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Nanocomposite Based on Natural Materials

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1. Introduction

Nanotechnology today is one of the most important ways of industrial manufacture of materials. A great variety of »nanomaterials« with controlled size and composition are developed with the aim of improving optical, mechanical, magnetic, electrical and other properties. With nanocomposite in principal, we will be able to develop structures not previously observed in nature. Also, in this way we expect to produce nanocomposite with better properties using natural raw materials as starting compound.

The most abundant natural materials at the surface of the earth are clay minerals. Clay is material less than 2 μm with specific properties (plasticity, shapeability, rheology, slip formation, ion-exchangeable, etc.) related to the fact that natural clay is nanosized layer. The clay minerals are hydrous aluminum silicates and are classified as phyllosilicates, or layer silicates. Bentonite clay contains a high percentage of montmorillonite.

Montmorillonite clays are known as inorganic ion exchange materials which are composed of alluminosilicate layers stacked one above the other, so called 2:1 layer type silicates.

The layered structure, shown in Fig. 1., presents two silica tetrahedral (corner shared) sheets fused to one (edge shared) octahedral sheet of alumina (alluminosilicate) or magnesia (magnesium silicate)(Manocha, 2006; Wang,1998)

Each layer has a small net negative charge due to an isomorphous substitution of ions in the framework, shown in Fig. 2. This charge is compensated by interlayer hydrated cations, known as exchangeable cations. It is well known that montmorillonite can accommodate various types of compounds in its interlayer spaces to give an intercalation type of inclusion compounds (Moore, 1989; Colomban, 2003; Slade, 1987).

Modification of chemical and structural properties of raw bentonite clay makes possible new nanostructured materials preparation suitable for different applications.

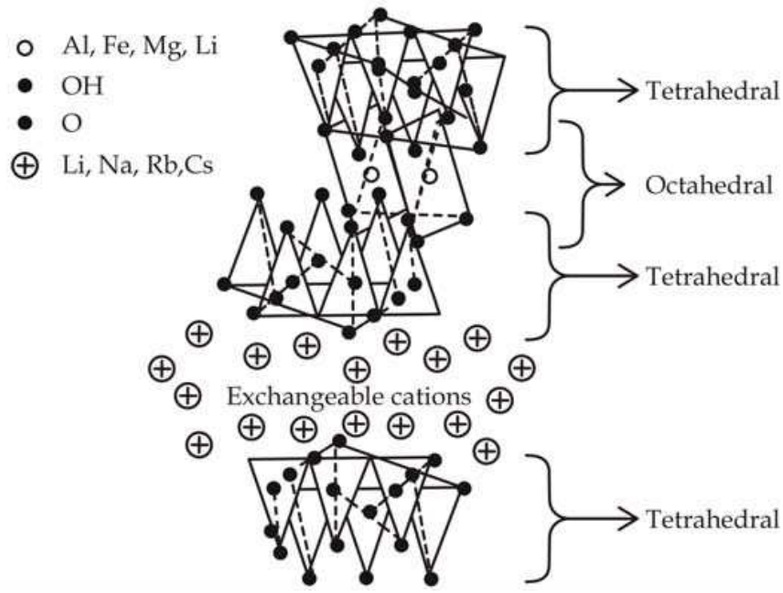


Fig. 1. Structure of montmorillonite clay

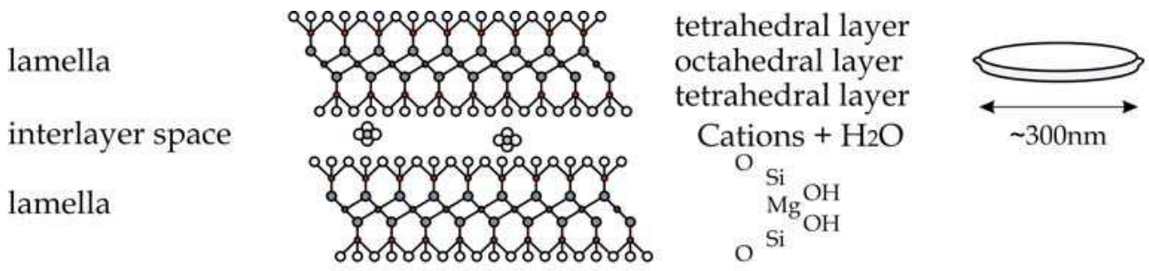


Fig. 2. The structure of montmorillonite, detailed particle view after Karnland (Kröhn, 2003).

With the aim to obtain stable new microporous material based on natural bentonite, we applied pillaring process. This is a multi-step process which involves replacement of the exchangeable interlayer cations by large inorganic polynuclear cations and calcination. Due to the calcination process, intercalated polycations transform into metal oxide clusters (named pillars) linking permanently silicate layers. New material is suitable for different applications (catalyst, catalyst support, etc.) due to their high specific area, chemical and thermal resistivity and micro- and mesoporosity (Ruiz-Hitzky, 1996).

Properties of pillared clays such as surface area, pore size distribution, acidity, depend on the synthesis treatment as well as nature minerals.

To obtain montmorillonite with increased catalytic properties and proton conductivity we have applied treatment which consisted of pillaring procedure and incorporation of different materials (polyoxomethalates -- 12-tungstphosphoric acid and ammonium decavanadate and transition metals Co and Ni) after that. The physicochemical characteristics (porosity, specific surface area, chemical composition, conductivity and catalytic properties) of obtained composite materials have been studded by porosimetry methods, atomic force microscopy, thermal analysis, X-ray diffraction (XRPD), and conductivity measurements. Several experimental techniques were employed to investigate the structure, textural and dynamic, as well as the conductivity properties of the composites.

2. Material preparation - Modification of the raw material

In our investigations we used natural bentonite clay "Šipovo" (Bosnia and Herzegovina) as starting material. The main component part of bentonite is the mineral montmorillonite (75%). Modification of the raw material consists of several steps (Sredić, 2004):

Step 1. Raw material is purified by sieving and sedimentation

Step 2. Ion-exchange step
Aqueous dispersion of purified clay is used and for Na+ exchange, a triple washing with NaCl solution followed by repeated washing until complete elimination of chloride ions is achieved. We expect largely hominid cations exchanged clays.

Step 3. Pillaring
Exchangeable cations can be substituted by large polynuclear cations which, after the thermal treatment, form nanoparticle oxides linking permanently the silicate layers. We used polyhydroxy cation of aluminium as pillaring agent to become thermally stable microporous solids. Al-pillaring reagent was prepared by slowly mixing 0.4 M solutions of $Al(NO_3)_3$ and NaOH until OHAl ratio was fixed at 2.4-2.5. Clay's dispersion was treated with pillaring reagent under continuous magnetic stirring at 80^0C over 3 hours and than allowed to cool to room temperature. Resulting sample was washed several times until complete elimination of nitrate ions, air-dried at 60^0C and calcinated at 400^0C. So we obtained pillared clays (PILCs). Heating causes dehydroxylation of the Al-polyhydroxy cations with formation of alumina clusters, water and protons. It has been proposed that protons generated during these processes migrate to the octahedral layer to charge compensate for the presence of divalent ions in octahedral sites. The exact nature of the alumina clasters that form pillar are not known. Some authors (Ocelli at al.) belive that AlOOH units connect to form the Al-pillar. Informations about dynamic of proton species can provide new knowledges about structure of pillars. There are two different stages of pillars: after drying in air at 100 0C and after calcination at 400^0C with different concentracion of hydrogen.

Chemical composition after three steps of material preparation is given in Table 1.

Chemical Characteristics	Samples			
	Starting raw material (Bentonite Sipovo)	Purified (I step)	Na-exchanged Clay (II step)	Al-pillared clay (III step)
SiO2 content (%)	53,50	50,96	49,10	46,32
Al2O3 content (%)	24,39	24,12	25,21	30,09
Na2O content (%)	0,09	0,09	4,37	0,20
K2O content (%)	0,41	0,44	0,24	0,27
CaO content (%)	2,86	2,62	0,60	0,45
MgO content (%)	1,03	1,62	1,62	0,68
Fe2O3 content (%)	4,82	4,69	3,88	3,89
TiO2 content (%)	0,41	0,39	0,67	0,68

Table 1. Chemical composition of the raw material

Experimentally obtained results on Sorptomat (Table 2) show that the chemical changing of the raw montmorillonite (ionic exchange and pillaring) indicate transparent texture changes

manifesting as increase in total pore volume (16.3%), total microspore volume (64.0%) and increasing in the specific surface area by 46.8%. At the same by increasing in micro pore volume, total volume of the mezo pore is decreasing by 23.2%, which is consistent with the increase of specific surface area of the modified material. Chemical modification of the raw montmorillonite gave the slight increase in pore width from 3.740 to 3.947nm while the concentration of pores size from 3 to 6nm increased for 27.9% in ratio to started raw material.

	MM (raw)	Ion Exchange MM	Pillared Ion Exchanged MM
Pore volume (cm^3/g)	0.098	0.092	0.107
Micro pore volume (cm^3/g)	0.0364	0.0386	0.0597
Specific surface area (m^2/g)	79.9	85.2	117.3
Maximum pore width (nm)	3.740	3.791	3.947
Pore (3-6 nm) concentration (%)	73.5	78.4	94.0

Table 2. Textural characteristic of the samples after first, second and third treatment

The textural change evident from experimentally obtained results on Sorptomat (Table 2) is also visible on the AFM measurements, Fig. 3.

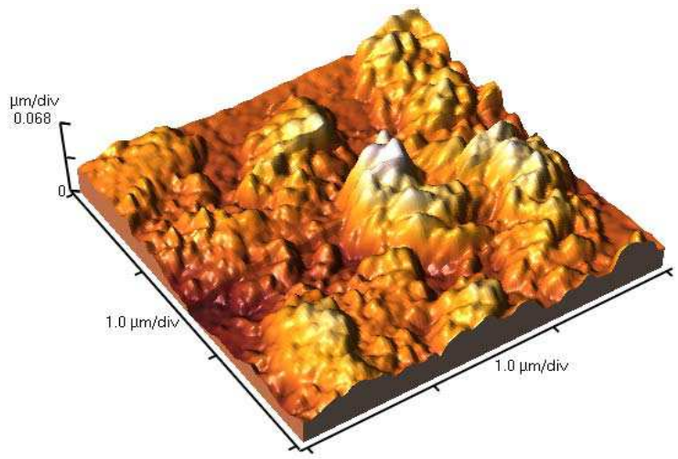


Fig. 3. AFM image of the surface area Al-pillared sample

Step 4. Composite preparation

- A new WPA-PILC material has been prepared by the sol-gel method. The heteropoly acid used in this work was 12-tungstophosphoric acid hydrate $H_3PW_{12}O_{40} \cdot nH_2O$ (WPA-n). The WPA-PILC composite materials were prepared by using water solutions of WPA-6 and pillared clay. We prepared samples with different WPA contents (16, 67 mass %, 28, 57 mass % and 37.50 mass %). The solutions were stirred at room temperature (25^0C) for 2 hours, and kept at this temperature for 24 hours to transfer to a gelatine. The gelatine was dried at the temperature of 70^0C (Čajkovski, 2005).
- Preparation of new ADV-PILC MM materials by the sol-gel method. The ADV-PILC MM composite materials were prepared by using aqueous ADV

(ammonium decavanadate, solution and MM pillared clay suspension. The ADV content was 2 and 5 mass %. The solutions were stirred at room temperature for 24 hours, and then dried at a temperature of 60 ^{0}C (Sredić, 2008).

Textural characteristics of samples after the first, second and third treatment and of the composite sample with incorporated WPA and ADV are given in Table 3.

	Pillared Ion Exchanged MM	Pillared Ion Exchanged MM+ WPA (28,57 mass%)	Pillared Ion Exchanged MM+ADV (5 mass%)
Pore volume (cm^3/g)	0.107	0.038	0.114
Microspore volume (cm^3/g)	0.0597	0.0291	0.0474
Specific surface area (m^2/g)	117.3	53.46	102.0
Maximum pore width (nm)	3.947	3.857	3.701
Pore (3-6 nm) concentration (%)	94.0	81.6	59.9

Table 3. Textural characteristics of samples after the first, second and third treatment and of the composite sample with incorporated WPA and ADV

3. Dielectric measurements

Polyoxometalates are widely used as industrial catalysts and there is a possibility of using them as materials of specific electric properties. New composite materials have better properties in comparison to starting material.

This resulted especially in a substantial increase of the electrical conductivity.

Investigation of dielectrical and conductivity properties of pillared montmorillonite with incorporated 12-tungstophosphoric acid (PILC-WPA) and ammonium-decavanadate (PILC-ADV) has shown that the new materials exhibits improved electrical conductivity which is higher than the conductivity of both starting compounds.

3.1 PILC-WPA

Using broad band dielectric relaxation spectroscopy (DRS), electrical properties of the obtained material were investigated. Thermally stimulated depolarization current technique was also used due to its high sensitivity and high resolving power. It has been established that pillared montmorillonite doped with WPA-6 ($H_3PW_{12}O_{40}6H_2O$) shows conductivity better than that of the pure components, as shown in Fig. 4.

TSDC plots for PILC montmorillonite are shown in Fig. 5.

The high values of ε'' indicate that these relaxations are caused not only by water molecules but we think also by ion movements affected by the presence of water molecules (Fig. 6.)

In Fig. 7., a comparison of TSDC plots for MM+28.57 mass % of WPA and WPA is shown. We again observe that the conductivity of the MM+28.57 mass % of WPA sample is higher than that of WPA. In the inset of the figure a peak is seen probably indicating phase transition. This phenomenon is observed only for MM+28.57 mass % of WPA, but not for WPA, probably due to its higher conductivity.

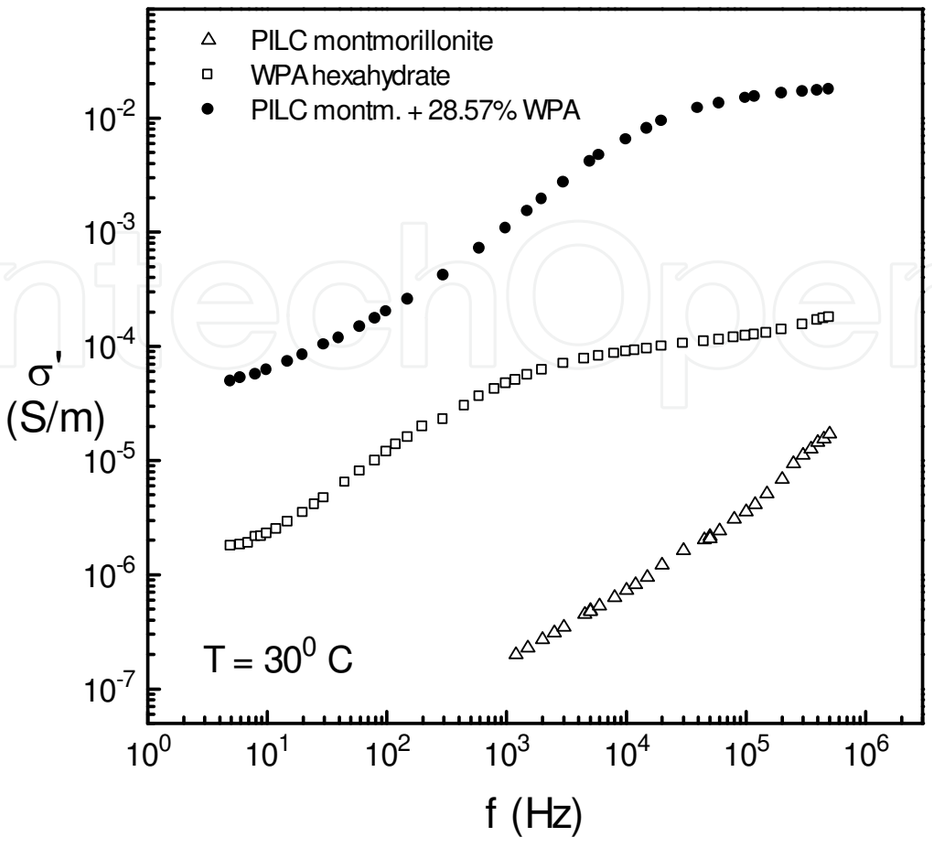


Fig. 4. Conductivity versus frequency for the investigated materials.

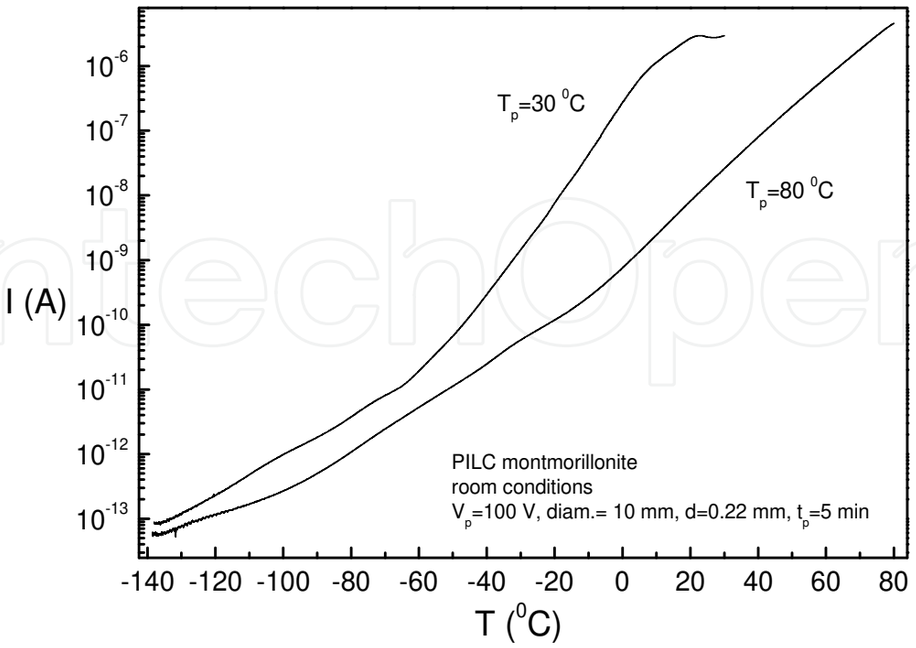


Fig. 5. TSDC for montmorillonite for two polarization temperatures: Tp=30⁰ C and Tp=80⁰ C.

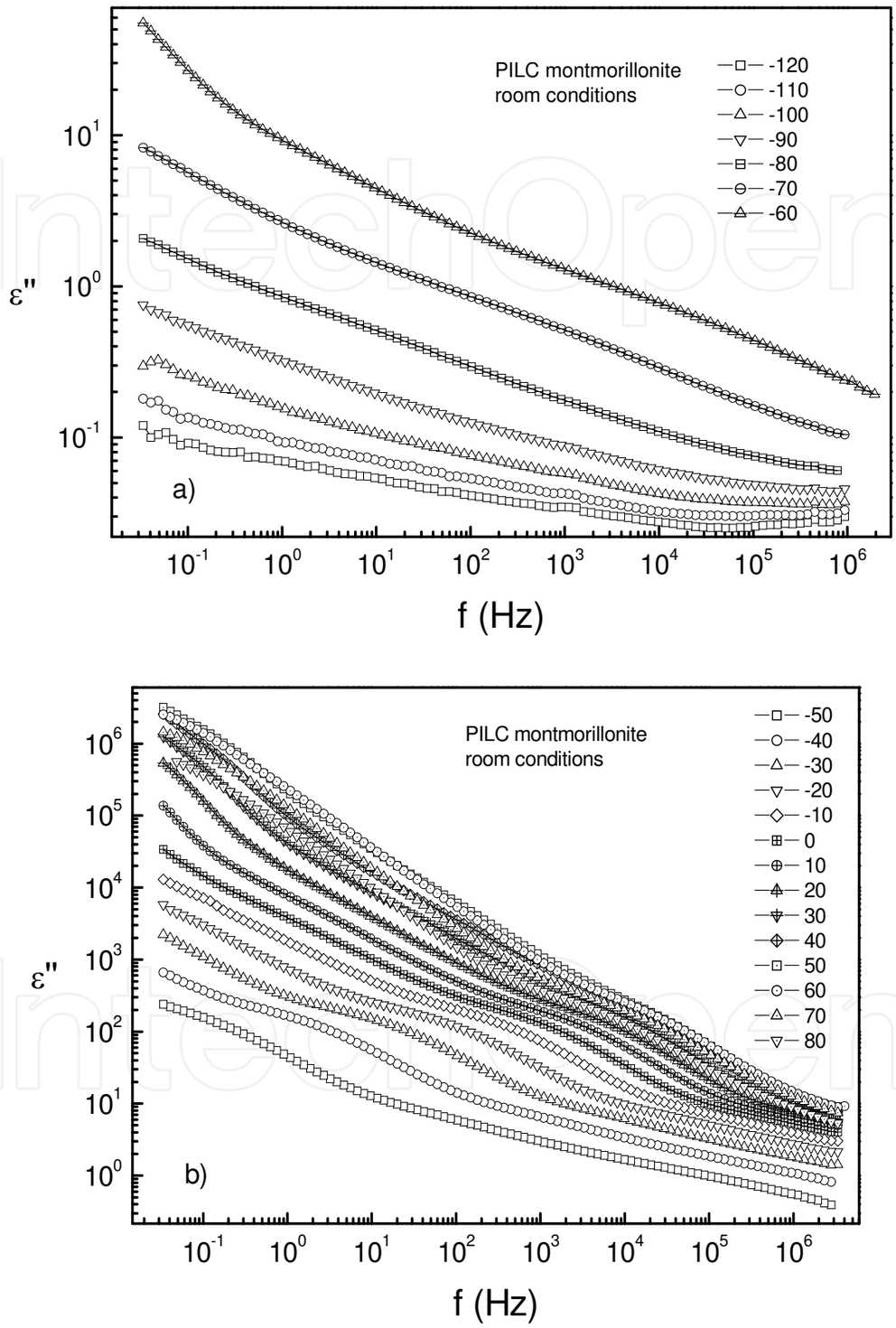


Fig. 6. a) and 6. b) Frequency dependence of imaginary part ε'' of the complex permittivity ε* of PILC montmorillonite at temperatures indicated on the plots.

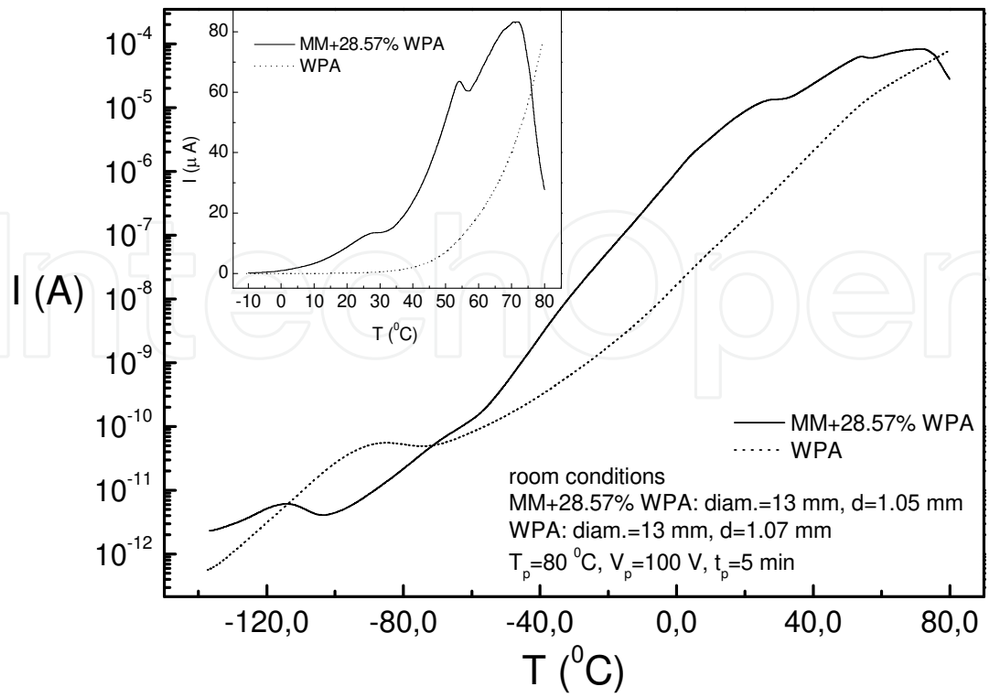


Fig. 7. Comparison of TSDC plots of WPA and MM + 28.57 mass% of WPA.

3.2 PILC-ADV

Comparative TSDC and DRS measurements of all samples were carried out in ambient relative humidity conditions. At this stage, no efforts were made to measure and control the water content in the samples.

Fig. 8. presents the results of TSDC measurements. The polarization temperature was 80 0C. In all samples, the depolarization current rising with rising temperature over several orders of magnitude, indicating rising dielectric activity. Relatively high values of depolarization current, in particular at higher temperatures, suggest that the main contribution to the dielectric response arises from conductivity rather than dipolar effects (Čajkovski, 2005; Sredić, 2008). Above 30^{0}C depolarization current is higher for ADV-Al-PILC than for the pure ADV and in all investigated temperature region doped samples show significantly higher responses than pure MM This finding could be explained by greater contribution of ionic conductivity to total one. In addition to the overall increase of dielectric response with increasing temperature, the TSDC thermo grams in Fig.8. have the feature reflecting the presence of relaxations. The high depolarization current values suggest that these relaxations arise from the motion of charge carriers. In the case of doped MM samples three relaxations are evident, located at about -125, -95 and -55^{0}C.

For pure MM i.e. pure ADV and the sample doped with 2 mass % ADV the frequency dependence of ac conductivity, σ_{ac}, at 30^{0}C, calculated from the ε''(f) plots of Fig. 9. by means of equation (1)

$$\sigma_{ac}(f) = 2\pi f \varepsilon_0 \varepsilon''(f) \quad (1)$$

where ε_0 is the permittivity of free space.

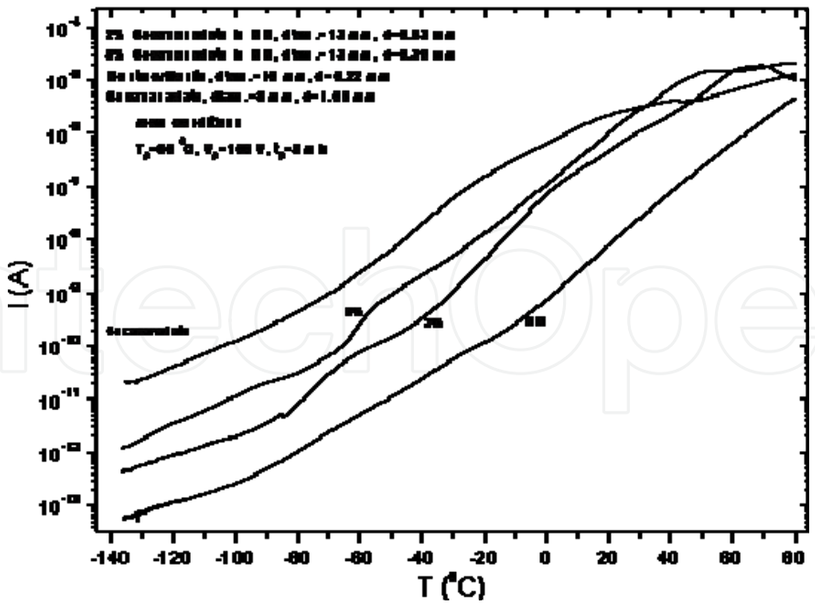


Fig. 8. TSDC thermograms obtained with the samples indicated on the plot

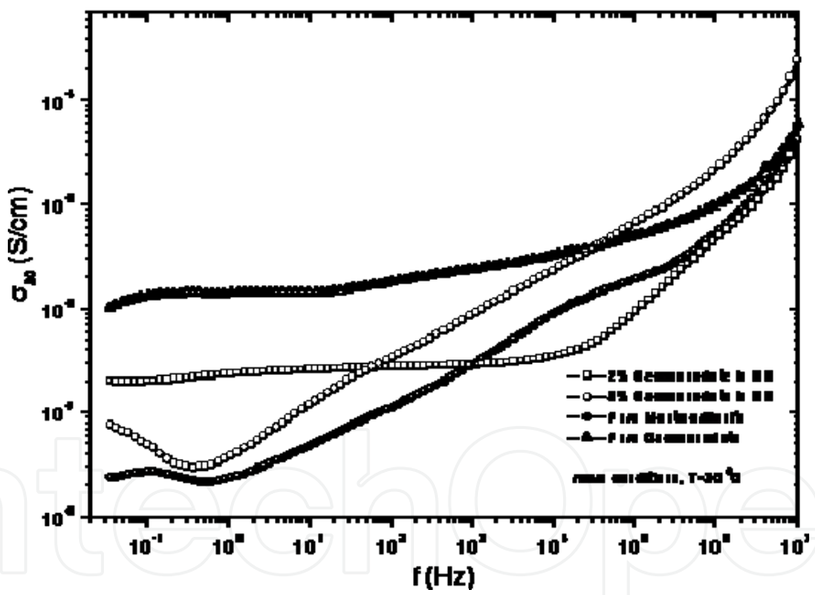


Fig. 9. Shows ac conductivity σ_{ac} versus frequency for the samples indicated on the plot at 30^0C and ambient relative humidity

The relaxation processes observed as shoulders in Fig. 9., mask the typical behaviour of an ionic conductor, i.e. the change from a frequency independent value at low frequencies (σ_{dc}, dc conductivity plateau) to a steady increase of σ_{ac} with increasing frequency at higher frequencies (Mioč, 2010). The results allow, however, direct reading of the values of σ_{dc} at the temperature and experimental conditions of the measurements. So, we get the values of about $2x10^{-8}$ S/cm in pure MM, $1x10^{-6}$ S/cm in pure ADV and $2x10^{-7}$ S/cm in the doped sample. It is interesting to note that that σ_{dc} increases by one order of magnitude after

doping of MM with only 2 mass % of ADV. This result is interesting also with respect to possible applications. Please note that the absolute values of dc conductivity refer to samples equilibrated in air (ambient relative humidity conditions).

4. Catalytic properties

4.1 Heteropoly compounds supported on montmorillonite as catalysts for wet peroxide oxidation of toluene

Acid and redox properties of heteropoly acids (HPAs) and their salts render them suitable catalysts. One of the disadvantages of HPA catalysts, their low surface area and high solubility, can be overcome by impregnation of porous supports by HPAs or by neutralization of the HPA with different cations. In present study catalytic activity of montmorillonite based catalysts with different heteropoly compounds was further investigated.

Catalytic wet peroxide oxidation (CWPO) of toluene by Al-pillared montmorillonite (PILM) doped with 12-tungstophosphoric acid, $H_3PW_{12}O_40 \cdot nH_2O$ (WPA), before and after calcination and by neutral and acidic Cs salts of WPA was investigated and compared to catalytic activity of Al-Cu pillared bentonite clay (PILM-Cu) as the reference sample.

Raw material obtained from "Šipovo" bentonite deposits, Republic of Srpska, was modified and doped with WPA according to the procedure described elsewere. Cs salts were synthesized by drop wise addition of solution of Cs_2CO_3 (0.1mol/L) to solution of WPA (0.08mol/L). The precipitates were separated and dried at 40^0C overnight. The calcination was performed at 300^0C for three hours. The amount of WPA incorporated into PILM was determined from ICP spectrometric measurements and was 25,3%.

The characterization of catalysts was performed previously by IR spectrophotometry, DTA and TGA, while BET surface areas and pore size distributions were calculated from nitrogen adsorption isotherms at 77 K. Samples were outgassed at 353 K.

Oxidation of toluene

The obtained solids were tested as catalysts in wet oxidation of toluene by H_2O_2 at 40^0C. Filtrates were taken during the reaction and analyzed for the toluene content by gas chromatography. It is shown that after one hour about 80% of toluene was oxidised to CO_2.

4.2 Modification of pillared clays with cobalt functionality

The supported samples were prepared by impregnation of the pillared solids using $Co(NO_3)_2 \times 6H_2O$ solutions as a impregnation agenses.

The amount of the metal salts was equivalent to a content of 1,5,10 and 20 mass.% Co in the final samples. After the impregnation, the samples were dried (24 h, room temperature, 18h, 60^0C) and calcinated (4h, 295^0C).

4.3 XRD characterization

All the samples showed a type IV isotherm with a hysteresis loop, which is usually observed for mesoporous materials. The dimensions of pores in PILM samples are large enough for incorporation of Keggin ion (r~1.2 nm).

Adsorption-desorption isotherms for Cs2.5 H0.5 WPA are shown in Fig. 10.

Reaction kinetics of wet toluene oxidation over various montmorillonite based catalysts is shown in Fig. 11.

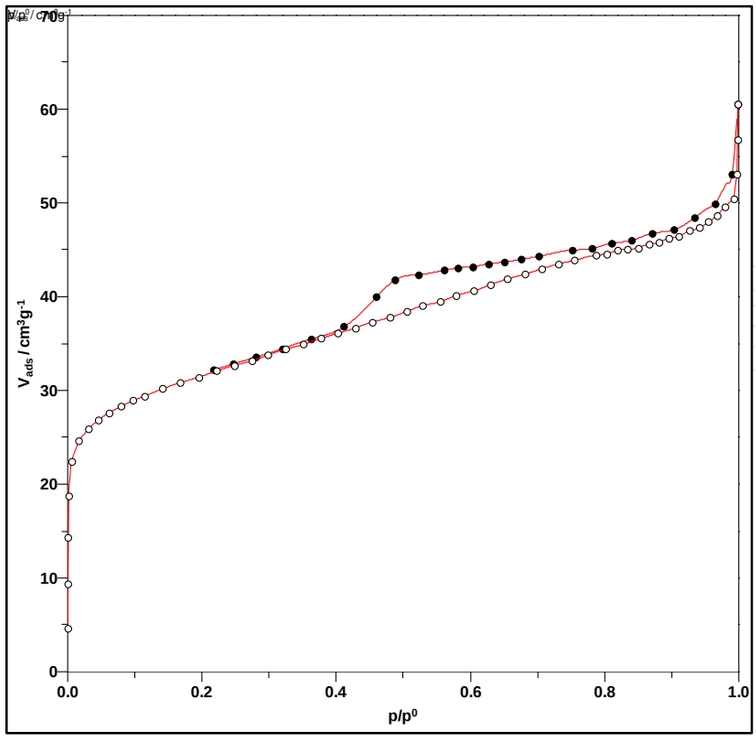


Fig. 10. Adsorption-desorption isotherms for Cs2.5 H0.5 WPA

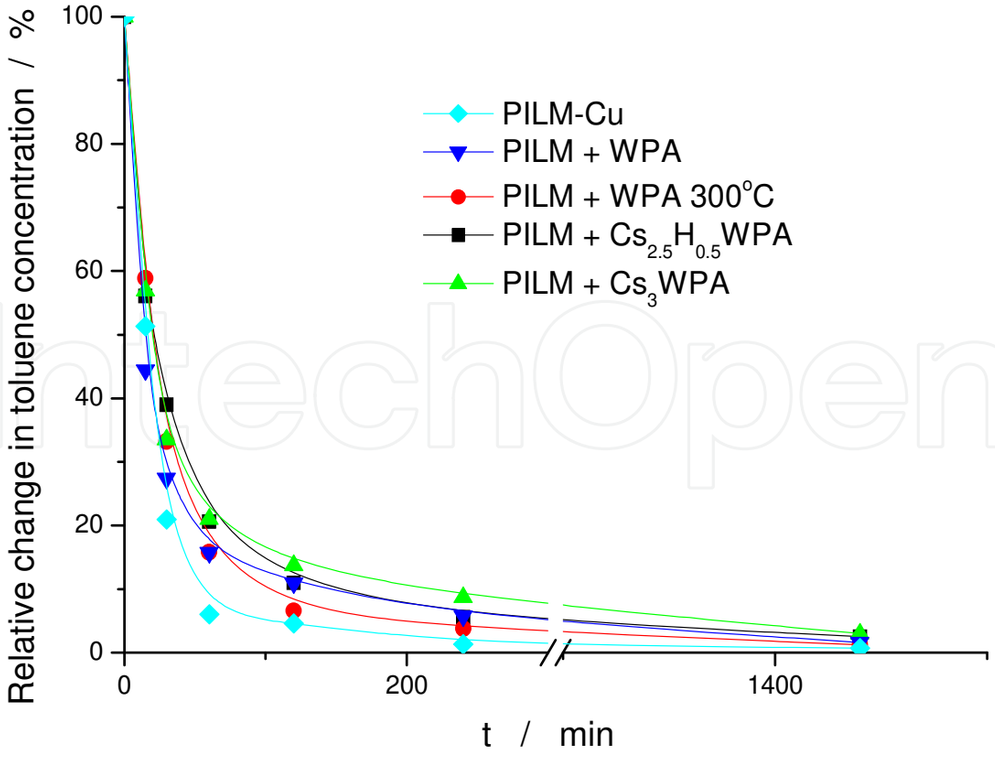


Fig. 11. Reaction kinetics of wet toluene oxidation over pillared montmorillonite catalysts

Statistical parameters of various models are compared in Table 4.
Table 5 presents rate constants for model with parallel first and second order reactions.

Sample	$Tol \xrightarrow{k_1} P1$	$Tol + Tol \xrightarrow{k_2} P2$	$Tol \xrightarrow{k_1} P1$ $Tol + Tol \xrightarrow{k_2} P2$
PILM-Cu	2.7320	9.7614	4.9724
PILM + WPA	7.3759	3.3605	0.9151
PILM + WPA 300oC	4.9623	3.4395	2.3565
PILM + Cs2.5H0.5WPA	7.8425	2.2392	1.1575
PILM + Cs3WPA	8.2171	2.9924	1.7793

Table 4. Standard error of the fit with tested reaction models, for different samples. The first and second order reactions are tested.

Sample	PILM-Cu	PILM+WPA	PILM+WPA (300)	PILM+C2.5H0.5 WPA	PILM+C3WPA
k1	5.6375E-02	9.5279E-02	4.4655E-02	2.3820E-02	5.4794E-02
k2	5.1602E+00	4.6719E+01	2.8530E+01	6.7017E+01	2.9349E+01

Table 5. Rate constants for toluene wet peroxide oxidation over various catalyst samples. Best fitting model with parallel first and second order reactions is used.

According to the results given in Table 1, sample of reference PILM-Cu shows kinetics of the first order reaction, contrary to the Al-pillared montmorillonite doped with WPA and its Cs salts, which can be described by the mixed first and second order reaction kinetics. The highest value of second order rate constant (Table 2) is obtained for Al-pillared montmorillonite doped with acidic Cs salt of WPA (C2.5 H0.5WPA).
The structure properties of the new-doped material have been studied using X-ray powder Diffraction (XRPD) method, presented in Fig. 12. The analyses were performed on Siemens D500 diffractometer.
Data were processed using Siemens Diffrac Plus software and JCP database. Data were collected in the 2θ range from 2 to 80 ° having a continuous scan with the step of 0.02 °2θ and the time of 1 s per step.
Reflections of the Co_2O_3 samples of the pillared clays impregnated with Co are distinguished from individual phase of Co_2O_3 but some numbers of these oxides can be incorporated in montmorillonite. In the sample of Co where the reflex ions in samples of Co_2O_3 are weaker in the case of samples with 20% Co, and reflexion of (100) in case of montmorillonite is widen in direction of d values.
The results of kinetic tests during cyclohexane oxidation are presented in Figure 13.
The oxygen uptake is given in Figure 14.
The increase of cyclohexanone and cyclohexanol is liner after short induction period and both products have similar yield. The further oxidation leads to unwanted byproducts.
All samples gain activity comparable with previously tested catalysts. Unexpectedly, the samples with lower Co content were more active. This observation is another evidence of

the inhibition effects in the cyclohexane oxidation system, and implies the need for the optimization of the catalysts.

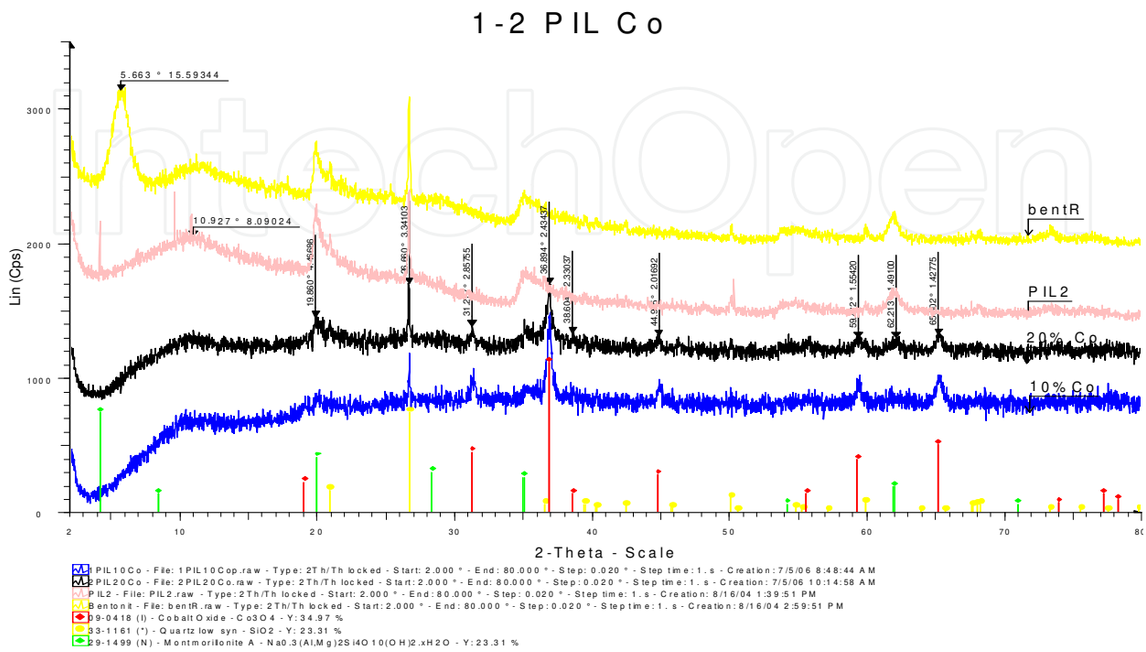


Fig. 12. The structure properties of the new-doped material have been studied using X-ray powder Diffraction (XRPD) method

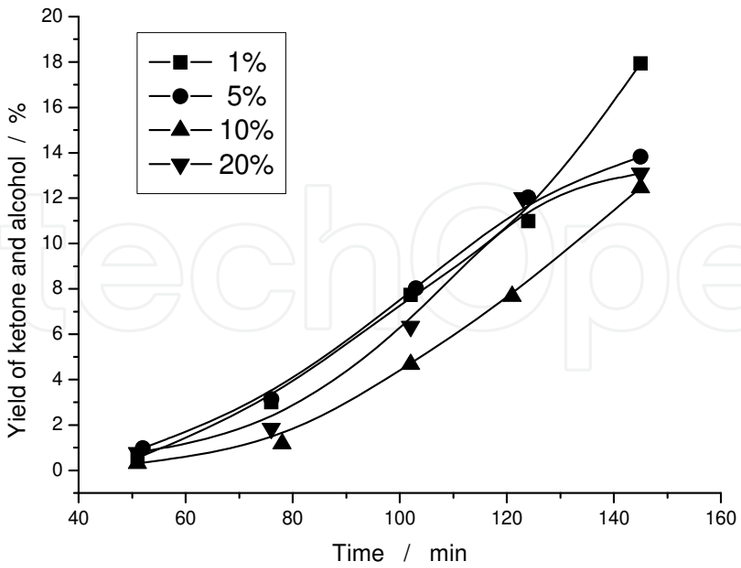


Fig. 13. The yield of useful products of the cyclohexane oxidation (cyclohexanone, cyclohexanol and cyclohexylhydroperoxide), at montmorilonite supported Co catalysts with indicated Co content.

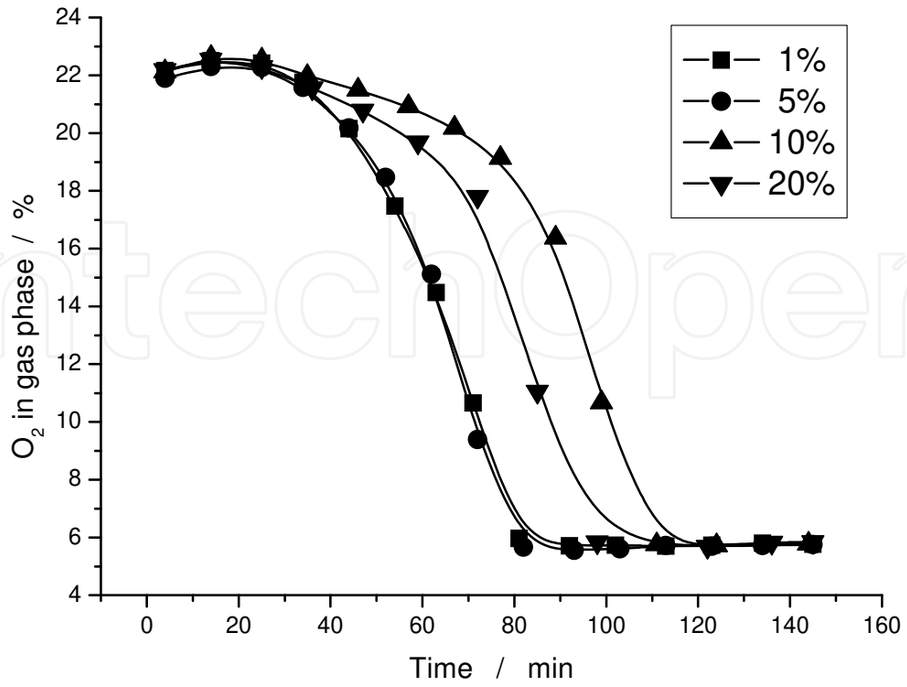


Fig. 14. The oxygen concentration in gas phase during the cyclohexane oxidation, at montmorilonite supported Co catalysts with indicated Co content.

5. Applications

The field of polyoxometalates (POMs), although a mature field, continues to attract significant attention (Katsoulis, 1998).

Montmorillonite structure differs from the others kind of natural minerals by having an interlayer space that gives it a swelling behaviour and restricts the water movement. The other clays are non-swelling.

Nanostructured materials have received much attention due to their potential to achieve properties superior to conventional engineering materials. Nanoscale reinforcements such as nanoclays can be used for fabrication of polymer-clay nanocomposites or polymer matrix composite with nanotubes. Although resulting in enhanced yield stress, tensile strength and Young's modulus in the former case, while in latter case electrical conductivity can be incorporated in the polymer in addition to increase in tensile strength. Thus, incorporation of nanoparticles, nanoclays and nanotubes in polymer matrix or ceramic matrix leads to the formation of composites with better properties for applications.

In recent years significant progress has been achieved in the synthesis of various types of polymer-nanocomposites and in the understanding of the basic principles, that further defines their optical, electronic and magnetic properties. Nanocomposite-based devices, such as light emitting diodes, photodiodes, photovoltaic solar cells and gas sensors, have been developed, often using chemically oriented synthetic methods such as soft lithography, lamination, spin-coating or solution casting. The key moment of an application development, of nanocomposite-based devices, is discovery of the possibility of filling conductive polymer matrices of types: polyaniline, substituted poly (paraphenylenevinylenes)

or poly (thiophenes), with semiconducting nanoparticles. The possibility to fill the polymer matrix, both n- and p- conductivity types with nanoparticles, thus providing access to peculiar morphologies, like interpenetrating grid, p-n semiconductors or fractal p-n interfaces, not achievable by traditional microelectronics technology.
The peculiarities in the conduction mechanism through a grid of semiconductor nanoparticle chains provide the basis for the manufacture of highly sensitive gas sensors. These sensors combine the properties of the polymer matrix with those of the nanoparticles. It allows the fabrication of sensor devices selective to some definite components in mixtures of gases.
The basic properties and functions of material structures and systems can be changed as a function of the organization of matter via molecular interactions (such as hydrogen bonds, electrostatic dipole, van der Waals forces, various surface forces, electro-fluidic forces, etc.)
Tables 6 and 7 present potential applications of ceramic-, metal- and polymer-based nanocomposites, respectively. Metal and ceramic nanocomposites are expected to generate a great impact over a wide variety of industries. These tables summarize the possible developments associated with these materials in catalysts, sensors, structural materials, electronic, optical, magnetic, mechanical and energy conversion devices suggested by researchers in the field.

Nanocomposites	**Applications**
SiO2/Fe	High performance catalysis, data storage technologies
Metal oxides/Metal	Catalysis, sensors, optoelectronic devices
SiO2/Ni	Chemical sensors

Table 6. Potential application of ceramic Nanocomposite systems

Nanocomposite	**Application**
Fe/MgO	Catalysis, magnetic devices
Fe/TiN	Catalysis

Table 7. Potential application of metal Nanocomposites systems

Materials with defined pore-size in the nanometer range are of special interest for a wide range of industrial applications because of their outstanding properties with regard to thermal insulations, controllable material separation and release and their applicability as templates or fillers for chemistry and catalysis. One example of nanoporous material is aerogel, which is produced by sol-gel chemistry. A wide range of potential applications of these materials include catalysis, thermal insulation, electrode materials, environmental filters and membranes as well as controlled release drug carriers.
The applications of POMs are based on combinations of so-called "value-adding properties" which are summarized in Table 1. such as:

1. metal oxide like
2. stable (H2O/air, T): processing advantage
3. large size (diameter, 6-25 Å)

4. discrete size/discrete structure (confined geometric factors)
5. anions (charge from -3 to -14)
6. high ionic weight (103 - 104)
7. fully oxidized compounds/reducible
8. variable oxidation numbers for the addenda atoms (E1/2) 0.5 to -1.0 V vs SCE)
9. colour of oxidized forms different from colour of reduced forms
10. photoreducible
11. arhenius acids (pKa < 0)
12. incorporate over 70 elements and form large number of structures: processing advantage
13. acid forms very soluble in H2O & other oxygen carrying solvents (ethers, alcohols, ketones)
14. also soluble or transferable into nonpolar solvents: processing advantage
15. hydrolysable to form deficient structures: processing advantage

From the above listed properties, the applications of POMs are centred primarily on their redox properties, photochemical response, ionic charge, conductivity, and ionic weights. Primarily $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ are used as the main examples for many applications for different purposes: coatings, analytical chemistry, processing radioactive waste, membranes, sensors, dyes/pigments, electrooptics, electrochemistry/electrodes, capacitors, dopants in sol-gel matrixes, flammability control, etc.
The majority of the applications of POMs are found in the area of catalysis.

Coatings

A nanocoating can produce high quality with super properties in the coating layers. Sustainable products can be produced with super ability to resist the stress and loads for different applications.
Of the most widely used methods to combat corrosion of metal surfaces is the utilization of corrosion inhibitors such as chromates, phosphates, or silicates. The main concern with the use of chromate inhibitors is their toxic nature.
Polyoxometalates have relatively low toxicity as compared to chromates; they accept electrons without major changes of their structures and form insoluble salts with large cations. These properties make them attractive as oxidizing and film-forming corrosion inhibitors (Katsoulis, 1998).
The high solubility of heteropolyacids in water is a drawback since it renders them unstable under humid conditions, and thus various hydrophobic hosts are required to preserve their value-adding properties. As one might expect the primary application of composite systems is in coatings where attributes such as optical properties, adhesion, hardness and abrasion resistance are desirable.

Analytical chemistry

The recent explosive growth of sol-gel science and technology offers several examples of utilization of POMs as additives in inorganic or organic matrixes. The number of examples is not as large as one might have anticipated based on the advantages that POMs offer in the ease of incorporation into sol-gel matrixes and on their rich combinations of properties analytical chemistry such as ion conductivity, photochromicity, and electrochromicity. This trend is changing, and more material scientists are investigating the interactions of POMs with organic and inorganic matrixes.

Substances of high electrical conductivity have the potential to function as effective antistatic agents. POM acid (Keggin type) are among the many compounds that have been claimed to function as such. Their function is based on the synergy between their hygroscopic and ionic character.

Processing radioactive waste

The ideal nanocomposite would not only resist radiation damage. It would also not itself become radioactive by absorbing neutrons.
A good number of applied analytical publications deal with the usage of POMs as process aids for the processing of radioactive nuclei. (Katsoulis, 1998)
Their presence renders the processing and solidification (vitrification) of these wastes more difficult because they evaporate to a noticeable degree and leach out of the vitrified products that are intended for permanent storage such as glass blocks, cement blocks, and bitumen blocks.
Limitation of these approaches is the fact that $H_3PMo_{12}O_{40}$ is also soluble in the aqueous phase and causes interference with the subsequent process of MAW such as vitrification.
It could still take years before such materials are approved for use, but the modelling methods will greatly speed up the process.

Membranes and Sensors

Composite membrane has good permeability and selectivity for gases, which depends upon the operating conditions. The solubility and diffusivity of the penetrants in the polymer matrix control the transport through non-porous dense membrane (Vijay, 2006).
A large number of application patents and publications deal with the building of membrane-based devices and sensors that exploit the high ionic conductivity of POMs, their capability to form a plethora of salts with virtually any cation, and their ability to undergo redox processes under many mild conditions. The most common uses of these membranes are in selective electrodes, in gas detection apparatuses, in solid-state electrochromic devices, and in liquid and solid electrolytic cells.
Many of the selective electrodes described in the literature were constructed for use in clinical chemistry.
Campiglio (1994) described an ion selective electrode for the potentiometric microtitration of vitamin B_1.
The sensor biosensor for the determination of the neurotransmitter acetylcholine, based on a two-layer selective poly(vinyl chloride)-poly(vinyl acetate) membrane consisting of a choline phosphotungstate as the electroactive compound (Katsoulis, 1998; Eppelsheim, 1994)
The membranes were used in gas sensors for the detection of hydrogen and gaseous compounds capable of dissociating into or combining with hydrogen ions.
The gas sensors are prepared by organic-inorganic polymer membranes made of water soluble organic polymers (i.e. poly(vinyl alcohol), poly(ethylene oxide), poly(ethylene glycol), cellulose acetate, etc.) and heteropolyacids or their salts.
Improvements of the functional life of such sensors have been achieved with the use of various porous solid-state encapsulants that encapsulate at least one component of the chemical sensor (Katsoulis, 1998; Goldstein, 1996).

Dopants in sol-gel matrixes

Common inorganic matrixes are usually derivatives of Al, Si, Ge, Ti, or Zr alkoxides and to lesser degree derivatives of Sn, Pb, or Nb alkoxides. The acid catalysis properties of POMs

are used in conjunction with their photochromic, electrochromic, and ion conductive properties to produce composite siloxane materials through the sol-gel approach. (Katsoulis, 1998; Katsoulis, 1995; Tasumisago, 1993)

Substances of high electrical conductivity have the potential to function as effective antistatic agents. POMs are among the many compounds that have been claimed to function as such. Their function is based on the synergy between their hygroscopic and ionic character.

The electrodes had excellent optical uniformity due to properties of $H_4SiW_{12}O_{40}$ compacted to a disk in a form of electrochromic display (Katsoulis, 1998).

Dyes/pigments

The ability of POMs to form stable precipitates with cationic dyes has resulted in considerable patent activity from industries related to pigments, dyes, and inks.[83-95] There continues to be a need for better control of particle size, particle size distribution, surface activity, surface area, porosity, and color quality.

Silicomolybdic acid was the most preferred complex heteropolyacid for preparing pigments for printing inks, particularly for quick set offset printing.

The compounds had excellent utility as pigments, primarily in textiles (i.e. denims) and inks (replacement for indigo dyes) (Katsoulis, 1998)

Electrochemistry and electrodes

The storage of energy today is a great technology challenge and ongoing activity, especially the process of charging and recharging of light weight batteries and/or capacitors in compact forms.

For modification and improvement of activating electrodes and their storage charge capacity, the polyoxometalates are used. Subsequently, the polyoxometalates are applied for fabrication of electric double-layer capacitors with optimized energy storage properties.

Due to their capability, reversible redox reactions provide a secondary charge storage mechanism without decreasing the charge storage ability of the activated electrode's materials.

During the past few years, significant developments on electrode modification by POMs have taken place aiming to improve the reaction rates of fuel cells and produce economically sufficient currents for practical uses (Katsoulis, 1998; Ndzebet, 1995; Savadogo, 1990)

Capacitors

Heteropolyacids and their salts have been claimed as electrolytes for capacitors (solids and solutions) (Katsoulis, 1998).

The capacitors also maintained good reliability at high temperature operation up to 150 °C. Aging studies at 125 °C for 310 h showed constant resistivity (Katsoulis, 1998).

Fuel cell

Fuel cell applications include nanocomposite in the proton exchange membrane, binder for the electrodes and matrix for bipolar plates.

Improvement of the mechanical properties for proton exchange membrane and enhanced proton conductivity of it yield the nanoparticles to be incorporated into proton exchange membrane structure.

When the direct methanol fuel cells are considered, nanoparticles are applied for reduction of methanol crossover (Paul, 2008; DeLuca, 2006)
Heteropolyacids like $H_3PW_{12}O_{40}$ are applied to proton exchange membranes to yield improved proton conductivity at higher temperatures while retaining good mechanical properties (Paul, 2008; Kim, 2003; Wang, 2006)

6. Brief conclusion

In the first line of interest, natural nanostructures have potential to overtake the primate of conventional engineering materials by means of properties and application. Nanomaterials as nanoclays can be modified to polymer-clay nanocomposites or matrix composites and for result they form the pre-products with improved characteristics.
In accordance with the properties of natural nanocomposite materials and their possibilities for application, the need of interdisciplinary science approach is arising, involving encompassing physics, chemistry, biology, materials science and engineering. Synergy of knowledge will result in new science discipline and very new technologies and therefore especially materials. Furthermore, development and implementation of nanocomposites will impact the society in various areas: electronic, chemical, transportation, medicine and health care, energy and environmental protection. It is expected that natural nanocomposites will make significant positive influence on life quality in future (Camargo, 2009).

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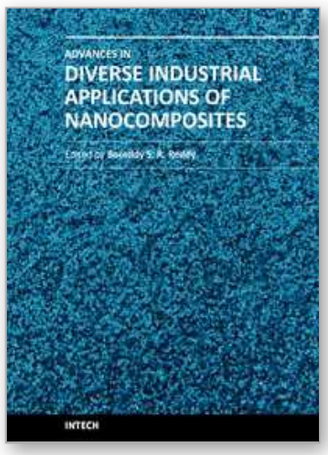
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Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

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