PHOTOCATALYTIC OXIDATION OF PHENOL, CYCLOHEXANOL AND HEXANOL BY TITANIA DISPERSED ON MESOPOROUS SILICA MCM-41

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I dedicated this work to my beloved parents, Mohd Nor Ahmad and Salamah Ahmed, my loving husband, Elham Mazalan, as well as my brothers Mohd Nuraffandi, Nur Izzat and my sisters Nur Umi Rasyidah, Nur Umi Umairah who have always been there for me. I love you all.

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ABSTRAK

Alkohol adalah sebatian yang berguna tetapi pendedahan kepada alkohol yang berlebihan adalah berbahaya kepada manusia dan perlu dirawat. Oleh itu, fotopemangkinan telah dicadangkan sebagai kaedah alternatif untuk pengoksidaan alkohol dan titanium dioksida (TiO_2) dikenal pasti sebagai fotomangkin yang paling berpotensi. Dalam kajian ini, untuk meningkatkan keberkesanan TiO_2, siri TiO_2-MCM-41 telah disediakan dengan kaedah pengisitepuan. Corak pembelauan sinar-X dan analisis penjerapan-penyaherapan mendedahkan kejayaan pembuatan MCM-41. Corak pembelauan sinar-X juga menunjukkan bahawa fasa tulen TiO_2 yang disediakan adalah anatas. Struktur MCM-41 dapat dikekalkan apabila jumlah muatan TiO_2 adalah rendah (sehingga 5 wt%). Kejayaan pembentukan TiO_2-MCM-41 juga telah disahkan oleh spektroskopi pendarfluor. Sebaliknya, spektrum pantulan serakan ultralembayung-cahaya nampak menunjukkan sampel dengan muatan 5 wt% TiO_2 adalah yang paling tersebar di kalangan sampel TiO_2-MCM-41. Penyebaran TiO_2 yang baik pada MCM-41 juga dapat dilihat melalui analisis mikroskopi imbasan elektron pancaran medan dan pemetaan tenaga sebaran sinar-X. TiO_2-MCM-41 dengan berat 5% TiO_2 (TiO_2(5)-MCM-41) juga menunjukkan nombor perolehan (TON) yang paling tinggi iaitu 0.27 untuk pengoksidaan fenol. Penyelerakan TiO_2 dan pengekalan struktur MCM-41 dicadangkan sebagai parameter yang penting untuk aktiviti yang tinggi bagi fotomangkin tersebut. Kajian kinetik mendedahkan bahawa pengoksidaan fenol mengikuti tindak balas tertib pertama dengan kadar pemalar 0.33 h^{-1}, manakala kajian terhadap mekanisme tindak balas mencadangkan bahawa lubang positif bertindak sebagai tapak aktif dalam pengoksidaan fenol. Aktiviti fotomangkin yang terbaik, TiO_2(5)-MCM-41 juga diuji untuk pengoksidaan sikloheksanol dan heksanol. Fotomangkin menunjukkan peningkatan aktiviti pengoksidaan mengikut urutan heksanol<sikloheksanol<fenol. Adalah disarankan bahawa interaksi dan penjerapan yang paling kuat antara fenol dan fotomangkin mendorong kepada aktiviti yang tertinggi. Sebaliknya, pengoksidaan sikloheksanol mengikuti tertib kedua dengan kadar pemalar 0.026 $M^{-1} h^{-1}$ manakala, pengoksidaan heksanol mengikuti tertib pseudo pertama dengan kadar pemalarnya 0.014 h^{-1}. Keputusan ujian pemerangkap mencadangkan radikal superoksida bertindak sebagai spesies aktif untuk kedua-dua pengoksidaan sikloheksanol dan heksanol.

ABSTRACT

Alcohol is a useful compound, but the excessive exposure of alcohol is hazardous to human and must be treated. Therefore, photocatalysis has been proposed to be an alternative method to oxidize the alcohol and titanium dioxide (TiO_2) has been recognized as the most potential photocatalyst. In this study, in order to increase the efficiency of TiO_2, TiO_2-MCM-41 series were prepared by an impregnation method. The X-ray diffraction patterns and nitrogen adsorption-desorption analysis revealed the successful formation of MCM-41. The X-ray diffraction patterns also showed that the pure phase of TiO_2 is anatase. The structure of MCM-41 was maintained when the loading amount of TiO_2 was low (up to 5 wt%). The successful formation of TiO_2-MCM-41 was also confirmed by fluorescence spectroscopy. On the other hand, diffuse reflectance ultraviolet visible spectrum showed that the sample with 5 wt% of TiO_2 (TiO_2(5)-MCM-41) loading has the most dispersed TiO_2 among the TiO_2-MCM-41 samples. The good dispersion of TiO_2 on the MCM-41 was also observed by field emission scanning electron microscopy and the energy dispersive X-ray mapping analyses. The TiO_2-MCM-41 with 5 wt% of TiO_2 loading showed the highest turnover number (TON) which is 0.27 for phenol oxidation. The dispersion of TiO_2 and well maintained MCM-41 structure were proposed to be the important parameters for the high activity of the photocatalyst. The kinetic study revealed that phenol oxidation followed first order with the rate constant of 0.33 h^{-1}, while the study on the mechanism of reaction proposed that the positive holes acted as the active sites in phenol oxidation. The activity of the best photocatalyst, TiO_2(5)-MCM-41 was also tested for oxidations of cyclohexanol and hexanol. The photocatalytic activity increased in the order of hexanol < cyclohexanol < phenol. It is suggested that the strongest interaction and adsorption between phenol and the photocatalyst led to the highest activity. In contrast, cyclohexanol oxidation followed second order with the rate constant of 0.026 $M^{-1} h^{-1}$ while, the hexanol oxidation followed pseudo-first order with the rate constant of 0.014 h^{-1}. Scavenger tests results proposed that the superoxide radicals acted as the active species for both cyclohexanol and hexanol oxidations.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

arb.u	-	Arbitrary unit
cm	-	Centimeter
eV	-	Electron volt
UV	-	Ultra Violet
Å	-	Angstrom
K	-	Kelvin
W	-	Watt
GC-FID	-	Gas Chromatography-Flame Ionization Detector
GC-TCD	-	Gas Chromatography-Thermal Conductivity Detector
wt%	-	Weight percent
ppm	-	Part per million
mV	-	Millivolt
g	-	Gram
V	-	Volt
μm	-	Micrometer
mL	-	Milliliter
nm	-	Nanometer
h	-	Hour
s	-	Second
min	-	Minute
mmol	-	Millimol
L	-	Litre
XRD	-	X-ray Diffraction
DR UV-Vis	-	Diffuse Reflectance Ultra Violet-Visible
FESEM	-	Field Emission Scanning Electron Microscopy
EDX	-	Energy Dispersive X-ray

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Alcohol is widely used in many industrial applications. However, the excessive amounts of alcohol in our environment will give bad impacts to human being, such as lung cancer, bronchitis, brain damage and others. Therefore, before its disposal to our environment, alcohol should be converted to more useful compounds, such as aldehyde that can be used in drug delivery, perfumery, pharmacist and food industries and carboxylic acid that is an intermediate for organic synthesis. Another approach is to convert alcohol to harmless compounds, such as CO_2 and H_2O (Adan *et al.*, 2009; Augugliaro *et al.*, 2008).

In the early 80's, some strong oxidation reagents such as $KMnO_4$ and CrO_3 were introduced to increase the performance of alcohol oxidation reaction. Unfortunately, some drawbacks have been recognized, which are expensive, can cause explosion if misuse them and not environmentally friendly. In order to overcome these problems, heterogeneous catalysts have been proposed. Compared to the homogeneous catalysts, heterogeneous catalysts are easier to be handled and can be reused, thus giving more benefits for industrial processes (Anpo *et al.*, 2009; Endud & Wong, 2007).

Recently, photocatalytic oxidation of alcohol has become one of the alternative methods to convert alcohol to more useful or harmless compounds via partial or complete oxidation processes, respectively. This is due to the fact that the

photocatalytic oxidation process can occur at ambient temperature and pressure in the presence of photocatalyst and light source, either UV or visible light. Light is considered as non-toxic and ideal to be used in the environmentally friendly green process. Light also generates no waste and can be obtained from the renewable source, which is the sun (Higashimoto *et al.*, 2009).

Titanium dioxide (TiO_2) is one of the most studied photocatalysts. TiO_2, especially anatase phase, has been investigated in various photocatalytic reactions due to its large band gap (3.2 eV), which gives a strong absorption in the ultraviolet (UV) region. TiO_2 is usually active for total oxidation reaction (Lachheb *et al.*, 2011), for instance it is active for complete oxidation of phenol (Zheng *et al.*, 2000). It has been proposed that the continuous irradiation should produce many electrons and holes on the surface of titanium that could degrade the organic pollutant.

On the other hand, the highly dispersed TiO_2 on supports, such as silica showed good activity for partial oxidation reaction (Yoshida, 2003). Unfortunately, there are still no clear comparison studies between TiO_2 and highly dispersed TiO_2 when they are used for oxidation of specific alcohols under the same conditions. In this study, TiO_2 and highly dispersed TiO_2 series were prepared by impregnation method. Mesoporous silica, MCM-41 was used as the support material for the dispersion of TiO_2. This is due to the remarkable properties of MCM-41, which are uniform cylindrical pores of diameter varying from 15 to 100 Å, high surface area of around 1000 m^2/g and long range ordering structure of hexagonal arrangement (Atchudan & Pandurangan, 2012; Zhao *et al.*, 1996).

In this study, the performance of bulk and dispersed TiO_2 were examined for oxidation of alcohols. In the photocatalytic reactions, many parameters would affect the activity of the degradation of alcohols such as crystallinity of photocatalyst, concentration of pollutant, oxidation potential of pollutants and others. The use of different types of alcohols might also give influences in the performance of the photocatalysts since it gives different results in the terms of activity and also selectivity for partial or complete oxidation reactions (Koodali & Zhao, 2010). These points were revealed in this study.

1.2 Statement of Problem

TiO_2 has been recognized as the most appropriate and potential photocatalyst for the oxidation of organic pollutants to form non-hazardous compounds, which are CO_2 and H_2O. However, there are some drawbacks of TiO_2, such as low crystallinity due to the agglomeration of active site, which resulted in low activity of the reaction (Reddy *et al.*, 2004). Therefore, modification of TiO_2 using support material is important in order to decrease the agglomeration of the active site of TiO_2 and also produce high quantum yield. It has been reported that the use of MCM-41 as support material for TiO_2 would increase performance of the photocatalyst for photocatalytic oxidation reaction (Davydov *et al.*, 2001).

On the other hand, the highly dispersed TiO_2 on inert support has been reported to be the selective for some partial oxidation reactions (Yoshida, 2003). However, there are still no clear comparison studies when TiO_2 and the dispersed one are both used for oxidation of the same alcohol compound under the same conditions. Moreover, the type of alcohol might also give the effect on the type of oxidation reactions, which however, has never been reported before.

The different types of alcohol might be oxidized following different reaction order and mechanism. Since the kinetic study and the reaction mechanism for different types of alcohols are still not clear, there are still many rooms to be investigated. Moreover, the interaction between the type of alcohol and the photocatalyst might play the significant role for the photocatalytic oxidation reaction. Therefore, it would be important to study the properties of photocatalyst and their effects on the photocatalytic oxidation of different types of alcohol.

1.3 Objectives

The main objectives of this research are:

1) To synthesize the bulk TiO_2 and dispersed TiO_2 on MCM-41 photocatalysts.

2) To study the properties of the prepared bulk TiO_2 and dispersed TiO_2 on MCM-41.
3) To investigate the photocatalytic activity, kinetic and mechanism reactions of bulk TiO_2 and dispersed TiO_2 on MCM-41 for oxidation of phenol, cyclohexanol and hexanol.

1.4 Scope of Study

The scope of this study is shown as below. The bulk TiO_2 was prepared by hydrolysis of titanium isopropoxide, followed by calcination at 773 K. The MCM-41 was prepared by using tetraethyl orthosilicate (TEOS) as the silica source and cetyltrimethylammonium bromide (CTABr) as the surfactant. Furthermore, the surface area of MCM-41 was determined by using Brunauer-Emmett-Teller (BET) specific surface area and Barret-Joyner-Halenda (BJH) pore siza distribution. The dispersed TiO_2 on MCM-41 series with various amounts of TiO_2 loadings were prepared by impregnation method. The amounts of loaded TiO_2 were 3, 5, 7, and 9 wt%. The prepared materials were characterized in details by using the following instruments, which were X-ray diffraction (XRD), diffuse reflectance ultraviolet-visible (DR UV-Vis), fluorescence spectroscopy and field emission scanning electron microscopy (FESEM).

Photocatalytic reaction was conducted at room temperature under an 8 W UV lamp with wavelength centered at 254 nm using a closed reactor system attached with water system cooling. The investigated alcohols were phenol as the model of aromatic alcohol, cyclohexanol and hexanol as the model of aliphatic alcohol. The products were analyzed by gas chromatography equipped with a flame ionization detector (GC-FID) and a thermal conductivity detector (GC-TCD) for liquid and gas products, respectively. The mechanism of the reaction was investigated using benzoquinone, silver nitrate, ammonium oxalate, and *tert*-butyl alcohol as scavengers for superoxide radical, electron, holes, and hydroxyl radical, respectively.

1.5 Significance of Study

The development of photocatalyst design that can enhance the properties of the active site is an important approach in material science. This study would reveal some important parameters to improve the efficiency of the TiO_2 photocatalyst. Moreover, the simple preparation of the photocatalysts shown in this study would give also benefits for photocatalysis field. Furthermore, this research also could give us deepen knowledge about the characteristics of the photocatalysts so that they could be used for other applications. This study also would help us to give better understanding in fundamental requirements of active sites responsible in the oxidation reactions.

On the other hand, this study might improve our technology in terms of handling organic pollutants in our environment. The successful degradation of organic compounds from the wastewater industries absolutely would give great advantages to our environment as well as human being. This research can be considered as one of the green technologies due to the capability of the photocatalysts to oxidize the harmful pollutants into non-hazardous compounds via a green process using light as a source of energy. Besides the photocatalytic reaction, this study also could give knowledge about fundamental studies on the oxidation reactions by studying their kinetics and mechanisms.

REFERENCES

Aboul-Gheit, A. K., Abdel-Hamid, S. M., Mahmoud, S. A., El-Salamony, R. A., Valyon, J., Mihályi, M. R., & Szegedi, Á. (2011). Mesoporous Ti-MCM-41 materials as photodegradation catalysts of 2, 4, 6-trichlorophenol in water. *Journal of materials science,* **46** (10), 3319-3329.

Adan, C., Carbajo, J., Bahamonde, A., & Martínez-Arias, A. (2009). Phenol photodegradation with oxygen and hydrogen peroxide over TiO_2 and Fe-doped TiO_2. *Catalysis Today,* **143** (3), 247-252.

Ahmed, S., Rasul, M., Martens, W. N., Brown, R., & Hashib, M. (2010). Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments. *Desalination,* **261** (1), 3-18.

Akpan, U., & Hameed, B. (2009). Parameters affecting the photocatalytic degradation of dyes using TiO_2 based photocatalysts: A review. *Journal of Hazardous Materials,* **170** (2), 520-529.

Anpo, M., Kim, T.-H., & Matsuoka, M. (2009). The design of Ti-, V-, Cr-oxide single-site catalysts within zeolite frameworks and their photocatalytic reactivity for the decomposition of undesirable molecules. The role of their excited states and reaction mechanisms. *Catalysis Today,* **142** (3), 114-124.

Artkla, S., Kim, W., Choi, W., & Wittayakun, J. (2009). Highly enhanced photocatalytic degradation of tetramethylammonium on the hybrid catalyst of titania and MCM-41 obtained from rice husk silica. *Applied Catalysis B: Environmental,* **91** (1–2), 157-164.

Atchudan, R., & Pandurangan, A. (2012). The use of bimetallic MCM-41 mesoporous catalysts for the synthesis of MWCNTs by chemical vapor deposition. *Journal of Molecular Catalysis A: Chemical,* **355**, 75-84.

Augugliaro, V., Bellardita, M., Loddo, V., Palmisano, G., Palmisano, L., & Yurdakal, S. (2012). Overview on oxidation mechanisms of organic compounds by TiO_2 in heterogeneous photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* **13** (3), 224-245.

Augugliaro, V., Kisch, H., Loddo, V., López-Muñoz, M. J., Márquez-Álvarez, C., Palmisano, G., Palmisano, L., Parrino, F., & Yurdakal, S. (2008). Photocatalytic oxidation of aromatic alcohols to aldehydes in aqueous suspension of home-prepared titanium dioxide: 1. Selectivity enhancement by aliphatic alcohols. *Applied Catalysis A: General,* **349** (1), 182-188.

Auguliaro, V., Davi, E., Palmisano, L., Schiavello, M., & Sclafani, A. (1990). Influence of hydrogen peroxide on the kinetics of phenol photodegradation in aqueous titanium dioxide dispersion. *Applied Catalysis,* **65** (1), 101-116.

Barrera, A., Tzompantzi, F., Padilla, J., Casillas, J., Jácome-Acatitla, G., Cano, M., & Gómez, R. (2014). Reusable PdO/Al_2O_3 photocatalysts in the UV photodegradation of phenol. *Applied Catalysis B: Environmental,* **144**, 362-368.

Behnajady, M., Modirshahla, N., & Hamzavi, R. (2006). Kinetic study on photocatalytic degradation of CI Acid Yellow 23 by ZnO photocatalyst. *Journal of Hazardous Materials,* **133** (1), 226-232.

Bellardita, M., Augugliaro, V., Loddo, V., Megna, B., Palmisano, G., Palmisano, L., & Puma, M. A. (2012). Selective oxidation of phenol and benzoic acid in water via home-prepared TiO_2 photocatalysts: Distribution of hydroxylation products. *Applied Catalysis A: General,* **42**, 79-89.

Chaudhari, S., Waghulde, A., Samuel, V., Bari, M., & Chumbhale, V. (2013). Characterization of ZnO and Modified ZnO Catalysts for Anaerobic Oxidation of Cyclohexanol. *Research Journal of Chemical Sciences,* **3** (7), 38-44.

Chen, J., Eberlein, L., & Langford, C. H. (2002). Pathways of phenol and benzene photooxidation using TiO_2 supported on a zeolite. *Journal of Photochemistry and Photobiology A: Chemistry,* **148** (1), 183-189.

Cheng, S., Tsai, S.-J., & Lee, Y.-F. (1995). Photocatalytic decomposition of phenol over titanium oxide of various structures. *Catalysis Today,* **26** (1), 87-96.

Comninellis, C., & Pulgarin, C. (1993). Electrochemical oxidation of phenol for wastewater treatment using SnO_2, anodes. *Journal of Applied Electrochemistry,* **23** (2), 108-112.

Dąbrowski, A., Podkościelny, P., Hubicki, Z., & Barczak, M. (2005). Adsorption of phenolic compounds by activated carbon a critical review. *Chemosphere,* **58** (8), 1049-1070.

Dalrymple, O. K., Stefanakos, E., Trotz, M. A., & Goswami, D. Y. (2010). A review of the mechanisms and modeling of photocatalytic disinfection. *Applied Catalysis B: Environmental,* **98** (1–2), 27-38.

Davydov, L., Reddy, E. P., France, P., & Smirniotis, P. G. (2001). Transition-metal-substituted titania-loaded MCM-41 as photocatalysts for the degradation of aqueous organics in visible light. *Journal of Catalysis,* **203** (1), 157-167.

Devlin, H. R., & Harris, I. J. (1984). Mechanism of the oxidation of aqueous phenol with dissolved oxygen. *Industrial & engineering chemistry fundamentals,* **23** (4), 387-392.

Ding, Z., Lu, G., & Greenfield, P. (2000). A kinetic study on photocatalytic oxidation of phenol in water by silica-dispersed titania nanoparticles. *Journal of colloid and interface science,* **232** (1), 1-9.

Endud, S., & Wong, K. L. (2007). Mesoporous silica MCM-48 molecular sieve modified with $SnCl_2$ in alkaline medium for selective oxidation of alcohol. *Microporous and Mesoporous Materials,* **101**, 256-263.

García, A., & Matos, J. (2010). Photocatalytic Activity of TiO_2 on Activated Carbon Under Visible Light in the Photodegradation of Phenol. *Open Materials Science Journal,* **4**, 2-4.

Gimeno, O., Carbajo, M., Beltrán, F. J., & Rivas, F. J. (2005). Phenol and substituted phenols AOPs remediation. *Journal of Hazardous Materials,* **119** (1), 99-108.

Górska, P., Zaleska, A., & Hupka, J. (2009). Photodegradation of phenol by UV/TiO_2 and Vis/N,C-TiO_2 processes: Comparative mechanistic and kinetic studies. *Separation and Purification Technology,* **68** (1), 90-96.

Guo, M. L. (2004). Quaternary ammonium decatungstate catalyst for oxidation of alcohols. *Green Chem.,* **6** (6), 271-273.

Harren, F., Berkelmans, R., Kuiper, K., te Lintel Hekkert, S., Scheepers, P., Dekhuijzen, R., Hollander, P., & Parker, D. (1999). On-line laser photoacoustic detection of ethene in exhaled air as biomarker of ultraviolet radiation damage of the human skin. *Applied physics letters,* **74** (12), 1761-1763.

Hasanzadeh, M., Karim-Nezhad, G., Mahjani, M., Jafarian, M., Shadjou, N., Khalilzadeh, B., & Saghatforoush, L. (2008). A study of the electrocatalytic oxidation of cyclohexanol on copper electrode. *Catalysis Communications,* **10** (3), 295-299.

Higashimoto, S., Kitao, N., Yoshida, N., Sakura, T., Azuma, M., Ohue, H., & Sakata, Y. (2009). Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes by molecular oxygen on titanium dioxide under visible light irradiation. *Journal of Catalysis,* **266** (2), 279-285.

Kohtani, S., Yoshioka, E., & Miyabe, H. (2012). Photocatalytic Hydrogenation on Semiconductor Particles. Journal of Catalysis, **4** (7), 212-214.

Koodali, R. T., & Zhao, D. (2010). Photocatalytic degradation of aqueous organic pollutants using titania supported periodic mesoporous silica. *Energy & Environmental Science, **3*** (5), 608-614.

Lachheb, H., Ahmed, O., Houas, A., & Nogier, J. P. (2011). Photocatalytic activity of TiO_2–SBA-15 under UV and visible light. *Journal of Photochemistry and Photobiology A: Chemistry,* **226** (1), 1-8.

Laoufi, N., Tassalit, D., & Bentahar, F. (2008). The degradation of phenol in water solution by TiO_2 photocatalysis in a helical reactor. *Global NEST Journal,* **10** (3), 404-418.

Liu, Z., Zhang, X., Nishimoto, S., Jin, M., Tryk, D. A., Murakami, T., & Fujishima, A. (2007). Anatase TiO_2 nanoparticles on rutile TiO_2 nanorods: a heterogeneous nanostructure via layer-by-layer assembly. *Langmuir,* **23** (22), 10916-10919.

Macwan, D., Dave, P. N., & Chaturvedi, S. (2011). A review on nano-TiO_2 sol–gel type syntheses and its applications. *Journal of materials science,* **46** (11), 3669-3686.

McCarthy, R., & MacLachlan, A. (1961). Kinetics of some radiation-induced reactions. *Transactions of the Faraday Society,* **57,** 1107-1116.

Minero, C., Catozzo, F., & Pelizzetti, E. (1992). Role of adsorption in photocatalyzed reactions of organic molecules in aqueous titania suspensions. *Langmuir,* **8** (2), 481-486.

Mukherjee, S., Basak, B., Bhunia, B., Dey, A., & Mondal, B. (2013). Potential use of polyphenol oxidases (PPO) in the bioremediation of phenolic contaminants

containing industrial wastewater. *Reviews in Environmental Science and Bio/Technology,* **12** (1), 61-73.

Murata, C., Yoshida, H., Kumagai, J., & Hattori, T. (2003). Active sites and active oxygen species for photocatalytic epoxidation of propene by molecular oxygen over TiO_2-SiO_2 binary oxides. *The Journal of Physical Chemistry B,* **107** (18), 4364-4373.

Otto, D. (1942). Oxidation of cyclohexanol: US Patent **2 (285)** 914.

Peral, J., Casado, J., & Domenech, J. (1988). Light-induced oxidation of phenol over ZnO powder. *Journal of Photochemistry and Photobiology A: Chemistry,* **44** (2), 209-217.

Petkov, V., Holzhüter, G., Tröge, U., Gerber, T., & Himmel, B. (1998). Atomic-scale structure of amorphous TiO_2 by electron, X-ray diffraction and reverse Monte Carlo simulations. *Journal of Non-Crystalline Solids,* **231** (1–2), 17-30.

Qu, Q., & Gu, Z. (2014). Facile synthesis of hierarchical MCM-41 spheres with an ultrahigh surface area and their application for removal of methylene blue from aqueous solutions. *Analytical Methods,* **6** (5), 1397-1403.

Reddy, E. P., Davydov, L., & Smirniotis, P. G. (2002). Characterization of titania loaded V-, Fe-, and Cr-incorporated MCM-41 by XRD, TPR, UV-vis, Raman, and XPS techniques. *The Journal of Physical Chemistry B,* **106** (13), 3394-3401.

Reddy, E. P., Sun, B., & Smirniotis, P. G. (2004). Transition metal modified TiO_2-loaded MCM-41 catalysts for visible-and UV-light driven photodegradation of aqueous organic pollutants. *The Journal of Physical Chemistry B,* **108** (44), 17198-17205.

Reddy M., K., Manorama, S. V., & Reddy R., A. (2003). Bandgap studies on anatase titanium dioxide nanoparticles. *Materials Chemistry and Physics,* **78** (1), 239-245.

Rotko, G., & Kurek, S. (2011). Electrooxidation of neat higher alcohols catalysed by cobalt porphyrin. *Czasopismo Techniczne. Chemia,* **108**, 211-219.

Sadjadi, M. S., Farhadyar, N., & Zare, K. (2009). Synthesis of nanosize MCM-41 loaded with TiO_2 and study of its photocatalytic activity. *Superlattices and Microstructures,* **46** (1–2), 266-271.

Saravanan, P., Pakshirajan, K., & Saha, P. (2009). Degradation of phenol by TiO_2-based heterogeneousphotocatalysts in presence of sunlight. *Journal of Hydro-environment Research,* **3** (1), 45-50.

Sharma, P., Durga Kumari, V., & Subrahmanyam, M. (2008). Photocatalytic degradation of isoproturon herbicide over TiO_2/Al-MCM-41 composite systems using solar light. *Chemosphere,* **72** (4), 644-651.

Shishido, T., Miyatake, T., Teramura, K., Hitomi, Y., Yamashita, H., & Tanaka, T. (2009). Mechanism of photooxidation of alcohol over Nb_2O_5. *The Journal of Physical Chemistry C,* **113** (43), 18713-18718.

Sobczyński, A., Duczmal, Ł., & Zmudziński, W. (2004). Phenol destruction by photocatalysis on TiO_2: an attempt to solve the reaction mechanism. *Journal of Molecular Catalysis A: Chemical,* **213** (2), 225-230.

Tamaki, Y., Furube, A., Murai, M., Hara, K., Katoh, R., & Tachiya, M. (2006). Direct observation of reactive trapped holes in TiO_2 undergoing photocatalytic oxidation of adsorbed alcohols: Evaluation of the reaction rates and yields. *Journal of the American Chemical Society,* **128** (2), 416-417.

Teramura, K., Tanaka, T., Kani, M., Hosokawa, T., & Funabiki, T. (2004). Selective photo-oxidation of neat cyclohexane in the liquid phase over V_2O5/Al_2O_3. *Journal of Molecular Catalysis A: Chemical,* **208** (1), 299-305.

Togbe, C., Dagaut, P., Mzé-Ahmed, A., Diévart, P., Halter, F., & Foucher, F. (2010). Experimental and detailed kinetic modeling study of 1-hexanol oxidation in a pressurized jet-stirred reactor and a combustion bomb. *Energy & Fuels,* **24** (11), 5859-5875.

Wang, X., Lian, W., Fu, X., Basset, J.-M., & Lefebvre, F. (2006). Structure, preparation and photocatalytic activity of titanium oxides on MCM-41 surface. *Journal of Catalysis,* **238** (1), 13-20.

Wallington, T. J., Dagaut, P., Liu, R., & Kurylo, M. J. (1988). Rate constants for the gas phase reactions of OH with C5 through C7 aliphatic alcohols and ethers: Predicted and experimental values. *International Journal of Chemical Kinetics,* **20** (7), 541-547.

Xu, Y., & Langford, C. H. (1995). Enhanced photoactivity of a titanium (IV) oxide supported on ZSM5 and zeolite A at low coverage. *The Journal of Physical Chemistry,* **99** (29), 11501-11507.

Yang, H., Deng, Y., & Du, C. (2009). Synthesis and optical properties of mesoporous MCM-41 containing doped TiO_2 nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **339** (1–3), 111-117.

Yi, Q., Zhang, J., Huang, W., & Liu, X. (2007). Electrocatalytic oxidation of cyclohexanol on a nickel oxyhydroxide modified nickel electrode in alkaline solutions. *Catalysis Communications,* **8** (7), 1017-1022.

Yin, C. Y., Aroua, M. K., & Daud, W. M. A. W. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Separation and Purification Technology,* **52** (3), 403-415.

Yoshida, H. (2003). Silica-based quantum photocatalysts for selective reactions. *Current Opinion in Solid State and Materials Science,* **7** (6), 435-442.

Yuliati L., Itoh H. & Yoshida H. (2007). Photocatalytic Direct Conversion of Methane on Silica-Titania Catalysts. *Science and Technology in Catalysis,* July **3** (28), 2006.

Zhang, Y., Zhang, N., Tang, Z.-R., & Xu, Y.-J. (2012). Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer. *ACS nano,* **6** (11), 9777-9789.

Zhao, X. S., Lu, G., & Millar, G. J. (1996). Advances in mesoporous molecular sieve MCM-41. *Industrial & engineering chemistry research,* **35** (7), 2075-2090.

Zheng, S., Gao, L., Zhang, Q.-h., & Guo, J.k. (2000). Synthesis, characterization and photocatalytic properties of titania-modified mesoporous silicate MCM-41. *J. Mater. Chem.,* **10** (3), 723-727.

Zhou, G., Xu, Z., Guo, X., Zhuang, H., Li, Y., Lü, X., Cheng, T., Li, W., & Zhen, K. (2005). Transition metal substituted tungstophosphoric compound catalyzed oxidation of hexanol to hexanal with hydrogen peroxide. *Reaction Kinetics and Catalysis Letters,* **85** (1), 57-64.

Zmudziński, W., Sobczyńska, A., & Sobczyński, A. (2007). Oxidation of phenol and hexanol in their binary mixtures on illuminated titania: Kinetic studies. *Reaction Kinetics and Catalysis Letters,* **90** (2), 293-300.

Zou, J. J., Zhang, M.-Y., Zhu, B., Wang, L., Zhang, X., & Mi, Z. (2008). Isomerization of norbornadiene to quadricyclane using Ti-containing MCM-41 as photocatalysts. *Catalysis letters,* **124** (1-2), 139-145.