Inorganic Chemistry Communications 59 (2015) 13–16

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A new hybrid porphyrin-heteropolyacid material: Synthesis, characterization and investigation as catalyst in Baeyer–Villiger oxidation. Synergistic effect

K. Pamin [a], M. Prończuk [b], S. Basąg [c], W. Kubiak [d], Z. Sojka [c], J. Połtowicz [a],*

[a] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland
[b] Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland
[c] Jagiellonian University, Department of Chemistry, Ingardena 3, 30-060 Kraków, Poland
[d] Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Mickiewicza 30, 30-059 Kraków, Poland

ARTICLE INFO

Article history:
Received 15 March 2015
Received in revised form 21 May 2015
Accepted 4 June 2015
Available online 10 June 2015

Keywords:
Organic-inorganic hybrid
Poyoxometalate
Porphyrin
Cyclohexanone oxidation

ABSTRACT

A new tetraphenylporphyrin-tungstophosphoric acid hybrid was synthesized and physico-chemically characterized by different techniques. This hybrid, its molybdenum analogue, tungstophosphoric and molybdophosphoric acids as well as their Mn, Fe and Co salts were applied in Baeyer–Villiger oxidation of cyclohexanone to caprolactone with molecular oxygen. Due to the synergistic effect porphyrin-heteropolyacid hybrids exhibit similar catalytic activity as appropriate heteropoly salts and much higher activity than parent heteropolyacids.

Baeyer–Villiger oxidation of cyclic ketones to the corresponding lactones (Scheme 1) has received considerable attention in organic synthesis because products are very important industrial intermediates in the production of polymers, pharmaceuticals and herbicides [1–3]. Polyoxometalates are inorganic metal–oxygen clusters well-known as efficient catalysts for the selective oxidation of hydrocarbons [4–6]. Their redox properties, acidity and solubility in various solvents can be finely tuned by choosing constituent elements or counter cations [7]. Polyoxometalates are known to behave as electron reservoir and they are useful for electron transfer oxidation reactions [8]. In addition, these compounds are stable under thermal and oxidative conditions. Porphyrins as multidentate compounds are also the subject of many studies as effective and selective catalysts for oxidation of hydrocarbons [9,10]. Their catalytic properties can be easily modulated by changing substituents in macrocyclic ring. Therefore, polyoxometalates and porphyrin are selected as building blocks to obtain organic–inorganic hybrids. Polyoxometalate based organic–inorganic hybrid materials with application in catalysis have been designed via covalent [11–22] or electrostatic interaction [23–27].

A new organic–inorganic hybrid with formula $[H_4TPP][HPW_{12}O_{40}] \cdot 3 \cdot THF \cdot 6 \cdot H_2O$ **1**, was synthesized (Scheme 2) according to the procedure of Shi et al. [28] from the tetraphenylporphyrin H_2TPP **2** and tungstophosphoric acid $H_3PW_{12}O_{40}$ **3** [29]. Synthesized hybrid was characterized by UV–Vis and FT-IR spectroscopy, differential scanning calorymetry DSC, thermogravimmetric analysis TG and cyclic voltammetry CV.

The formation of organic–inorganic hybrid was evidenced by UV–Vis spectroscopy. The absorption spectrum of the tetraphenylporphyrin H_2TPP shows four Q bands in the visible range of spectra with maxima at 615, 562, 518, 488 nm and an intense Soret band at 418 nm in THF (Fig. S1 in Supplementary data) [30]. Fig. 1 shows the changes in the absorption spectra of tetraphenylporphyrin H_2TPP upon stepwise addition of a THF solution of $H_3PW_{12}O_{40}$ ($6 \cdot 10^{-5}$ mol L^{-1}) in 5 µl portions. During the titration, absorbance observed at 269 nm and 208 nm increases regularly due to the heteropolyacid added but the intensity of Soret and Q bands decreases [31]. The appearance of two new bands at 658 nm and 448 nm (Soret band) confirms the formation of di-protonated porphyrin H_4TPP^{2+} [32] and reveals the strong interaction between porphyrin and polyoxometalate indicating the formation of a hybrid complex by electrostatic interactions.

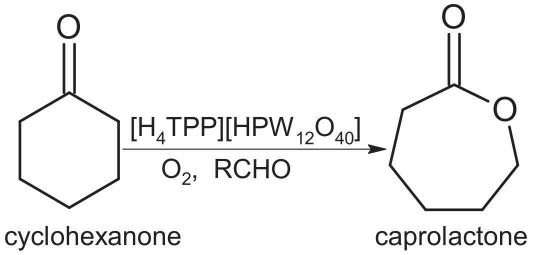
The electrochemical properties of the hybrid compound **1** were investigated by cyclic voltammetry [33]. Fig. 2 shows the typical cyclic voltammogram of the organic–inorganic hybrid. The oxidation wave is visible at $Epa = -5.2$ mV and reduction wave can be observed at $Epc = -81.5$ mV. The anodic potential of $H_3PW_{12}O_{40}$ reaches $Epa = 6.6$ mV and catodic potential $Epc = -62.0$ mV.

As mentioned above, upon attachment of electron-donating porphyrin to tungstophosphoric acid which is the electrons reservoir, the

---

* Corresponding author.
E-mail address: ncpoltow@cyf-kr.edu.pl (J. Połtowicz).

http://dx.doi.org/10.1016/j.inoche.2015.06.005
1387-7003/



Scheme 1. Oxidation of cyclohexanone to caprolactone.

electron density of the hybrids increases. In consequence, reduction of hybrids becomes more difficult rendering their easier oxidation.

The FT-IR spectrum of tungstophosphoric acid is presented in Fig. 3. It shows four characteristic bands in the region 1100–400 cm^{-1}, observed at 1080, 982, 893 and 812 cm^{-1}, which can be assigned to the stretching vibrations of P–O, W═, interoctaedral W–O–W and intraoctaedral W–O–W bands, respectively [34]. The bonds that are present in H_2TPP are C═C, C–H, C═N, and N–H. The C═C aromatic bonds oscillate with a wavenumber around 1500 cm^{-1}, hence, they can be attributed to the peaks at 1593, 1556, 1469, and 1440 cm^{-1}. The 1348 cm^{-1} peak corresponds to the C═N and the C–H bonds which appear at 794, 721, and 696 cm^{-1}, one is also visible at 3050 cm^{-1}. The N–H bonds can be seen at 3300 cm^{-1} and 964 cm^{-1}. The hybrid spectrum contains all the characteristic important bands of both the porphyrin and the heteropolyacid and proves the synthesis of organic–inorganic hybrid.

Fig. 4 presents DTA profile for organic–inorganic hybrid which was compared with parent H_2TPP porphyrin and heteropolyacid $H_3PW_{12}O_{40}$ [35,36]. For H_2TPP porphyrin a large exothermic effect observed at about 450 °C is related to the complete decomposition of porphyrin [37,38]. In the case of $H_3PW_{12}O_{40}$ two large endothermic effects at 123 °C and 264 °C are visible. The first one is connected with the loss of crystallization water and the other originates from the loss of water hydrating protons. The complete decomposition of the heteropolyacid with formation of WO_3 and P_4O_{10} corresponds to the large exothermic effect at 616 °C. Two small endothermic effects responsible for the loss of water were also observed for porphyrin-polyoxometalate hybrid. At 471 °C a broad exothermic effect connected with the burning of an organic part of hybrid (ligand TPP) was observed. Large exothermic effect visible at 591 °C is connected with the complete decomposition of hybrid. Lower decomposition temperature of hybrid in comparison with tungstophosphoric acid indicates that stability of the former is lower than the stability of $H_3PW_{12}O_{40}$.

New organic–inorganic hybrid $[H_4TPP][HPW_{12}O_{40}]$ and its molybdenum analogue $[H_4TPP][HPMo_{12}O_{40}]$, presented in Fig. 5, were applied as catalysts in the oxidation of cyclohexanone to caprolactone with molecular oxygen in the presence of an aldehyde [39]. Additionally, catalytic activity of heteropolysalts $HMPMo_{12}O_{40}$ and $HMPW_{12}O_{40}$ with transition metals (M = Mn, Fe, Co) in the positions of compensating cations, prepared according to the procedure of [40], was studied. For comparison, parent heteropolyacids $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ were also applied in the oxidation of cyclohexanone. The catalytic results are shown in Table 1. As it can be seen, all the synthesized catalysts (except H_2TPP) are active in the oxidation of cyclohexanone. Molybdophosphoric acid $H_3PMo_{12}O_{40}$, due to its higher oxidizing ability, is more active than tungstophosphoric acid $H_3PW_{12}O_{40}$ [41]. It is understandable since tungstophosphoric acid possesses much stronger acidic properties than its molybdenum analogue.

Introduction of the metal atom into heteropoly structure enhances its catalytic activity and all heteropolysalts show higher catalytic activity

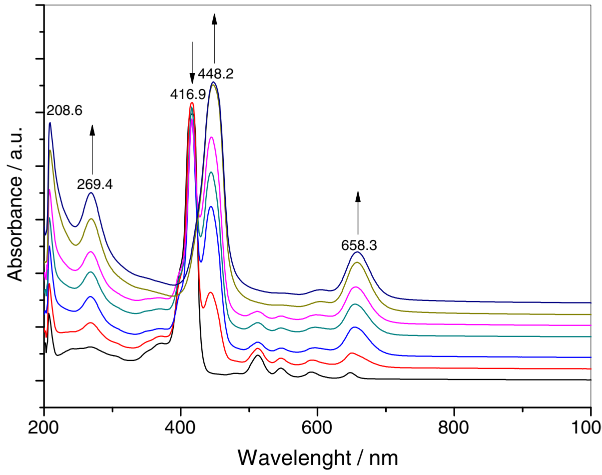


Fig. 1. Spectroscopic titration of a $8°10^{-6}$ mol L^{-1} THF solution of tetraphenylporphyrin H_2TPP (black line) by a heteropolyacid $H_3PW_{12}O_{40}$ solution (in 5 μL portions of $6°10^{-5}$ mol L^{-1} $H_3PW_{12}O_{40}$ in THF).

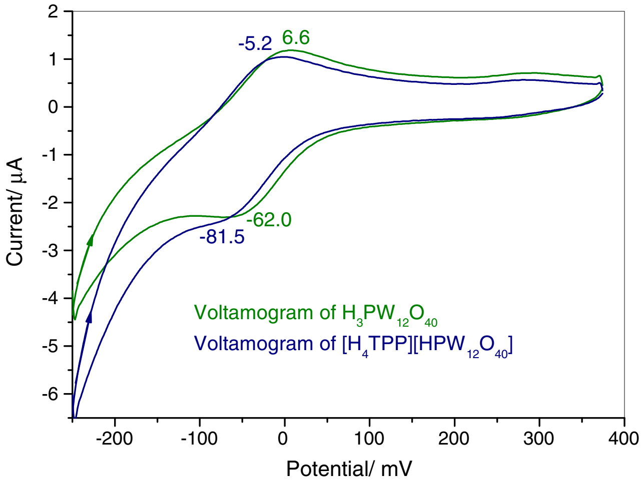
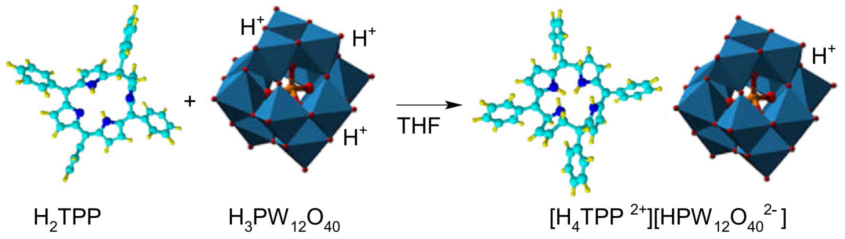


Fig. 2. Cyclic voltammograms of tungstophosphoric acid $H_3PW_{12}O_{40}$ and organic–inorganic hybrid $[H_4TPP][HPW_{12}O_{40}]$ in tetrahydrofuran medium. A glass carbon electrode was used as a working electrode, Pt wire as an auxiliary electrode, scan rates 50 mV s^{-1}. The reference electrode was an Ag/AgCl electrode.



Scheme 2. Synthesis of the hybrid organic–inorganic catalyst.

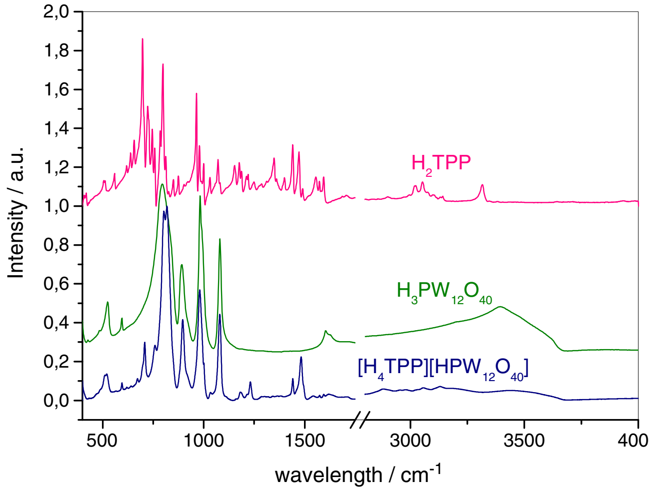


Fig. 3. FT-IR spectra of H_2TPP (pink), $H_3PW_{12}O_{40}$ (green) and organic–inorganic-hybrid $[H_4TPP]$ $[HPW_{12}O_{40}]$ (navy). Fourier transform infrared (FT-IR) absorption spectra were recorded using Nicolet 6700 spectrometer under atmospheric conditions. Spectra of solid samples were recorded as KBr pellets in range of 4000–400 cm^{-1} with resolution of 2 cm^{-1} and collecting 64 scans.

than appropriate parent heteropolyacid. Cobalt tungstophosphate catalyst, $HCoPW_{12}O$, is the most active among all the studied catalysts and displays three times higher activity than parent tungstophosphoric acid. Generally, catalysts of tungsten series are considerably more active than their molybdenum analogues. Introduction of the metal atoms into the heteropolyacids increases conversion of ketone in comparison with parent heteropolyacids. In the case of organic–inorganic hybrids, tungstophosphate hybrid $[H_4TPP][HPW_{12}O_{40}]$ shows catalytic activity similar to tungstophosphate heteropolysalts and higher than the parent heteropolyacid. The activity of molybdophosphate hybrid $[H_2TPP][HPMo_{12}O_{40}]$ is comparable to that of molybdophosphate Keggin type complexes. Both heteropolyacids, $HPW_{12}O_{40}$ and $HPMo_{12}O_{40}$ demonstrate the lowest catalytic activity in the cyclohexanone oxidation whereas porphyrin is not active at all in this reaction. High catalytic activity of hybrid catalysts arises from the synergistic effect. The following order of activity was observed for tungsten catalysts: $HCoPW_{12}O_{40} > HFePW_{12}O_{40} > [H_4TPP][HPW_{12}O_{40}] > HMnPW_{12}O_{40} > H_3PW_{12}O_{40}$. Reactivity of molybdenum catalysts has changed in a quite similar manner: $HFePW_{12}O_{40} > HCoPMo_{12}O_{40} > [H_4TPP][HPMo_{12}O_{40}] > HMnPMo_{12}O_{40} > H_3PMo_{12}O_{40}$. The influence of the nature of the metal atoms on the catalytic activity and the redox potential of polyoxometalate complexes can be explained as follows. The reduction potentials of cation-exchanged heteropolyacids can be controlled by the electronegativity of the counter-cation [42]. When two protons from $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ acid were replaced by less electronegative cations like cobalt, manganese or iron, the reduction potential of synthesized heteropolysalts decreased, which implied an increase of their oxidation potential. The similar phenomenon was observed for studied organic–inorganic hybrids. Since H_2TPP porphyrin can be treated as an electron-donating group, the negative charge on the heteropolyacid is expected to increase. In consequence the decrease of the reduction potential of the hybrids occurs and, according to expectations, the increase of their catalytic activity is noted as in the case of polyoxometalate catalysts. The similar synergistic effect was also observed in the cyclohexane hydroxylation catalyzed by metallocomplex-porphyrin hybrid catalyst [43] and Suzuki coupling reaction catalyzed by salen-polyoxometalate hybrid catalyst [44]. In both cases, catalytic activity of hybrid catalysts is higher than catalytic activity of their organic or inorganic components.

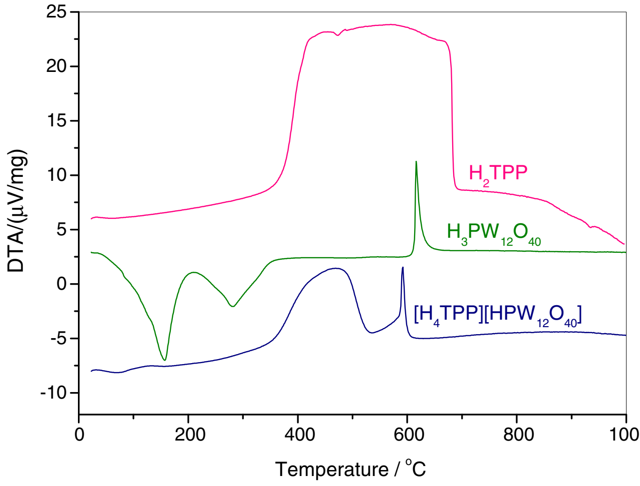


Fig. 4. DSC measures of H_2TPP (pink), $H_3PW_{12}O_{40}$ (green), and organic–inorganic hybrid $[H_4TPP][HPW_{12}O_{40}]$ (navy). The simultaneous differential thermal analysis was performed using NETZSCH STA 409 apparatus: temperature range from ambient to 923 K, heating rate 25 K/min, dynamic air atmosphere with the flow rate 30 mL/min, sample 8–10 mg.

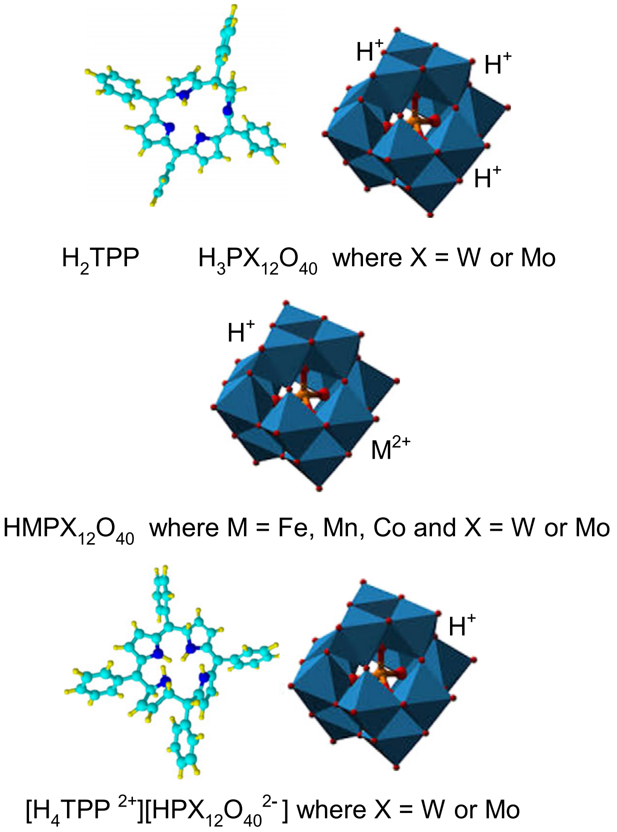


Fig. 5. Investigated catalysts.

Tungstophosphate hybrid catalyst was recycled three times with only a small decrease of catalytic activity in the second run and in the third run (Table 1).

1. Conclusions

In summary, a new organic–inorganic hybrid $[H_4TPP][HPW_{12}O_{40}]$ was synthesized and characterized by UV–Vis and FT-IR spectroscopy, differential scanning calorymetry DSC, thermogravimmetric analysis TG and cyclic voltammetry CV. This new hybrid, its molybdenum analogue and iron, manganese or cobalt salts of tungstophosphoric and molybdophosphoric acids were applied for the first time in the

Table 1
Oxidation of cyclohexanone to caprolactone with molecular oxygen catalyzed by polyoxometalates and their hybrids with porphyrin[a].

Entry	Catalyst		Conversion[a] of cyclohexanone, %	Yield of caprolactone, %	Selectivity %	TON[b]
1	$[H_4TPP][HPW_{12}O_{40}]$	(1)	56.1 54.1[c] 52.8[d]	24.2 23.5 23.2	43.1 43.4 43.8	111.3 108.1 106.7
2	H_2TPP	(2)	–	–	–	–
3	$H_3PW_{12}O_{40}$	(3)	18.5	6.0	32.4	27.6
4	$HFePW_{12}O_{40}$	(4)	60.3	25.6	42.5	117.7
5	$HCoPW_{12}O_{40}$	(5)	58.7	38.9	66.4	178.9
6	$HMnPW_{12}O_{40}$	(6)	52.8	23.3	44.1	107.2
7	$[H_4TPP][HPMo_{12}O_{40}]$	(7)	30.2	15.6	58.3	71.8
8	$H_3PMo_{12}O_{40}$	(8)	26.5	7.8	29.4	35.9
9	$HFePMo_{12}O_{40}$	(9)	32.3	18.4	57.0	84.6
10	$HCoPMo_{12}O_{40}$	(10)	33.9	16.5	48.7	75.9
11	$HMnPMo_{12}O_{40}$	(11)	30.1	13.1	43.5	60.2

[a] Reaction conditions: cyclohexanone = 4.6 mM, aldehyde = 14 mM, catalyst 0.01 mM in a 10 mL of acetonitrile, reaction time = 5 h, temp. = 40 °C.
[b] TONs were calculated as [mol of product]/[mol of catalyst].
[c] Second run.
[d] Third run.

oxidation of cyclohexanone to caprolactone with molecular oxygen. Tungsten derived heteropolysalts and tungstophosphate hybrid show three times higher catalytic activity in comparison to $H_3PW_{12}O_{40}$. Molybdenum derived heteropolysalts and molybdophosphate hybrid demonstrate similar trend in the catalytic activity increase but it is not so spectacular like for tungsten series. Catalytic activity of heteropolysalts is governed by introduction of metal atom — new catalytic centre, while catalytic activity of porphyrin-heteropolyacid hybrids is connected with the synergistic effect.

Acknowledgment

This research received funding from the Marian Smoluchowski Kraków Research Consortium — a Leading National Research Center KNOW supported by the Ministry of Science and Higher Education.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2015.06.005.

References

[1] M. Renz, B. Meunier, Eur. J. Org. Chem. 4 (1999) 737–750.
[2] G.-J. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, Chem. Rev. 104 (2004) 4105–4123.
[3] F. Cavani, K. Raabova, F. Bigi, C. Quarantelli, Chem. Eur. J. 16 (2010) 12962–12969.
[4] A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane, Chem. Rev. 110 (2010) 6009–6048.
[5] N. Mizuno, K. Kamata, K. Yamaguchi, Top. Organomet. Chem. 37 (2011) 127–160.
[6] F. Cavani, L. Ferroni, A. Frattini, C. Lucerelli, A. Mazzini, K. Raabova, S. Alini, P. Accorinti, P. Babini, Appl. Catal. A Gen. 391 (2011) 118–124.
[7] I.K. Song, M.A. Barteau, J. Mol. Catal. A Chem. 212 (2004) 229–236.
[8] M. Misono, Catal. Rev. Sci. Eng. 29 (1987) 269–321.
[9] R.A. Sheldon (Ed.), Metalloporphyrins in Catalytic Oxidations, Marcel Dekker, New York, 1994.
[10] F. Montanari, L. Cassela, Metalloporphyrins Catalyzed Oxidation, Kluwer Academic Publisher, Dordrecht, 1994.
[11] D. Schaming, C. Costa-Coquelard, I. Lampre, S. Sorgues, M. Erard, X. Liu, J. Liu, L. Sun, J. Canny, R. Thouvenot, L. Ruhlmann, Inorg. Chim. Acta 363 (2010) 2185–2192.
[12] M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Boltork, Dalton Trans. 41 (2012) 3087–3094.
[13] A. Yokoyama, T. Kojima, K. Ohkubo, S. Fukuzumi, Chem. Commun. (2007) 3997–3999.
[14] A. Yokoyama, T. Kojima, K. Ohkubo, S. Fukuzumi, Inorg. Chem. 49 (2010) 11190–11198.
[15] M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Boltork, Dalton Trans. 41 (2012) 11745–11752.
[16] X. Meng, H.-N. Wang, X.-L. Wang, G.-S. Yang, S. Wang, K.-Z. Shao, Z.-M. Su, Inorg. Chim. Acta 390 (2012) 135–142.
[17] M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Boltork, M.M. Javadi, Polyhedron 29 (2010) 648–654.
[18] I. Bar-Nahum, H. Cohen, R. Neumann, Inorg. Chem. 42 (2003) 3677–3684.
[19] X. Meng, H.-N. Wang, G.-S. Yang, S. Wang, X.-L. Wang, K.-Z. Shao, Z.-M. Su, Inorg. Chem. Commun. 14 (2011) 1418–1421.
[20] Q. Wu, X. Hao, X. Feng, Y. Wang, Y. Li, E. Wang, X. Zhu, X. Pang, A hexa-{MnIII-Schiff-base}-decorated cyclic polyoxovanadate as photocatalyst for dye degradation, Inorg. Chem. Commun. 22 (2012) 137–140.
[21] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Boltork, E. Shams, N. Rasouli, Appl. Catal. A Gen. 334 (2008) 106–111.
[22] J. Ettedgui, R. Neumann, J. Am. Chem. Soc. 131 (2009) 4–5.
[23] I.C.M.S. Santos, S.L.H. Rebelo, M.S.S. Balula, R.R.L. Martins, M.M.M.S. Pereira, M.M.Q. Simoes, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, J. Mol. Catal. A Chem. 231 (2005) 35–45.
[24] M. Najafi, A. Abbasi, M. Masteri-Farahani, V.H. Rodrigues, Inorg. Chem. Commun. 46 (2014) 251–253.
[25] S.-Q. Liu, J.-Q. Xu, H.-R. Sun, D.-M. Li, Inorg. Chim. Acta 306 (2000) 87–93.
[26] D. Schaming, C. Costa-Coquelard, S. Sorgues, L. Ruhlmann, I. Lampre, Appl. Catal. A Gen. 373 (2010) 160–167.
[27] H. Kameyama, F. Narumi, T. Hattori, H. Kameyama, J. Mol. Catal. A Chem. 258 (2006) 172–177.
[28] Z. Shi, Y. Zhou, L. Zhang, S. ul Hassan, N. Qu, J. Phys. Chem. A 118 (2014) 6413–6422.
[29] Supporting Information.
[30] D.F. Marsh, L.M. Mink, J. Chem. Educ. 73 (1996) 1188–1190.
[31] M. Hye Youn, H. Kim, J. Chul Jung, I. Kyu Song, K.P. Barteau, M.A. Barteau, J. Mol. Catal. 241 (2005) 227–232.
[32] M.M. Kruk, A.S. Starukhin, W. Maes, Macroheterocycles 4 (2011) 67–79.
[33] Supporting Information.
[34] T. Okuhara, N. Mizuno, M. Misono, Advances in Catalysis, vol. 41Academic Press, Inc., 1996. 129.
[35] C. Racchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22 (1983) 207–216.
[36] C. Rocchiccioli-Deltcheff, M. Fournier, J. Chem. Soc. Faraday Trans. 87 (1991) 3913–3920.
[37] D.W. Smithenry, K.S. Suslick, J. Porphyrins, Phthalocyanines 8 (2004) 182–190.
[38] S.F. Pop, R.M. Ion, M.C. Corobea, V. Raditoiu, J. Optoelectron. Adv. Mater. 13 (2011) 906–911.
[39] Supporting Information.
[40] G.A. Tsigdinos, Ind. Eng. Chem. Prod. Res. Dev. 13 (1974) 267–274.
[41] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171–198.
[42] K. Tanaka, A. Ozaki, J. Catal. 8 (1967) 1–7.
[43] J.-W. Huang, Z.-L. Liu, X.-R. Gao, D. Yang, X.-Y. Peng, L.-N. Ji, J. Mol. Catal. A Chem. 111 (1996) 261–266.
[44] J. Tong, H. Wang, X. Cai, Q. Zhang, H. Ma, Z. Lei, Appl. Organomet. Chem. 28 (2014) 95–100.