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

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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 heteropolycarids.

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 [H4TPP][HPW12O40 · 3 · THF · 6 · H2O] 1, was synthesized (Scheme 2) according to the procedure of Shi et al. [28] from the tetraphenylporphyrin H2TPP 2 and tungstophosphoric acid H3PW12O40 3 [29]. Synthesized hybrid was characterized by UV–Vis and FT-IR spectroscopy, differential scanning calorimetry DSC, thermogravimetric analysis TG and cyclic voltammetry CV.

The formation of organic–inorganic hybrid was evidenced by UV–Vis spectroscopy. The absorption spectrum of the tetraphenylporphyrin H2TPP shows four Q bands in the visible range of spectra with maxima at 418, 518, 615, 562 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 H2TPP upon stepwise addition of a THF solution of H3PW12O40 (6 · 10−3 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 H2TPP2+ 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 H3PW12O40 reaches Epa = 6.6 mV and cathodic potential Epc = −62.0 mV.

As mentioned above, upon attachment of electron-donating porphyrin to tungstophosphoric acid which is the electrons reservoir, the
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=O, interoctaedral W–O–W and intraoctaedral W–O–W bonds, respectively [34]. The bonds that are present in H$_2$TPP 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 C–H bands 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$_2$TPP porphyrin and heteropolyacid H$_3$PW$_{12}$O$_{40}$ [35,36]. For H$_2$TPP 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$_3$PW$_{12}$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$_2$O$_4$ 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$_3$PW$_{12}$O$_{40}$.

New organic–inorganic hybrid [H$_4$TPP][HPW$_{12}$O$_{40}$] and its molybdenum analogue [H$_4$TPP][HMPW$_{12}$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 H$_3$PMo$_{12}$O$_{40}$ and H$_3$PW$_{12}$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$_3$PMo$_{12}$O$_{40}$ and H$_3$PW$_{12}$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$_2$TPP) are active in the oxidation of cyclohexanone. Molybdophosphoric acid H$_3$PMo$_{12}$O$_{40}$, due to its higher oxidizing ability, is more active than tungstophosphoric acid H$_3$PW$_{12}$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.

Scheme 1. Oxidation of cyclohexanone to caprolactone.

Fig. 1. Spectroscopic titration of a $8\times10^{-6}$ mol L$^{-1}$ THF solution of tetraphenylporphyrin H$_2$TPP (black line) by a heteropolyacid H$_3$PW$_{12}$O$_{40}$ solution (in 5 μL portions of $6\times10^{-5}$ mol L$^{-1}$ H$_3$PW$_{12}$O$_{40}$ in THF).

Fig. 2. Cyclic voltammograms of tungstophosphoric acid H$_3$PW$_{12}$O$_{40}$ and organic–inorganic hybrid [H$_4$TPP][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.
than appropriate parent heteropolyacid. Cobalt tungstophosphate catalyst, HCoPW12O, 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 [H4TPP][H2PW12O40] shows catalytic activity similar to tungstophosphate heteropolysalts and higher than the parent heteropolyacid. The activity of molybdophosphate hybrid [H2TPP][HPMo12O40] is comparable to molybdophosphate Keggin type complexes. Both heteropolyacids, HPW12O40 and HPMo12O40 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: HCoPW12O > HFePW12O > [H4TPP][HPW12O40] > HMnPW12O40 > H3PW12O40. Reactivity of molybdenum catalysts has changed in a quite similar manner: HFePW12O > HCoPMo12O > [H4TPP][HPMo12O40] > HMnPMo12O > H3PMo12O40. 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 H3PW12O40 or H3PMo12O40 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 H2TPP 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.

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 [H4TPP][HPW12O40] was synthesized and characterized by UV–Vis and FT-IR spectroscopy, differential scanning calorimetry DSC, thermogravimetric 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
oxidation of cyclohexanone to caprolactone with molecular oxygen. Tungsten derived heteropolysalts and tungstophosphate hybrid show three times higher catalytic activity in comparison to $H_2PW_{12}O_{40}$. 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-heteropolypolygacids is connected with the synergistic effect.

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**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**

[29] Supporting Information.
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