Enhanced photocatalytic activity of zeolitic imidazolate framework-8 by modification with phosphor tungstic acid

Jiahui Guo¹, Lili Yang²*, Ruhuai Guo³, Shuo Yang², Jianbin Chen²

¹Centre for Training, Guangdong Polytechnic of Environmental Protection Engineering, Nanhai District, Foshan 528216, China
²School of Materials and Environment, Beijing Institute of Technology, Zhuhai 519088, China

*Corresponding author e-mail: yllgdut@126.com

Abstract. Phosphor tungstic acid (PTA)-modified zeolitic imidazolate framework-8 (ZIF-8) catalysts were synthesized for photocatalytic degradation of methylene blue under UV irradiation. The as-prepared catalysts were characterized by the powder X-ray diffraction, N₂ adsorption-desorption, Fourier transform infrared spectroscopy, Raman spectroscopy and UV-vis diffuse reflectance spectroscopy techniques. The optimum reaction conditions for photocatalytic degradation of methylene blue on the obtained materials were investigated. The results show that PTA evidently improved the activity of ZIF-8 catalysts because of its fast reversible multi-electron redox transformations. In addition, the reaction mechanism underlying the process was proposed.

1. Introduction

Organic dyes are major sources of environmental contamination, and the removal of these organic pollutants is very important for both academic and industrial societies. Since the first artificial photo catalyst TiO₂ was discovered for pollutants degradation,[1] many metal oxides including ZrO₂ and WO₃ have been identified as photo catalysts for solving environmental problem.[2, 3] The degradation capacity towards organic pollutants using these developed metal oxides as catalysts, however, is still moderate at present. Thus, it is of great interest to search for the novel higher effective photo-catalysts.

Metal organic frameworks (MOFs), composed of organic and inorganic building blocks, have emerged as a novel kind of porous crystalline materials. Their excellent properties, such as uniform microspores, accessible pore volumes, and large surface areas,[4] have opened the door for MOFs in many potential applications.[5-11] In particular, MOFs have the ability to behave as semiconductors when exposed to light, making them unique platforms for light harvesting and photoinduced catalysis.[12-14] Some MOFs can act as a charge-carrier transporting system because of the existence of the open metal sites and the catalytically active organic linkers.[15-17] Majima investigated the photoinduced charge-transfer process between excited MOF-5 nanoparticles and organic compounds by using time resolved emission and diffuse reflectance spectroscopies.[18, 19] In addition, as the host porous materials for photocatalytic reactions, MOFs can also provide extra pathways for the migration of photoinduced electrons and thus facilitate charge-carrier separation, increasing the photocatalytic efficiency.[23] Besides, the presence of coordinatively unsaturated metal sites in MOFs allows their...
post-functionalization by grafting of active species. Recently, an increasing number of papers have appeared to indicate that MOFs, such as MOF-5, provide a unique opportunity for integrating different molecular functional components to achieve light harvesting and to drive photocatalytic hydrogen evolution and CO₂ reduction.[14] However, the slight exposure of MOF-5 to the ambient atmosphere or residual water in the solvent remarkably lowers their photocatalytic activity because of the destruction of the pore structures.

The zeolitic imidazolate frameworks (ZIF-8, (Zn(MIM)₂, MIM=2-methylimidazole), a subclass of MOF, was selected in this study as the photo catalyst because of its high stability.[22] The secondary building units of ZIF-8 are Zn₄(MIM)₈ and Zn₄(MIM)₄ rings, and each Zn(I) ion is tetrahedrally coordinated by four nitrogen atoms from bridging MIM to furnish an infinite 3D frameworks.[20-21]

To the best of our knowledge, photocatalytic degradation of methylene blue (MB) by ZIF-8 has rarely been studied. Unfortunately, the obtained results show that the degradation capacity towards MB using ZIF-8 as catalyst in this paper is still moderate. Phosphotungstic acid (PTA), which consists of heteropolyanions PW₁₂O₄₀³⁻ with W-O octahedra as the basic structure unit, has received largely attentions in the past decades.[24] The properties such as extremely high proton mobility, fast reversible multi-electron redox transformations and well stability make PTA an excellent catalytic candidate. Several compounds that PTA was introduced into the MOF segments have been reported. [25] However, highly efficient, truly heterogeneous catalysis over well-defined PTA /MOF materials had not been presented until now. Maksimchuk et al.[26] recently demonstrated that PTA /MIL-101 could be utilized as oxidation catalysts, but they did not determine their crystal structures. Herein, we try to anchor highly dispersed PTA on the ZIF-8 frameworks via a facile room-temperature synthetic strategy and expect that the as-synthesized PTA/ZIF-8 can act as a solid-state photo catalyst with high activity. To illustrate the activities of PTA/ZIF-8 catalysts, photo degradation of methylene blue has been carried out. Interestingly, the results show that the PTA/ZIF-8 catalysts exhibit an excellent reusability and higher catalytic performance for methylene blue degradation than that of bare ZIF-8 under UV light illumination. It is expected that our current research could provide a new way to design ZIF semiconductor photo catalysts for organic pollutants degradation.

2. Experimental Section

2.1. Preparation of ZIF-8 and PTA/ZIF-8
ZIF-8 was prepared according to the procedure described by Moises A. Carreon et al.[27]: a solution of 2-methylimidazole (C₉H₈N₂, 6.4x10⁻³ mol) in methanol (1.4 mol) was added to a solution of zinc nitrate hexahydrate ([Zn(NO₃)₂·6H₂O, 8x10⁻³ mol]) in methanol (1.4 mol), then vigorously stirred for 10 min. White polyhedral crystals appeared immediately. Finally, this solution was centrifuged at 2000 rpm and washed 3 times with methanol, then dried overnight at 60 °C.

For the preparation of PTA/ZIF-8 (impregnation of PTA in ZIF-8), PTA (0.1 g) was dispersed in acetone (10 mL), while ZIF-8 (0.1 g) was added and stirred for 12 h at room temperature. The resulting materials were recovered by filtration and washed twice with acetone and dried overnight at 60 °C.

2.2. Page Numbers Photo degradation of MB
The photo catalytic activities of ZIF-8 and PTA/ZIF-8 were evaluated by the photo degradation of MB dye under a 30W Xe lamp irradiation at room temperature. The distance between the light and the beaker containing reaction mixture was about 10 cm. The original solution was prepared by MB solution (20 mg/L, 100 mL) and the catalyst (4 mg) in a 250 mL beaker. Prior to irradiation, the mixture was stirred in dark for 1 h to ensure the establishment of an adsorption-desorption equilibrium. Then the mixture reacted at room temperature under stirring. A small quantity of reaction mixture (3 mL) was withdrawn at definite intervals until the end of the reaction and immediately centrifuged to remove the catalyst before analysis.
3. Results and Discussions

3.1. Catalyst and Characterizations

Fig 1. Characterizations of ZIF-8, PTA and PTA/ZIF-8 materials: (a) Powder X-ray diffraction patterns of ZIF-8, PTA and PTA/ZIF-8. (b) N$_2$ adsorption-desorption isotherms of ZIF-8, PTA and PTA/ZIF-8 at 77 K. (c) Pore size distribution curves of ZIF-8 and PTA/ZIF-8. (d) FT-IR spectra of ZIF-8, PTA and PTA/ZIF-8. (e) Raman spectra of ZIF-8, PTA and PTA/ZIF-8. (f) UV-Vis diffuse spectra of ZIF-8 and PTA/ZIF-8 at ambient temperature.
The XRD patterns of ZIF-8, PTA, and PTA/ZIF-8 materials are illustrated in Fig 1-a. The sharp peaks of ZIF-8 indicate its excellent crystallinity, and all the diffraction peaks are well matched with the previous results.[28] The as-prepared PTA/ZIF-8 materials possess similar XRD patterns as that of ZIF-8. After the impregnation of PTA, no obvious loss of crystallinity of ZIF-8 is found in the XRD patterns, suggesting that the integrity of the ZIF-8 framework is maintained. Furthermore, the characteristic diffractions of PTA are not found from the XRD patterns of PTA/ZIF-8. This is probably due to the fact that the content of PTA in the synthesized PTA/ZIF-8 materials is relatively low, which is further proved by the ICP-AES. ICP-AES is used to quantify the amounts of W produced as a function of PTA loading in the PTA/ZIF-8 (2.690 wt%).

The surface area and porosity of the obtained materials are analyzed by N\textsubscript{2} adsorption experiments at 77 K. As shown in Fig1-b, the sorption isotherms of ZIF-8 and PTA/ZIF-8 indicate that micropores are retained. The langmuir surface areas of PTA/ZIF-8, ZIF-8 and PTA were calculated to be 1799 cm\textsuperscript{2}/g, 1485 cm\textsuperscript{2}/g and 18 cm\textsuperscript{2}/g, respectively. The surface area of ZIF-8 is also in good agreement with the recently reported values.[28] The higher surface area of PTA/ZIF-8 is probably attributed to the fact that PTA with small particle size distributed on the ZIF-8 surface uniformly, instead of blocking of the open pores in ZIF-8. The pore size distribution curve of ZIF-8 (Fig.1-c) calculated by Horvath-Kawazoe (HK) method gives two types of micropores located at 6.7 Å and 9.4 Å, respectively, which consistent with the reported literature. Furthermore, the addition of PTA increased the volume of these two types of micropores, corresponding to the larger surface area of PTA/ZIF-8.

To confirm the presence of PTA in the PTA/ZIF-8 catalysts, FT-IR spectroscopy and Raman spectroscopy are performed. Fig 1-d shows the FT-IR spectra curves of ZIF-8, PTA and PTA/ZIF-8, suggesting that three characteristic peaks of PTA are observed in the PTA/ZIF-8. A small peak at around 880 cm\textsuperscript{-1} is attributed to a P-O bond, and a strong peak at approximately 990 cm\textsuperscript{-1} is corresponded to the W=O bond. Furthermore, an additional peak at around 1080 cm\textsuperscript{-1} is observed, which might have resulted from the stretching vibration of W-O-W.[29] The Raman spectra of ZIF-8, PTA and PTA/ZIF-8 in Fig.1-e further demonstrated the above results. And for the crystalline PTA,[30] stretching vibration of P-O lied in 1007 cm\textsuperscript{-1}, stretching vibration of W=O lied in 986 cm\textsuperscript{-1}, stretching vibration of W=O-W lied in 900 cm\textsuperscript{-1}, and stretching vibration of O-P-O lied in 550 cm\textsuperscript{-1}. Besides the characteristic bands of ZIF-8, the spectra of PTA/ZIF-8 also exhibited a new small stretching vibration locating at 1100 cm\textsuperscript{-1}, which was assigned to W=O.

The photoabsorption property plays a key role in determining the photocatalytic activity, the UV-vis diffuse reflectance absorption spectroscopy (DRS) of the samples are measured. Fig.1-f displays the DRS of the as-prepared ZIF-8 and PTA/ZIF-8 materials. As can be observed, the main optical absorption band of them lied at approximately 212 nm, which was assigned to ligand-to-metal charge transfer.[13] In other words, under the interference of the ligands and UV irradiation, electron transfer occurred in the d orbital of transition metal Zn ions. In addition, the introduction of PTA enhanced the light absorption intensity of ZIF-8 ranging from 200 nm to 350 nm, which is expected to improve the photocatalytic performance of ZIF-8. This inference is well identified by the photocatalytic testing of ZIF-8 and PTA/ZIF-8 toward degradation of MB under UV light irradiation.
3.2. Photo degradation of MB

![UV-Vis absorption spectra of MB with PTA/ZIF-8 (10 mg) and H$_2$O$_2$ (0.5 mL).](image)

Fig 2. UV-Vis absorption spectra of MB with PTA/ZIF-8 (10 mg) and H$_2$O$_2$ (0.5 mL).

The photo catalytic performance of PTA/ZIF-8 is evaluated by monitoring the decolorization of the UV-vis absorption spectra of MB solutions ($\lambda_{max}$=665 nm). To determine the optimum reaction conditions, a number of experiments have also been carried out to demonstrate the photo catalytic nature of the reactions. Specially, H$_2$O$_2$ plays double roles in the reaction: on one hand, when the concentration of H$_2$O$_2$ is relatively low, catalytic efficiency become higher with the increasing of concentration; On the other hand, when the concentration of H$_2$O$_2$ is much more, H$_2$O$_2$ will become the scavenger of ·OH. In addition, ·OH, ·O$_2$H even between ·OH and ·O$_2$H are able to occur the coupling reaction, [31] resulting in the reduction of radicals. Results also showed that the reaction went well when the H$_2$O$_2$ volume is equal to 0.5 mL. All the reactions were carried out with the optimum reaction conditions in the following studies. Fig.2 presents the typical temporal evolution of the spectral changes of MB solutions at various intervals in the presence of PTA/ZIF-8. With the increase of irradiation time, the absorption peak at 665 nm ascribed to MB decreases gradually, and it almost disappears after 20 min of irradiation.

![Reaction kinetic plots](image)

Fig 3. Reaction kinetic plots: (1) with the presence of PTA/ZIF-8 and H$_2$O$_2$, (2) with the presence of ZIF-8 and H$_2$O$_2$, (3) with the presence of PTA and H$_2$O$_2$, (4) with the presence of H$_2$O$_2$ only, (5) with the presence ZIF-8 only, (6) with the presence of PTA only, (7) without any catalyst or H$_2$O$_2$. 

As shown in Fig 3, only a small margin of MB was degraded after 120 min light irradiation in the control experiments without any catalysts. Instead, the degradation of MB proceeds smoothly in the presence of photo catalyst. In addition, PTA/ZIF-8 exhibits higher activity than that of ZIF-8 (Table 1), the degradation ratio is rapidly increased to 99% after UV light illumination for 20 min. The degradation rate of catalysts followed the order: PTA/ZIF-8 > ZIF-8 > PTA. It’s significant that impregnation of PTA improved evidently the activity of catalysts, and all of these results confirmed that the PTA/ZIF-8 showed extremely high catalytic activity. The enhanced photo catalytic activity of PTA/ZIF-8 may be ascribed to the intimate interfacial contact between PTA and ZIF-8, which provides short distance for photo-excited charge carrier transfer and reduce the electron-hole pair recombination efficiently. We also noted that the degradation process could be divided into two stages (Fig3): the demethylation of MB chromophoric group and the degradation of aromatic miscellaneous ring of MB.[31] The first stage in the first 30 minutes conformed to first-order kinetics model (1); the second stage, occurred from 40 minutes to 120 minutes, were consistent with second-order kinetics mode (2).

\[
\ln(C/C_0) = Kt
\]  
\[
1/C-1/C_0= Kt
\]

Wherein, \(C_0\) is the initial concentration of MB, \(C\) is the final concentration of MB, \(t\) is the reaction time, and \(K\) is the kinetic rate constant which was obtained from the slope of the linear plot.

**Table 1. Effect of different catalysts on the MB degradation rate constant under UV irradiation.**

| Entry | Catalyst               | \(K/\text{min}^{-1}\) |
|-------|------------------------|------------------------|
| 1     | -                      |                        |
| 2     | ZIF-8                  | 0.0749                 |
| 3     | PTA/ZIF-8              | 0.2216                 |
| 4     | PTA/ZIF-8 (1\textsuperscript{st}) | 0.2213           |
| 5     | PTA/ZIF-8 (2\textsuperscript{nd}) | 0.2212             |
| 6     | PTA/ZIF-8 (3\textsuperscript{rd}) | 0.2206             |

\(a\) Reaction conditions: \(m\) (catalyst) = 10 mg, \(V\) (\(\text{H}_2\text{O}_2\)) =0.5 mL;

\(b\) The apparent rate constant (\(K\)).

The stability and reusability of the photo catalyst are crucial. To evaluate the reusability of PTA/ZIF-8, three successive cycles for the photo-degradation of MB were carried out over the recycled catalysts. Photo catalyst PTA/ZIF-8 can be simply recovered by filtration, washing and drying. The XRD patterns of the samples before and after the reaction show no significant difference, suggesting the superior stability of PTA/ZIF-8 catalyst. As shown in Table 1, the PTA/ZIF-8 could retain its photo catalytic activity fairly well even after three cycles of application, indicating the high reusability of PTA/ZIF-8.
3.3. Photo degradation of MB Mechanism of Degradation

![Scheme 1. Mechanism for methylene blue (MB) degradation in when irradiated by UV light in presence of PTA/ZIF-8.](image)

Considering that the conduction band of TiO$_2$ was constructed by empty Ti 3d orbital, ZIF-8 containing transition metals Zn as structural nodes is also expected to be an active photo catalyst because the empty Zn d orbital mixed with the organic linkers would form the conduction band. Based on the reported mechanism for MB degradation [31] and the present observations, the photo catalytic reaction mechanism was proposed as shown in Scheme 1. Upon UV light irradiation, it took place that the electronic transition from valence band to conduction band when ZIF-8 received photons with energy, generating electron-hole pairs (h$^+$). Secondly, electron-hole pairs (h$^+$) with strong oxidant capacity could directly oxidized organic molecules or reacted with H$_2$O or OH$^-$ to generate hydroxyl radical (-OH) with stronger oxidant capacity. Consequently, the introduction of external electron acceptor H$_2$O$_2$ could enhance the activity of photo-catalyst by generating more -OH. Moreover, the impregnation of PTA improved clearly the activity of catalysts due to the fast reversible multi-electron redox transformations. The present study indicated that ZIF-8 and PTA/ZIF-8 can be used as the novel catalyst for photo degradation of MB dye pollutants.

4. Conclusion
A novel PTA/ZIF-8 photo-catalyst was prepared by impregnation of phosphotungstic acid at room temperature and applied in the photo degradation of methylene blue with the assistance of electron acceptor hydrogen peroxide. PTA evidently improved the activity of ZIF-8 photo-catalyst due to its fast reversible multi-electron redox transformations. The performance of PTA/ZIF-8 catalysts in the photo degradation of methylene blue was outstanding, indicating the suitable interaction between PTA and ZIF-8. We hope that our current work can widen the application range of the ZIF and provide a feasible way for tuning their photocatalysis properties. Further studies are in progress to design robust and efficient ZIF photo catalysts for visible light-driven degradation of methylene blue.

Acknowledgments
This work was financially supported by the Foundation of Guangdong Province (NO.10251009001000003), Fund of Higher Education of Guangdong Province (NO.ZX-2016-012), and Scientific Program of Beijing institute of technology Zhuhai (NO.XK-2015-08).

References
[1] Daghrir, R., Drogui, P., and El Khakani, M.A, Photo electrocatalytic oxidation of chlortetracycline using Ti/TiO2 photo-anode with simultaneous H2O2 production,
Electrochem Acta, 87 (2013) 18-31.

[2] S.S.K. Ma, K. Maeda, K. Domen, Modification of TaON with ZrO2 to improve photocatalytic hydrogen evolution activity under visible light: influence of preparation conditions on activity, Catal Sci Technol. 2(2012):818-823.

[3] Nithya Vaidyathanathan, David M. Hercules, Marwan Houalla, Surface characterization of WO3/ZrO2 catalysts, Anal Bioanal Tech. 373(2002):547-554.

[4] M.E. Haiilfan Li, M.O'Keeffe, O.M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal-organic framework, Nature, 402 (1999) 276-279.

[5] H.T. Kwon, H.K. Jeong, In situ synthesis of thin zeolitic-imidazolate framework ZIF-8 membranes exhibiting exceptionally high propylene/propane separation, J Am Chem Soc. 135(2013): 10763-10768.

[6] Y. Hu, Z. Liu, J. Xu, Y. Huang, Y. Song, Evidence of pressure enhanced CO2 storage in ZIF-8 probed by FTIR spectroscopy, J Am Chem Soc. 135(2013): 9287-9290.

[7] Y. Zhou, J. Song, S. Liang, S. Hu, H. Liu, T. Jiang, B. Han, Metal-organic frameworks as an acid catalyst for the synthesis of ethyl methyl carbonate via transesterification, J Mol Catal A: Chem. 308(2009):68-72.

[8] M. Zahmakiran, Iridium nanoparticles stabilized by metal organic frameworks (IrNPs@ZIF-8): synthesis, structural properties and catalytic performance, Dalton T.41(2012):12690-12696.

[9] Xueling Yi, and Xiaodan Zhang, MIL-53(Fe) MOF-mediated catalytic chemiluminescence for sensitive detection of glucose, Anal Bioanal Tech. 408(2016):8805-8812.

[10] T.T. Dang, Y. Zhu, J.S.Y. Ngiam, S.C. Ghosh, A. Chen, A.M. Seayad, Palladium Nanoparticles Supported on ZIF-8 As an Efficient Heterogeneous Catalyst for Aminocarbonylation, ACS Catal. 3(2013):1406-1410.

[11] O. Karagiari, L.M. Lalonde, W. Bury, A.A. Sarjeant, O.K. Farha, J.T. Hupp, Opening ZIF-8: a catalytically active zeolitic imidazolate framework of sodalite topology with unsubstituted linkers, J Am Chem Soc. 134(2012):18790-18796.

[12] M. Alvaro, E. Carbonell, B. Ferrer, F.X. Llabres i Xamena, H. Garcia, Semiconductor behavior of a metal-organic framework (MOF), Chemistry. 2007;13:5106-5112.

[13] C.G. Silva, A. Corma, H. Garcia, Metal-organic frameworks as semiconductors, J Mater Chem. 20(2010):3141-3156.

[14] J.-L. Wang, C. Wang, W. Lin, Metal-Organic Frameworks for Light Harvesting and Photocatalysis, ACS Catal. 2(2012):2630-2640.

[15] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, Copper-based metal-organic framework for the facile ring-opening of epoxides, J Catal. 257(2008):390-395.

[16] F. Llabresixamena, O. Casanova, R. Galiassotailleur, H. Garcia, A. Corma, Metal organic frameworks (MOFs) as catalysts: A combination of Cu2+ and Co2+ MOFs as an efficient catalyst for tetralin oxidation, J Catal. 255(2008):220-227.

[17] S.H. Shinpei Hasegawa, Ryotaro Matsuda, Shuhei Furukawa, Y.K. Katsunori Mochizuki, and Susumu Kitagawa, Three-Dimensional Porous Coordination Polymer Functionalized with Amide Groups Based on Tridentate Ligand: Selective Sorption and Catalysis, J. Am. Chem. Soc. 129(2007):2607-2614.

[18] J.R.C. Takashi Tachikawa, Mamoru Fujitsuka, and Tetsuro Majima, Photoinduced Charge Transfer Processes on MOF-5 Nanoparticles: Elucidating Differences between Metal-Organic Frameworks and Semiconductor Metal Oxides, J Phys Chem C. 112(2008):14090-14101.

[19] T.T. Jun Rye Choi, Mamoru Fujitsuka, and Tetsuro Majima, Evaluating Host-Guest Interactions in a Metal-Organic Framework Using a Polarity-Sensitive Probe, J Phys Chem Lett.1(2010):1101-1106.

[20] H.F. Rahul Banerjee, David Britt, Carolyn Knobler, Michael O’Keeffe, and, O.M. Yaghi, Control of Pore Size and Functionality in Isoreticular Zeolitic Imidazolate Frameworks and their Carbon Dioxide Selective Capture Properties, J. Am. Chem. Soc. 131(2009):3875-3877.
[21] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, Ligand-Directed Strategy for Zeolite-Type Metal-Organic Frameworks: Zinc(II) Imidazolates with Unusual Zeolitic Topologies, Angewandte Chemie. 118(2006):1587-1589.

[22] Alba González, Jessica Avivar, and Fernando Maya, In-syringe dispersive μ-SPE of estrogens using magnetic carbon microparticles obtained from zeolitic imidazolate frameworks, Anal Bioanal Tech. 409(2016):225-234.

[23] L. Shen, S. Liang, W. Wu, R. Liang, L. Wu, CdS-decorated UiO-66(NH2) nanocomposites fabricated by a facile photodeposition process: an efficient and stable visible-light-driven photocatalyst for selective oxidation of alcohols, J Mater Chem A.1(2013):11473-11482.

[24] I.V. Kozhevnikov, Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions, Chem Rev.98(1998):171-198.

[25] N. Maksimchuk, M. Timofeeva, M. Melgunov, A. Shmakov, Y. Chesalov, D. Dybtsev, V. Fedin, O. Kholdeeva, Heterogeneous selective oxidation catalysts based on coordination polymer MIL-101 and transition metal-substituted polyoxometalates, J Catal. 257(2008):315-323.

[26] L. Yang, H. Naruke, T. Yamase, A novel organic/inorganic hybrid nanoporous material incorporating Keggin-type polyoxometalates, Inorg Chem Commun.6(2003):1020-1024.

[27] M. Zhu, D. Srinivas, S. Bhogeswararao, P. Ratnasamy, M.A. Carreon, Catalytic activity of ZIF-8 in the synthesis of styrene carbonate from CO2 and styrene oxide, Catal Commun.32(2013):36-40.

[28] K.S. Park, Z. Ni, A.P. Cote, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, PNAS. 103(2006):10186-10191.

[29] C.M. Granadeiro, A.D.S. Barbosa, P. Silva, F.A.A. Paz, V.K. Saini, J. Pires, B. de Castro, S.S. Balula, L. Cunha-Silva, Monovacant polyoxometalates incorporated into MIL-101(Cr): novel heterogeneous catalysts for liquid phase oxidation, App Catal A: Gen. 453(2013):316-326.

[30] E. Caliman, J.A. Dias, S.C.L. Dias, A.G.S. Prado, Solvent effect on the preparation of H3PW12O40 supported on alumina, Catal Today. 107(2005):816-825.

[31] J.J. Du, Y.P. Yuan, J.X. Sun, F.M. Peng, X. Jiang, L.G. Qiu, A.J. Xie, Y.H. Shen, J.F. Zhu, New photocatalysts based on MIL-53 metal-organic frameworks for the decolorization of methylene blue dye, J Hazard Mater. 190(2011):945-951.