion was stable at 100% during 20 hours. After the second regenaration, MB conversion remain in a constant at 100% during 18 hours. Catalytic activity still remained the same initial value after the third regeneration. Hence, it can be concluded that as-prepared catalyst has high activity, long life time and easy to regenarate.

**3.2.3. INITIAL STUDY ON APPLICABILITY OF CATALYST IN HANDLING OF ORGANIC COMPOUNDS IN WASTE WATER**

Catalytic activity evaluation results of catalyst in degradation reaction of organic compounds in waste water from detergent production and pestiside production were indicated in Fig. 3.22.

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|  | **Fig. 3.22: COD index of waste water vs. reaction time over TiO2 TM/TiO2 sol-gel/CNT catalyst** |

The results showed that COD indexes of all three waste water samples decreased after 1 h reaction. The coresponding COD indexes were 30 mgO/l, 41 mgO/l and 52 mgO/l which almost meet the standard of A classification waste water and are equivalent to the conversion of 84% to 86% in comparison with intial COD indexes. These results also revealed the efficiency of organic compounds treatment over TiO2 TM/TiO2 sol-gel/CNT photo catalyst and practical applicability of this catatlyst.

**3.4. EVALUATE CATALYTIC ACTIVITY THROUGH OXIDATION ABILITY OF DIBENZOTHIOPHEN AND 4,6-DIMETYL DIBENZOTHIOPHEN**

**3.4.1. Determine suitable conditions for photo oxidation reaction**

In order to find out the suitable reaction conditions, DBT and 4,6-DMDBT photo oxidation reactions were carried out over TiO2 TM/TiO2 sol-gel/CNTcatalyst with weight ratio of = 0,8/0,2/0,05 (noted as XT-1). GC-MS and HPLC methods were used to analyse the reaction product.

HPLC and GC-MS spectrum of DBT and 4,6-DMDBT solution before and after photo oxidation reaction over XT-1 catalyst and after adsortion process were shown in from Fig.3.23 to Fig. 3.3.0.



**Fig. 3.23: HPLCspectra of (a) DBT, (b)DBT solution after photo-oxidation reaction and (c) DBT solution after photo-oxidation reaction and adsorption by silicagel**



**Fig.3.24: HPLCspectra of (a) 4,6-DMDBT, (b) 4,6-DMDBT solution after photo-oxidation reaction and (c) 4,6-DMDBT solution after photo-oxidation reaction and adsorption by silicagel**

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|  | | **Fig. 3.25: GC-MS spectra of DBT in tetradecane solvent** | | |
|  | | **Fig. 3.26: GC-MS spectra of DBT in tetradecanesolvent after photo-oxidation reaction** | | |
|  | | **Fig. 3.27: GC-MS spectra of DBT in tetradecaneafter phot-oxidation reaction and adsorption** | | |
|  | **Fig. 3.28: GC-MS spectra of 4,6-DMDBT in tetradecane** | | | |
|  | | | **Fig. 3.29: GC-MS spectra of 4,6-DMDBT in tetradecaneafter photo-oxidation reaction** | | |
|  | | | | **Fig. 3.30: GC-MS spectra of 4,6-DMDBT in tetradecaneafter phot-oxidation reaction and adsorption** | |

It can be seen that there were some products were formed after photochemical reaction and most of them were adsorbed by silicagel. Thus, chromatography analytical methods had proven that through photochemical process over TiO2-carbon nanotubes composite, S compounds which are difficul to be adsorbed by silicagel were transformed into more polarized compounds which are gentle to be adsorbed by silicagel. Consequently, S content was falled to very low value at soft conditions such as atmospheric temperature and pressure that current HDS methods can not achieve.

**3.4.2 Studycatalytic activity of catalysts in DBTand4,6-DMDBT photo oxidation reaction**

Catalysts:

XT-1: TiO2 TM/TiO2 sol-gel/CNT = 0,8/0,2/0,05

XT-2: TiO2 TM/TiO2 sol-gel/THT = 0,8/0,2/20

XT-3: TiO2 TM/CNT-(alginate) = 1/0,05

XT-4: TiO2 TM/CNT-(alginate) = 1/0,3

Conversion of DBT and 4,6-DMDBTcalculating based on the decrease of total S content of product after reaction and absorption process was illustrated in Fig.3.31and3.329.

|  |  |
| --- | --- |
|  | **Fig 3.31: DBT DMDBT conversion over different catalysts** |

As shown in Fig. 3.31, all catalysts exhibited higher activity than that of commercial TiO2. Especially, catalytic activity of XT-4 catalystwas almost 2 times higher than that of TiO2 TM and this catalyst was the most effective catalyst.

|  |  |
| --- | --- |
|  | **Fig. 3.32: 4,6-DMDBT conversion over different catalysts** |

The above results clearly showed the role of carbon nanotubes in the catalytic activityenhancement of TiO2.In other words,there was asynergistic effect between TiO2 and nanocarbon in photochemical process.

**3.4.3 Study on catalytic activity stability**

The study results were showed in Fig. 3.33.

|  |  |
| --- | --- |
|  | **Fig. 3.33.Conversion of DBT and 4,6 DMDBT vs catalyst reused times** |

For both sulfur compounds (DBT và 4,6 DMDBT), after 11 regeneration times, catalytic activity, which was reflected by conversion, began downward trend. Excluding catalytic shrinkage factor when separating catalyst for recycling,the reduction of catalytic activity can be explained by the presence of impurities in materials and products as well as other compoundsdeposited on surface of catalyst whichcould cover active sites.

**3.4.4 Preliminary research on catalyst regeneration process**

Organic solvents were employed to regenerate catalyst. Catalyt regeneration process consited of two stages as below:

* Stage 1: Using n- hexane solvent to separate non-polar compound such as hydrocarbons from catalyst.
* Stage 2: Using acetone solvent to separate polar compounds from catalyst.

After solvent washing process, catalyst was dried at 100ºC for 1h before using in next photochemical process.

**3.4.5. Initial study on sulfur compound removal abiltiy of catalyst**

Catalytic activity of XT-3 catalyst in photo oxidation reaction of sulfur compounds in diesel was compared to that of TiO2 TM. Total S content of two commercial diesel samples are 0.25%S and 0.05%S, corresponding to 1500 ppm and 4700 ppm, respectively. After preliminary treatment by silica, S content decreased by 714 ppm and 201 ppm, respectively.

S contetnt of two commercial diesel samples after photo oxidation versus reaction time were shown in Fig 3.34 and Fig. 3.35.

|  |  |  |
| --- | --- | --- |
|  | | **Fig.3.34: S content in diesel of 0.25 % S vs. reaction time** |
|  | **Fig.3.35: S content in diesel of 0.5 % S vs. reaction time** | |

The results in Fig. 3:34 and Fig.3:35 showed that for both diesel samples, the S content in dieselafter two hours of photocatalyst treatment over XT-3 and silicagel adsorption was very low (only trace), whereas, in case of TiO2 TM, the remaining sulfur content in diesel was still quite high. There was a fact that the conver sion of S compounds over TiO2 TM catalystwas lower than that of the TiO2 – CNT composite photocatalyst. This, once again showed the efficiency of synergistic effect between CNTs and TiO2 in the removal of sulfur compounds.

**CONCLUSION**

* + **Catalyst support based on nano carbon fiber developed on carbon felt was successfully synthesized and development mechanism of nano carbon fiber was proven. This is the first time** TIP Growth mechanism of **CNF formation was successfully demonstrated by SEM technique.**
  + TiO2 sol-gelsynthesis was systematically studied. This material was used as ahsevie to prepare TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/TiO2 sol-gel/CNF catalyst. The suitable synthesis conditions for TiO2 sol-gel were as follow: mol ratio of Ti/EtOH/HNO3 = 1/17/0,1; pH = 3; hydrolysis at room temperature for 5h; gelate at room temperature for 4 days; dry at 80oC for 3h; calcinate at 400oC for 3h;
  + TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/TiO2 sol-gel/CNF catalysts were well synthesized by adhesion of commercial TiO2 and CNT or CNF/C using TiO2 sol-gel adhesive. TiO2 TM/CNT-(alginat) was prepared by heterogeneous gelation of commercial TiO2­and CNT using sodium alginate as gelation agent. The optimum weight ratio of components in catalyst were0,8/0,2/0,05; 0,15/0,2/0,7 and 1/0,3, respectively.
* It is proven that synergistic effect between CNT and TiO2 composition in TiO2 TM/TiO2 sol-gel/CNT catalyst contributed to the catalytic activity improvement of this catalyst compared to the activity of individual components.
* **Effects of catalyst supports on catalytic activity were studied. The experimental results show that catalyst based on CNF/C support has high activity and stability. After many regeneration times, this catalyst still remain high and stable activity. In contrast, catalyst based on activated carbon has very low photochemical effectiveness and catalytic activity sharply decreased with reaction time**.
* Applicability of TiO2 TM/TiO2 sol-gel/CNTandTiO2 TM/TiO2 sol-gel/CNF catalyst in the treatment of persistent organic compounds in waste water from detergent production and pesticide production under visible light region was researched. The results reveal that both catalysts have high efficiency and COD index of waste water reduced about 84-88%.
* Photo catalytic activity of TiO2 TM/TiO2 sol-gel/CNT and TiO2 TM/CNT-(alginat) catalysts in DBT and 4,6-DMDBT photo oxidation reaction was studied in comparison with that of commercial TiO2 and TiO2 TM/TiO2 sol-gel/THT. It can be seen that catalyst based on TiO2 and nanocarbon had much higher activity thant that of commercial TiO2. Particularly, catalyst based on commercial TiO2 and carbon nanotubes composite with weight ratio of 1/0.3, prepared by heterogeneous gelation method shows highest activity. Moreover, the suitable parameters for DBT and 4,6-DMDBT photo oxidation process were as follow:

+ Catalyst: (1:0,3) TiO2 TM/CNT-(alginat)

+ Ratio of catalyst/feedstock: 0,5 g/60 ml

+Reaction time: 2-3 h

+ Reaction temperature: ambient temperature

+ Light sources: high pressure mercury lamp or sunlight.

* Applicability of TiO2 TM/CNT-(alginat) catalyst in photo oxidation reaction of sulfur compounds in diesel was investigated. The results showedTiO2 TM/CNT-(alginat) catalyst exhibited high activity in sulfur compounds thorought removement which is much higher than that of TiO2 TM.

Mechanism of photo oxidation reaction of sulfur compounds over TiO2/nanocarbon composite was preliminary explored. In addition, effect of reducing recombination between electrons and fiber optic holes thanks to the presence of CNT in catalyst was demonstrated by photoluminescence method, thus, the mechanism of strengthening photochemical reaction over TiO2/CNT composite was proposed.

**LIST OF PUBLICATION**

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