

CHALLENGES IN THE SYNTHESIS OF COMPOSITES BASED ON HETEROPOLY COMPOUNDS

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Abstract

Polyoxometalates (POMs) are divided into two groups, namely isopoly and heteropoly anions. While the isopoly anions are built by (1) oxygen and (2) a transition metal (V, Nb, Ta, Mo, W), the heteropoly anions consist of: (1) oxygen atoms, (2) a metal labeled the addenda atom (W, Mo or V), and (3) an element generally from the p-block of the periodic table termed the heteroatom (Si, P or As). Heteropoly acids (HPAs) are composed of heteropoly anions and acidic hydrogen atoms. Among a wide variety of heteropoly acids, the Keggin type is the most stable and more readily available. Important characteristics responsible for a wide variety of applications of this type of compounds are: acidity, catalytic ability, easily and reversibly reduction in one- or multiple-electron steps, and significant biological activity. All these features are a consequence of their characteristic structure.

The preparation of a composite material presents a complex experimental challenge. The combination of different components engineered in such a way that they preserve their useful properties could potentially enable a synergetic effect when investigated for a specific application.

More than decade long investigations of our group from University of Belgrade try to find the answers whether the obtained composites would unify suitable properties of both components and improve: adsorption behavior for pesticide removal, antibacterial, and catalytic activity, as well as the charge storage properties. The basis of our work is the investigation of HPAs and their salts supported as an active phase on zeolites (H-BEA zeolite), mesoporous molecular sieves (TiO₂, MCM-41, SBA-15), and carbon materials (active carbon, graphene oxide, HOPG).

The results indicate that the interaction of HPAs with supporting materials is of substantial importance in applications and it has been studied in detail using different methods, such as the Fourier-transform infrared and Raman spectroscopy, X-ray photoelectron spectroscopy, temperature-programmed desorption method, zeta potential measurements, thermogravimetric-differential thermal analysis, X-ray diffraction analysis, transmission electron microscopy, and others.

Keywords: heteropoly compounds, Keggin anion, composites, zeolites, carbon materials, mesoporous molecular sieves

INTRODUCTION

Polyoxometalates (POMs), structures discovered before almost two centuries, usually consist of three or more oxide structures of transition metals interconnected by common oxygen atoms [1]. In such way, a formed three-dimensional network is characterized with the delocalization of the negative charge as one of their important properties. The metal ion usually belongs to the sixth (Mo and W) or fifth (V, Nb and Ta) groups of transition metals, in the form of their higher oxidation states. POM are usually classified as isopoly oxometalates, i.e., isopolyanions, and heteropoly oxometalates, or heteropolyanions. Besides the oxide structures of the metal atom, heteropolyanions also contain the central hetero atom, i.e., the anion of the inorganic acid (most usually phosphoric, silicic or boric acid).

Heteropoly compounds (HPC) are characterized by the diversity of chemical structures. The Keggin anion (KA) structure, such as dodeca tungsto- and/or molybdophosphates, is the most explored subset of POM, Fig. 1.

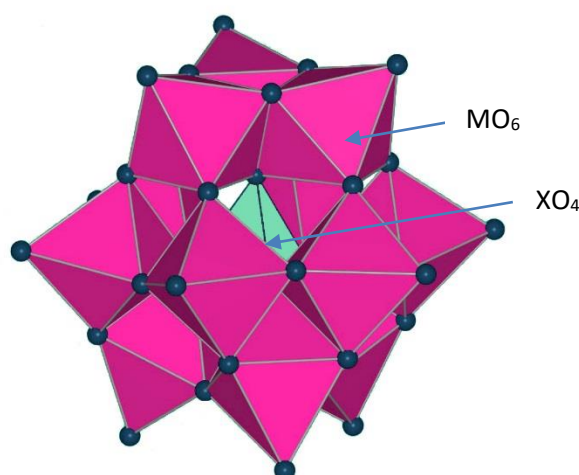


Fig. 1. Keggin anion structure (most frequently M – W, M or V; X – P, Si or B)

Keggin structured dodeca tungstophosphoric acid hydrates (WPA), characterized by strong acidity, are classified as “superacids” and the acidity is 100–1000 times that of H_2SO_4 . Also, they are soluble in water (1 g mL^{-1}), are very hygroscopic (up to 48 moles of water per mole of tungstophosphoric acid) and their surface area is relatively low ($<10\text{ m}^2\text{ g}^{-1}$) [2].

These properties which may be the disadvantages in certain applications, can be overcome by neutralization of the acid with large cations (e.g. K^+ , Rb^+ , Cs^+ , NH_4^+) to form porous insoluble salts. These salts are characterized by lower level of hydration and by less sensitivity to the surrounding conditions [3]. Another method, which is widely used, is incorporation of the acid into various stable porous supports, by the formation of different composites. These two basic types of procedures for the synthesis of new HPA-based materials are illustrated in Fig. 2.

Uncommon and fascinating properties of HPCs render them suitable for various applications. Thus, heteropoly acids (HPA) and their salts show high proton conductivity at room temperature [4], and high potential of numerous bioactivities [5]. Further, the acid and redox properties of these compounds make them good catalysts [6]. The interesting characteristics of the HPA is their tendency to decompose in solutions at high pH, whereby lacunar structures are formed [7,8].

HETEROPOLY ACIDS AND THEIR SALTS – THE STARTING POINT

With the aim to stabilize but to retain useful characteristics of HPA, the starting point was a synthesis of suitable salts. HPA salts can be divided into two groups according to their properties [4]. The salts of small cations such as Li^+ or Na^+ are classified to group A, and possess similar properties to the parent acid. They are non-porous, soluble in polar solvents, absorb polar molecules, and have low thermal stability. The salts of large cations (like Cs^+ or K^+) classified as B group salts are insoluble in polar solvents and have relatively high surface area and higher thermal stability.

HPA salts can be formed by replacing all protons in the acid, when neutral salts are formed, or partial replacement of protons, when acid salts are formed.

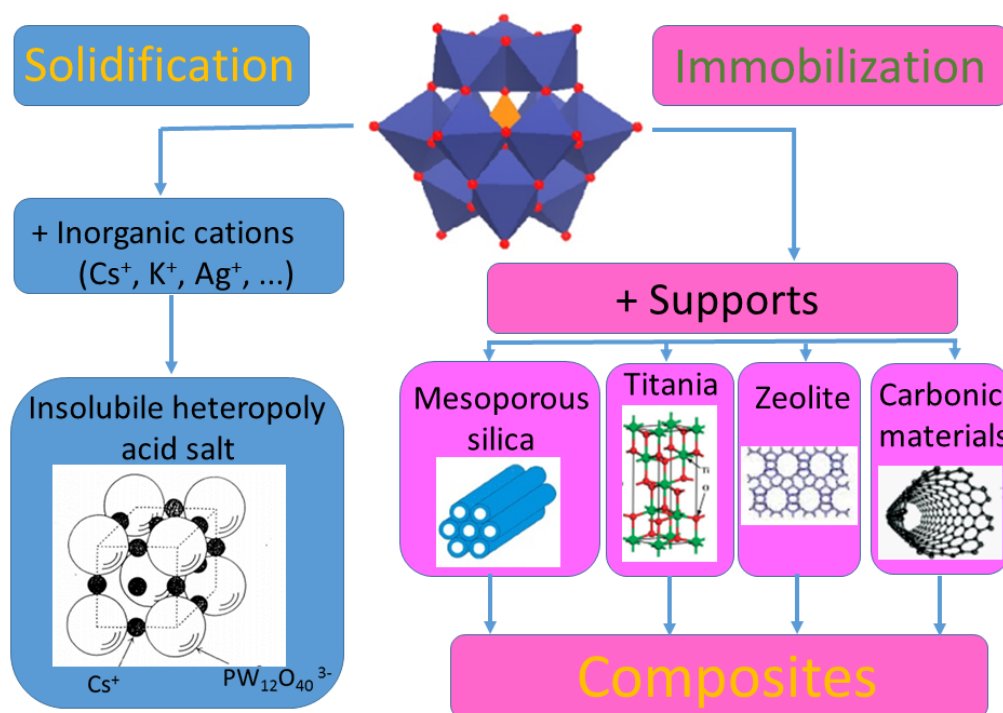


Fig. 2. Scheme of the synthesis procedures for obtaining HPA based materials

The experimental results confirm that potassium salts of WPA could be good candidates for application as proton exchange electrolytes in fuel cells due to their satisfactory proton conductivity, 7.2×10^{-5} (for K_3WPA), 8.7×10^{-5} (for K_2HWPA) and 1.4×10^{-4} (for KH_2WPA) S/cm, which are higher than the conductivity of WPA, whose value is 6.4×10^{-4} S/cm. Also, their possible washing out from electrolyte or membrane is avoided in contrast to soluble parent acid [9].

But, the stoichiometric ratio of the components used in the salts' synthesis does not necessarily result in the planned composition of the final compound, as it was reported for the case of potassium salts of WPA [9]. The characterization of obtained salts confirm that in the synthesis of neutral salts, the reaction of WPA with K_2CO_3 in the stoichiometric ratio causes precipitation of K_3WPA , as it was presumed. But, in the procedure of an acidic potassium salt (KH_2WPA) synthesis, a two-phase system of mesoporous neutral K_3WPA salt and unreacted cubic crystals of WPA was obtained as a result. Also, if the number of counter ions is 2, as in the case of potassium salt K_2HWPA , unreacted acid is dispersed over the grains of neutral salt.

The observed enhancement of proton conductivity of WPA potassium salts could be interpreted according to defect chemistry in heterogeneous polycrystalline and multiphase systems. Formation of extra defects (proton and proton vacancy) in the space-charge regions and internal interactions between defects, enables more developed network of hydrogen bonds. In addition to this, water, H^+ and protonic species in acid hydrate and in potassium salt hydrates are under the different influences. Higher proton conductivity of potassium salt WPA is enabled with defects in the space-charge region and higher statistical disorder of protonic entities [9]. Although the investigated salts have shown good chemical stability and satisfied conductivity, their potential as applicable materials can be reached by incorporation of this class of compounds into supports such as silica, alumina, titania, carbon or organic polymer.

WPA salts of elements from 1B and 3A groups of the periodic table, such as Ag and Tl, also possess behavior similar to alkaline metal WPA salts [6]. The exception is the thermal behavior of the silver salt, which is more like the parent WPA. Interestingly, neutral silver salt of WPA shows acidity about one order of magnitude higher than of neutral cesium salt. Probably, such high acidity is produced by

dissociation of water molecules coordinated to silver cations. According the physicochemical properties, this salt are between soluble A group and insoluble B group of salts.

The synthesis procedures can have a major impact on the morphology and properties of the final product. The influence of the synthesis procedures on silver WPA salts are reported in detail [10]. Neutral salt obtained by slow evaporation of the supernatant, labeled as AgWPA-E, forms randomly oriented aggregates of different shape and size. If the same salt is prepared by filtration of the supernatant, marked as AgWPA-F, porous aggregates of dodecahedral shape will be formed. The specific surface areas of the same salts, prepared by two different procedures are quite different: the specific surface area of AgWPA-F is about 16 times higher than the value of the AgWPA-E. The origin of these variances is different volume of micropores. At the same time, the contribution of the preparation procedure has no influence on the mesoporous region. The samples AgWPA-F and AgWPA-E show similar catalytic activity in dehydration of ethanol, as well as the selectivities of the main products (ethylene and diethyl ether) due to the same mesoporous surfaces and volumes. The low energy of activation of silver salt of WPA candidates makes this material a promising green catalyst for ethylene production.

Acid Ag salts of WPA have a specific surface area and thermal stability close to that of WPA [11]. They are less hydrated than the parent acid and partly insoluble in water. It was confirmed by Raman spectroscopy that the Keggin structure remains unaltered in salt, while an interaction between the Ag cation and tungstophosphate anion is mainly realized through terminal oxygen atoms. The XRD patterns of the acid salts with number of replaced protons less than 2 showed that these salts are two-phase mixtures consisting of neutral Ag salt and parent acid, as in the case of insoluble alkali salts of WPA. All the acid Ag salts $\text{Ag}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, where Ag content is $x = 1$ up to $x = 2.5$, proved to be less effective but more stable catalysts for dehydration of ethanol in gas phase compared to the parent acid. Their activity slightly decreases with increase of Ag mass%, while selectivity of ethylene and diethyl ether shows opposite dependence.

All the results indicate that the neutral and acid Ag salts of WPA are promising catalysts for ethylene production but their support on the micro and/or mesoporous matrices should be expected as more favourable.

COMPOSITES BASED ON HPC – THE NEXT LEVEL

As it has been stated previously, one of the possible ways to retain desirable characteristic of HPC and to overbridge some of not so appropriate characteristics, was to incorporate them into composites (where the immobilization of HPA on a suitable solid support may be performed by encapsulation, grafting, tethering and dispersion, [12]). Albeit, the preparing of composite materials for the particular application, in such a way to preserve the advantages of both components, requires creativity, theoretical knowledge and experimental skills.

This strategy seems to be promising, and as a result, numerous studies reported the application of great varieties of materials for those purposes, such as silica [13], titania [14], carbon [15], mesoporous materials [16], zeolites [17, 18] or montmorillonite clays [19]. Microporous materials, such as crystalline aluminosilicates (zeolites), are characterized by uniformly-sized channels. The pores in mesoporous materials (i.e., transitional aluminas or modified layered materials such as pillared clays and silicates), are generally irregularly spaced and broadly distributed in size. A problem may arise when strong chemical/physical interaction between the support and the HPA appears, which can lead even to destruction of HPA structure. For example, MgO , Al_2O_3 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ influence the decomposition of the Keggin anion [20, 21]. HPA supported materials depend mainly on the nature of the active phase and the support, concentration and pH of the impregnating solution, the solvent type, applied method of composite preparation as well as pre-treatment and post- synthesis procedures. In the explanation of the interaction between the active phase and the support, all the mentioned data should be taken into account [22].

Based on vibrational spectroscopy it is possible to monitor the interaction between HPA as the active phase and the support in the obtained samples, as well as the presence of “unbound” Keggin anions. The interaction of HPA with supports depends on the nature of both components. For example, microporous supports such as zeolites relatively strongly interact with HPA's. The formation of WPA and zeolite BEA composite is a consequence of the strong interaction of the Keggin anion and the zeolite, which is realized by H-bond, while in composite WPA and zeolite NaY, interaction is carried out via a decomposed form of the Keggin-anion. Also, TiO_2 strongly interacts with HPA and the hydrolysis of WPA occurs as a consequence of this interaction. On the other hand, silica mesoporous molecular sieves, as SBA-15 and MCM-41, and HPA show very weak mutual interaction. Information of the nature of interaction of HPC and supports gives a clue about the structure characteristics, and predict the catalytic activity potential of the investigated composites [22].

HPC COMPOSITES – APPLICATION IN CATALYSIS

Dispersion of HPA and their neutral or acid salts on solid supports with high specific surface area can improve the accessibility of the active sites and to advance their activity in various catalytic reactions. However, the sort of HPA and the support, the nature of interaction between the HPA and the support, as well as the experimental parameters during the synthesis considerably determine the activity of the obtained catalysts.

Modification of titania with WPA leads to more pronounced photocatalytic activity in degradation of various contaminants [14, 23-25] and other catalyzed organic transformations compared to pure titania [26-28]. The catalysts based on WPA supported by SBA-15 have been applied for various reactions such as synthesis, esterification, alkylation, isopropylation, and others [4]. The leaching of the WPA acid in polar media is a serious drawback to its application as active phase, so that insoluble WPA salts are preferred in these applications [29].

The deposition of silver acid salt $\text{Ag}_2\text{HPW}_{12}\text{O}_{40}$ (AgWPA) and the parent acid WPA (for comparison) on hydrothermally stable mesoporous molecular sieve SBA-15 and mesoporous TiO_2 , can be carried out via a simple incipient wetness impregnation method [30]. The composites AgWPA and WPA and these mesoporous carriers exhibited the high conversion and selectivity for ethanol dehydration. However, WPA supported catalyst tended to lose its activity due to the leaching of active heteropoly anion into the polar medium. Supported AgWPA on SBA-15 is more water-tolerant and thus important and promising as an ecofriendly solid acid catalyst.

Activated carbon (AC) is expected to be a catalyst supports due to a high surface area, suitable physical properties, stable inertness in harsh process conditions and low cost per cubic meter. Various reactions using catalysts based on AC have been carried out, among others and Keggin type heteropoly acids anchored to AC [15, 31-34]. Composites of WPA and its potassium salts (KH_2WPA and K_3WPA) supported on activated carbon (AC) showed very high activity in the vapor phase ethanol dehydration reaction, unlike pristine AC. The catalytic activity of pristine AC is extremely low due to its negligibly low acidity. The pure WPA, without support, shows the highest catalytic activity compared to salts in spite of the lowest surface area and no porosity for the reason that WPA is the strongest Brønsted acid [35]. In the case of composites AC and WPA, the surface area and pore volumes are higher in comparison to pure WPA, which result in improvement of their catalytic effect, dependent on WPA content. The almost 100 % ethanol conversion, for the first 200 min of time of streaming, is realized when catalyst with the highest content of WPA is supported to AC. However, in the case of $\text{K}_3\text{PW/AC}$ and $\text{KH}_2\text{PW/AC}$ composite samples, the amount of residual protonic entities are considerably lower and insufficient as active centers for catalysis of the ethanol dehydration reaction. It is clear that both surface area and acidity of the catalysts are important and should be considered in catalytic reactions.

The use of different zeolitic structures is attractive in this area, because of their ordered pore structures, high thermal stability and large surface area [36]. However, the applications of some zeolites for preparation composites based on HPA are limited because of their low stability in acidic medium and no resistance toward WPA decomposition. The zeolite BEA with three-dimensional

wide-pore system which comprises intersecting channels formed by 12-membered rings, is interesting for this purpose because Keggin anion in WPA/BEA composites remains unchanged. The HPC cannot fill the zeolite cavities because the diameter of 12-membered rings is 0.67 nm and isolate Keggin anion has diameter 1.2 nm, but is deposited on the external surface of the crystallites. Due to the better dispersion of the WPA active phase and larger surface area of the samples with lower WPA content, these samples show a higher catalytic activity [36]. The high ethanol conversion was associated with available Brønsted acid sites. When high loadings were accomplished, agglomerates of Keggin anion can reduce the number of active sites on WPA molecules. Also, excess of WPA blocks zeolite active sites and thus also lowers their accessibility to ethanol molecules. The different post-synthesis procedures including calcination and ultrasonication can lead to the formation of materials with improved characteristics. For example, samples obtained by ultrasound treatment possess better dispersion and homogeneous morphology, and thus increased and acid site distribution and availability for ethanol molecules.

HPC COMPOSITES – APPLICATION AS ADSORBENTS

Mentioned WPA/BEA zeolite composites were also investigated, using HPLC, as adsorbents of pesticide nicosulfuron [37]. The composite samples with different WPA/BEA ratios were found to be more efficient in nicosulfuron adsorption than parent BEA zeolite. The adsorption capacities are over 400 times higher than for active carbon, known in the literature as an excellent adsorbent. In addition, the preparation procedure which includes drying, calcination or ultrasonication, caused larger differences in adsorption behavior for the sample with the lowest amount of WPA, than with higher WPA content. The amount of WPA in the composite samples and the value of the particles surface charge are not essential for the adsorption behavior, it is rather the homogeneity of the zeolite surface coverage with the Keggin anion and distribution of active sites for adsorption.

In the preparation of composites intended for environmental pollutants treatment, the main issue is active component leaching. Successful preparation of insoluble K_3WPA/BEA zeolite composites is achieved through in situ synthesis, namely K^+ ion replacement in the external zeolite manifold and its subsequent reaction with WPA [38]. These composites were investigated as adsorbents of pesticide glyphosate. SEM imaging of the synthesized material detected similar morphology of composite and parent BEA zeolite but highly ordered and crystalline K_3WPA constituent parts could also be distinguished on micrograph of the composite sample. The primary structure of K_3WPA remained intact after immobilization on BEA zeolite, which was confirmed by vibrational spectroscopy. Also, this method indicated that the interaction of K_3WPA with zeolite is achieved via terminal oxygen atom of Keggin anion. Langmuir isotherm model, which assumed the binding on the energetically homogeneous adsorption centers, is highly suitable for the description of the adsorption behavior of K_3WPA/BEA composite. The adsorption of glyphosate is significantly affected by the synthesis procedure. In this case calcination, rather than drying, has produced materials with significantly high adsorption capacities. The interaction between KPW and glyphosate molecules is realized via hydrogen bond formation between secondary amine of glyphosate protonated form and unshared terminal oxygen atoms in structure. It was proved that regeneration of K_3WPA/BEA adsorbents can be performed by thermal treatment. Accordingly, supporting of K_3WPA on BEA zeolite-enabled the formation of highly efficient adsorbents for pesticide glyphosate with a significant perspective in environmental application.

HPC COMPOSITES – APPLICATION IN ELECTROCHEMISTRY

One of the possible fields of application of the composites based on HPC are electrochemical devices. HPC loaded nanocarbons are one of the examples used in energy related applications thanks to a synergy of physical capacitor effect and electrochemical redox reactions. The synthesis of those materials is very delicate because the interaction of HPC with carbon materials is of great importance in energy storage applications [39]. By the interaction between POMs and nanocarbon materials, one can obtain materials with adjustable physicochemical properties. The reasons for this are: the

tunability of POMs' size, structure and elemental composition, as well as rich surface chemistry of carbonaceous support. The interaction between POMs and carbon support is a complex process that can be described as strong and irreversible adsorption to a carbon support, resulting in a covalent bond formation [40]. Oppositely, some authors refer to this interaction as electrostatic repulsion between the electronegative oxygen-containing groups on carbon matrix and polyanions [41]. The thermal, mechanical and chemical stability together with a competitive cost, make graphene oxide (GO) an ideal candidate to be used as a support. The results of a recent study of GO/WPA nanocomposite show that surface chemistry, structural and thermal properties of the nanocomposite are significantly influenced by WPA loading, with the most pronounced changes in the range of 5-13wt % of WPA [42]. At low WPA loading, individual Keggin anions are allocated to the regions of GO matrix with higher content of oxygen functional groups, which leads to reduction of the amount of oxygen complexes and structural modification of the GO. At the same time, structural change of Keggin anion appears, as confirmed by FTIR spectroscopy, indicating the highest interaction of Keggin anion via terminal oxygen atom with protonated oxygen groups of GO. At high WPA loading (>13 wt%) the interaction between GO and Keggin anions is overpowered by the interaction between Keggin anions themselves in their agglomerations, and the properties of independent components of composites start to be manifested. Those facts are important since they are showing how it can be concluded that optimal ratio of components can be used for tuning of their interaction and thus adjust the properties of the final product.

Besides the ratio of components, the surface chemistry, i.e., the amount of surface oxygen functionalities of the obtained composite materials can be influenced by the choice of HPA or their suitable combination [43]. In case of anchoring WPA to AC surface, since the electrode potential of WPA has a more negative value than the peak of carbon redox process, the electrons will transfer spontaneously from WPA to AC, thus reducing it. The opposite redox abilities towards carbon surface chemistry is noticeable for another acid, molybdophosphoric acid (MoPA). Namely, the electrode potential of MoPA redox reactions is slightly more positive than the potential of the carbon redox process, so the electrons move spontaneously from AC to MoPA. MoPA acts as an oxidant, while water takes a role of the mediator in the formation of oxygen-containing groups CO and C=O functionalities at the AC surface.

HPC COMPOSITES- ANTIMICROBIAL STUDY

POMs, alone and as several kinds of composites, have a great potential for antimicrobial activity [5]. Recently, advanced composites of BEA zeolite and silver tungstophosphate were synthesized with three mass ratios of zeolite and Ag₃WPA (2/1, 4/1 and 10/1) by different preparation methods: two-step impregnation, ion-exchange and physical mixing [44]. Prepared samples were tested as antimicrobial agents against different laboratory control strains of bacteria: *Staphylococcus aureus*, *Enterococcus faecalis*, *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumoniae*, *Salmonella typhimurium* and *Pseudomonas aeruginosa*, as well as one yeast *Candida albicans*. For the composites samples obtained by the two-step impregnation procedure with the highest salt content, the existence of agglomerate anions is evident, unlike the samples obtained by an ion-exchange procedure. They showed more pronounced homogeneity in terms of the uniform arrangement of the Keggin anion on the zeolite surface. The best antimicrobial activity was obtained for the composite with highest salt content obtained by the two-step impregnation procedure. This procedure enables the formation of Ag₃WPA, which is crucial for antimicrobial activity, as the dominant species at the zeolite surface, in comparison with the ion-exchange procedure, which leaves some of the Keggin structure in form of WPA. Interestingly, those materials can be potentially used against pathogenic bacteria present in water resources, as well as in large scale removal of emerging water pollutants from the environment [44].

The highest antimicrobial efficiency was obtained for the samples with the highest level of AgPW prepared by the two-step impregnation procedure. The important result is that the content of silver in the liquid phase is not crucial. While more of the AgPW goes into the liquid phase under applied experimental conditions in comparison to composite samples, the AgPW itself shows lower

antimicrobial activity than composites. Hence, the silver ions that remain in the solid phase are of utmost significance for the antimicrobial activity.

CONCLUSION

The represented literature data survey gives a deep sight about the importance of all the steps during the synthesis of composites based on heteropoly compounds. Experimental conditions, including finding the optimal ratio of the components, temperature, the sequence of steps, purification methods, etc., tremendously influence on the properties of synthesized composite. Challenging, carefully designed experimental procedures may lead to the final composite material with desired characteristics. That is the only way to take full advantage of the amazing properties of the heteropoly compounds as promising materials in many application fields.

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