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Nano-structured catalysts immobilized onto polymer matrices

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INTRODUCTION

Among high-end technological achievements, nanoscience and nano-technology became an emblem and symbol of the transition to the XXI century. This is so since the small group of atoms with the same or different chemical nature generates properties essentially different from those of periodic solid state, due to its fundamentally new molecular arrangement or different degree of self-arrangement, specific structure, peculiar nature of the chemical bonds, manifestations of specificity in the interactions between the atoms or groups of atoms. Nano-science with its scientific basis and nanotechnology with the technical and technological background made "revolutionary" debut and are applied in electronics, microelectronics and communication, aviation and astronautics, power production and metallurgy, chemical industry and, in this respect, catalysis[1]. A new scientific field was developed-nano-catalysis and nanocatalysts. Major part of the latter are the deposited catalysts where the active component-an extremely small group of atoms, clusters, nano-structured particles, are attached, included, cross-linked or, generally, bonded to different extent to the substrate-carrier. The type of bonding stipulated by the interaction of the group with the carrier causes various physico-chemical phenomena-modification, consolidation, structural changes (on electron, crystal, magnetic or morphologic level)[1].

Recently, specific interest from applied scientific point of view aroused the so called polymer carriers with grafted and/or immobilized nano-structured groups. They are regarded as nano-catalysts.

The surface modification of polymeric materials by radiation and plasma grafting revealed new perspectives for the preparation of polymer carriers with suitable functional groups by surface introduction in nanostructures (ultra dispersed groups, clusters). The active groups in the grafted layer of the polymer are prerequisite for the co-ordination bonding of metal ions of different degrees of oxidation Thus, immobilized catalysts are obtained and some substantial disadvantages if homogeneous and heterogeneous catalysis like the necessity to isolate and regenerate the catalyst at the final stages of the process, gradual washing the catalyst off the surface and low catalytic activity are avoided.

Surface modification of polymer materials by radiation grafting holds out new perspectives for preparing polymer carriers with suitable functional groups on their surface. The active groups in the grafted layer are prerequisites for the co-ordination bonding of metal ions to a different degree of oxidation. This method make it possible to prepare immobilized catalysts so that some essential disadvantages of homogeneous catalysis coud be avoided such as the necessity of isolating and regenerating the catalyst at the final stages of the process.

Two main tasks form the basis of the concept of immobilized catalyst systems

- The first task is to prepare heterogenized catalysts with high concentration of active centers (for instance, metal-oxide groups, clusters and even nanoparticles). These centers should have well defined co-ordination sphere, i.e. different degree of bonding to polymer surface and potential to exert modifying and consolidating effects.
- The second task is related to the preparation of stable catalysts with good reproducibility, catalytic activity and selectivity, possibility for regeneration, utilization and easily removable from the reaction mixture.

Thus, in practical aspect, the immobilized catalysts should combine the advantages of the two main types of catalysts. These requirements, which the catalysts should conform to, would facilitate the solving of a fundamental problem-transition from empiric to scientifically based selection of immobilized catalyst and prediction of its catalytic properties under certain reaction conditions.

Review of the literature on the problem

The studies on radiation initiated grafting are interesting for the polymer chemistry due to the numerous possibilities it provides for solving various scientific problems and for the industrial implementation of the materials obtained.

Recently, polymer gtafting onto hydrophobic films has been achieved by plasma-induced polymerization. The treatment with 'cold' (low temperature) plasma is used to activate the surface for the consequent grafting of selected monomers[2-9]. The method allows obtaining material combining the properties of the polymer carrier and the monomer hosting the functional group. Furthermore, the method ensures tailoring of properties and contents of the grafted polymers[10-12].

A lot of publications report for plasma grafting of monomers on polymer films to obtain materials with modified surfaces and versatile application: ionomers for adsorption of metal ions from solutions[13], materials with biocontact properties and improved interaction with live cells[9], carriers for immobilization of biomolecules and other biomedical applications[14].

Acrylic acid (AA) is a rapidly polymerizing monomer under radiation initiation and the polymers based on polyacrylic acid (PAA) are well known for their ability to from stale complexes with metal ions of different valence. These materials are quite widely used-as separators in batteries, membranes for water desalination, catalytic systems, biomaterials and materials with potential biologic activity, etc[15].

Recently, the polymer-metal complexes attracted much attention due to their valuable electric, mechanical and thermal properties and are usd on industrial scale[16].

Hegazy et al.[17] have studied the preparation of metal complexes of polymers on the basis of radiation grafted AA onto terafluoroethene-ethene copolymers. Copolymers with degrees of grafting from 8.4 to 80.5% were used. The transformation of the grafted copolymers into acrylate complexes was performed by treating with various metal salts-$FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$. The authors proved that the chelate structure of the complexes of each metal ion formed by intermolecular of intramolecular bonding.

Different methods were used to clarify the formation of these complexes and their co-ordination structure: ultra-violet (UV) and infrared (IR) spectroscopy, colorimetry, as well as the method of X-ray fluorescent analysis. Some basic properties of the copolymer complexes with metal ions were determined-electric conductivity, moisture content and physico-chemical properties.

There are publications on radiation grafting of acrylic acid on other fluor containing copolymers including substrates of tetrafluoroethene-perfluorovinyl ether (TFE-PFVE) and metal complexes on their basis. Ghaffar et al.[18] obtained Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} acrylate complexes of grafted copolymers with degree of grafting from 18-76 to 54-19%. The authors have found that the formation of the metal complexes did not affect the crystalline structure of the copolymers. The polyacrylic acid grafted onto film of the copolymer mentioned above acts as chelate-forming center for certain ions of transition metals. The colorimetric studies confirmed the formation of grafted metal complexes with uniform distribution of the metal ions through the donor $-COOH$ groups in the grafted chains.

El-Sawy et al.[19] studied the radiation grafting of AA onto tetrafluoroethene-ethene (TFE) copolymer using γ-irradiation from ^{60}Co source at dose of D= 30 kGy. The spectral, structural and thermogravi metric characteristics of the materials obtained were determined. The formation of complexes with grafted polymer matrices was proved also by the method of electron paramagnetic resonance.

The effect of the metal complexes of Cu^{2+} on the thermal and electrochemical properties of the copolymers was studied[19]. The authors sustain the opinion that such materials are quite interesting for semiconductor production due to their increased resistance to decomposition at high temperature (above 573K).

In other publications, El-Sawy et al.[20] continued their investigations on the metal complexes of radiation grafted copolymers. Using γ-rays from ^{60}Co at dose rate [P(D)] from 0.06 to 1.74 Gy/s, they grafted AA onto TFE-PFVE copolymer. Based on the copolymers with P 25, 36 and 47%, metal complexes were prepared by treatment with 1.0 mass % aqueous solutions of $CuSO_4$ and $Cr_2(SO_4)_3$. The formation of the polymer-metal complexes was proved by spectrophotometric and colorimetric methods.

In other publications[21], the formation of complexes of rhodium with AA radiation grafted onto TFE-PFVE copolymer was studied. The copolymeization was carried out by the direct method of irradiation with γ-rays from ^{60}Co source at P(P) 0.84 Gy/s and D=25 kGy with aqueous solutions of rhodium chloride in concentrations from 0.05 to 0.8 mass% for 2h at 373K in nitrogen medium. The processes of complex formation were studied by measuring the change of pH of $RhCl_3$ aqueous solutions at different concentrations as function of time. The spectroscopic, optic, electric and thermal characteristics of the metal complexes synthesized were determined. The results obtained showed high stability of the metal complex formed. The radiation grafting of methacrylic acid onto polytetrafluoroethylene (PTFE) was also investigated[22]. The grafted copolymers were treated with solutions of iron, cobalt, nickel and copper nitrates to prepared the corresponding complexes. The catalytic activity of the materials synthesized was studied for the reaction of oxidation of CO to CO_2. It was found to change in the order Co>Ni> Cu>Fe and depended mainly on the amount of free dioxide obtained and the degree of separation of the reaction products.

Okamoto et al.[23] prepared various metal complexes (Hg^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}) by radiation grafting of acrylonitrile based copolymers onto tetrafluoroethene-ethene copolymer fibers. The grafted materials obtained (selective adsorbents) had high stability under aggressive treatment conditions (alkali treatment at 353K, contact with sea water for 24h at 303K) and were practically used for extraction of uranium from sea water. Some authors[24] reported for studies on the kinetics of graft copolymerization of metal acrylates onto powdery polyethene. Co^{2+}, Ni^{2+}, Cu^{2+} acrylates were used to prepare copolymer with 1.4 mass% metal content. The reaction rate was found to be 10 times lower than that of AA grafting and it did not depend on the concentration of metal-containing monomer in the interval 1-10 mass%[24].

Another publication[25] summarizes the literary data on the biologically active derivatives of PAA and the possibilities for their application. The salts of polyacrylic acid with metals, organic and metal-organic compounds, interpolymer complexes, copolymers of acrylic acid and its derivatives were studied for their pharmaco-medical activity and interacton with biological substrates. The choice of suitable nitrogen containing monomers for the grafting reactions is associated with the opportunity to introduce different ligands in the polymer carrier. By grafting 4-vinylpyridine (4VP) onto polymer matrices, including polyethene(PE) and polytetrafluoroethene, copolymers can be obtained combining the valuable characteristics of the initial polymers and hydrophilic properties. The preparation of metal complexes on their basis provides a greater possibility for synthesis of heterogeneous catalysts. Cheng and Chan [26] obtained rhenium complexes of poly-4-vinylpyridine (P4VP) and studied their morphology by X-ray analysis. Xi et al.[27] obtained palladium complexes of copolymers of 4VP with acrylic acid and estimated their catalytic activity in the hydrogenation of aromatic nitro-compounds. The optimum catalytic activity for nitrobenzene hydrogenation was determined when using a copolymer containing 57.4% P4VP. The immobilized catalysts showed a particularly high catalytic activity in the hydrogenation of nitrophenol and nitroanisol. The catalysts based on rhodium complexes immobilized onto P4VP have also been proved to present a special interest. Such polymer-supported catalysts were studied in the reaction of hydroesterification of 1-hexene in the presence of methanol and carbon oxide[28]. In another publication, Kabanov et al. reported on studying the structure of polyacrylic acid-Cu(II)-P4VP metal complex. Spectrophotometric and EPR analyses showed that complexing depends on both the conformation state of the cuprous ion in the co-ordination sphere and the number of functional groups which could take part in the process[29].

In his review, Mastrorilli[30] summarized the studies, conducted in the last decade and associated with the synthesis of heterogenized polymer catalysts prepared by copolymerization of suitable metal-containing monomers. These metal-containing complexes can be used as catalysts for the hydrogenation and oxidation of simple and functional alkenes, sulfates, alcohols and aldehydes. Recently, special attention has been paid to the use of metal-containing monomers as starting materials for the preparation of catalysts for the stereo-selective epoxidation of low reactivity alkenes. Chemical processes such as polymerization of alkenes and alkynes as well as allylic alkylation have been under extensive discussion as model reactions resulting in the formation of C-C bonds. The main comments in these publications were associated with the possible use of metal-containing monomers as precursors for the preparation of catalysts and catalyst supports.

The studies on catalytic epoxidation of alkenes using organic hydroperoxides in presence of immobilized catalysts are attracting the attention of researchers for some time. The search for highly active catalytic systems would allow to develop methods for synthesis of valuable oxygen containing compounds.

Valodkar et al. reported for the synthesis, characterization and observed catalytic activity of Mn(II) complexes based on chloromethylated copolymer of styrene and divinylbenzene[31], as well as the catalytic epoxidation of various olefins (styrene, cis-cyclooctene, nonbornene cyclohexene) using metal complexes in presence of tretbutylhydroperoxide. The effects of different reaction parameters like catalyst concentration, substrate nature, temperature and solvent on the conversion and selectivity were studied. The kinetic data showed that the catalysts can be recycled without significant destructon of the polymer matrix[31].

A general evaluation of the development of metal complexes immobilized onto polymer matrices which were employed as catalysts for epoxidation of alkenes has been presented in Sherrington's excellent review[32].

Highly selective immobilized catalysts for epoxidation were obtained based on copolymers of cross-linked polyoxyethene with 4-vinylpyridine, methacrylic acid, etc.[33,34]. It was found that the selectivity towards the decomposed hydroperoxide depends on the ligand type in the metal:ligand stoichiometry. The comparative study between homogeneous and heterogeneous catalysts showed that the heterogeneous catalysts excel the homogeneous ones.

In a number of publications[35-41], a group of researches has carried out studies on the synthesis of new multi-component polymer systems using modern methods for introduction of functional groups with hydrophilic-liophilic properties, which are expected to facilitate the implementation of new ideas in this field. Based on these copolymer materials, new types of catalysts were synthesized by complexing with various metal ions and their catalytic activities were studied. The authors analyzed the practical use of these nano-materials as catalysts in organic reactions important from ecological or industrial point of view. The test reaction employed was the oxidation of cyclohexene in presence of tertbutylperoxide(t-BHP). On the basis of gas-chromatographic separation of the epoxy products of the oxidation reaction, the indices of retention were determined with sufficient reproducibility, as well as the dependence between the physico-chemical properties of the epoxy products obtained and their parameters of gas-chromatographic retention using mathematical relationship, which allowed identifying epoxy compounds without reference compounds[42]. As a result of kinetic studies involving computer and mathematical methods, a kinetic model was developed describing the reaction proceeding within the temperature and concentration intervals studied. Novel information on the nature of active centers in the immobilized catalysts was obtained, as well as on the valent state of the metal ions and their ligand surrounding, the structure of the grafted groups, their stability and specific chemical behavior.

The processes involving homogeneous, heterogeneous and immobilized catalytic systems play an im-

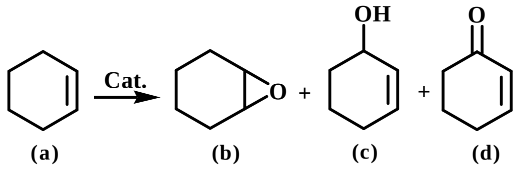
TABLE 1: Oxidation of cyclohexene with tert-butylhydroperoxide in presence of immobilized catalysts

No	Catalyst	Conversion, %	Yield*,%		
			Cyclohexene oxide	2-cyclohexene-1-ol	2-cyclohexene-1-on
1	PE-graft-P4VP- VO^{2+}	43.4	28.0	7.8	9.8
2	PE-graft-P4VP- MoO_2^{2+}	45.3	34.5	3.8	2.8
3	PE-graft-P4VP- WO_2^{2+}	6.8	<1	<1	4.8
4	PE-graft-P4VP- Co^{2+}	11.8	3.5	1.9	12.1
5	PE-graft-P4VP- Fe^{3+}	10.1	4.2	1.5	7.8
6	PTFE-graft-P4VP- VO^{2+}	38.4	26.0	5.8	12.4
7	PTFE-graft-P4VP- MoO_2^{2+}	54.1	31.1	4.2	4.3
8	PTFE-graft-P4VP- WO_2^{2+}	10.1	<1	<1	4.8
9	PTFE-graft-P4VP- Co^{2+}	9.8	1.5	2.6	6.7
10	PTFE-graft-P4VP- Fe^{3+}	11.5	2.5	4.8	4.1

***T= 358K, t=90min, solvent- toluene, cyclohexene (1.0ml, 0.8g), tert-butylhydroperoxide (0.1ml, 0.0081g), polymer complex 5× 10^{-3} mmol metal/l**

portant role in chemical industry. The oxidation of alkenes is a method for direct introduction of oxygen. These processes reguire the presence of a complex of transition metal and source of oxygen. The most often used oxidants with active oxygen : oxygen (100%), hydrogen peroxide(47%), ozone (33%), sodium hypochloride (21.6%), tert-butylhydroperoxide(17.8%), potassium persulphate (10.5%) and iodosylbenzene (7.3%), according to[43]. The immobilized complexes obtained were studied in the reaction of oxidation of cyclohexene(a). The data from the gas-chromatographic analysis showed that three products were obtained: cyclohexene oxide (b), 2-cyclohexene-1-ol (c) and 2-cyclohexene-1-one (d).

The yields of the goal products obtained by using immobilized catalysts based of PE-graft-P4VP are presented in TABLE 1. High yields of cyclohexene oxide were obtained in presence of molybdenum and vanadium complexes-45.3 and 43.4%, respectively. The results showed that these metal ions effectively decompose the hydroperoxide in the reaction of epoxidation. Significantly lower yields were observed with the same metal ions in the alyl oxidation of cyclohexene giving 2-cyclohexene-1-ol-3.8 and 7.8 %, respectively. The authors hoped to obtain higher yields with tungsten complexes but, as can be seen from TABLE 1, the only product of the reaction was 2-cyclohexene-1-one-4.8%. Lower yields were observed with Co and Fe complexes, 3.5 and 4.8 %, respectively. It is well known[44] that these metal ions decompose the organic hydroperoxides homolytically and they are not effective catalysts for epoxidation of alkenes. The yields of 2-cyclohexene-1-one of 12.1 and 7.8 % were quite higher compared to the other products of the reaction.



SCHEME 1

Similar results were obtained with immobilized catalysts based on PTFE-graft-P4VP (TABLE 1, No 6-10). In this case, the highest yield of epoxy compound was observed also with molybdenum and vanadium complexes-31.1 and 26.0 %, respectively. It can be seen from the experimental results shown in TABLE 1 that the carriers PE and PTFE did not have specific effect on the catalytic activities of the immobilized complexes of the same complex-forming agent-P4VP. The yields of the goal products were probably connected with the decreased swelling of poly-4-vinylpyridine in toluene.

Further, the catalytic activities of the polymer metal complexes prepared from Mo(VI), V(IV), W(VI), Co(II), Cu(II) and Fe(III) with poly(2-N,N-dimethylaminoethyl)methacrylate(PDMAEM) were studied in the same reaction[40]. All the experiments were carried out under the same conditions presented in TABLE 1.

The experimental data for the polymer complexes of (PDMAEM) with divinylbenzene (DVB) 5% and 10 % are shown in TABLE 2. As can be seen, high yields of cyclohexene oxide were observed with molybdenum and vanadium catalysts, 58 and 47%, respectively. The yields of 2-cyclohexene-1-ol and 2-

TABLE 2: Oxidation of cyclohexene with *tert*-butylhydroperoxide in presence of immobilized catalysts

No	Complexes No 1-6;5% (DVB) No 7-12;10% (DVB)	Conversion*, %	Yield**,%		
			Cyclohexene oxide	2-cyclohexene-1-ol	2-cyclohexene-1-one
1	PDMAEM-VO^{2+}	63	47	13	11
2	PDMAEM-MoO$_2^{2+}$	67	58	4	2
3	PDMAEM-WO$_2^{2+}$	37	18	11	9
4	PDMAEM-Co $^{2+}$	64	8	8	3
5	PDMAEM-Fe $^{3+}$	78	4	6	8
6	PDMAEM- Cu $^{2+}$	45	3	8	6
7	PDMAEM-VO^{2+}	51	42	11	10
8	PDMAEM-MoO$_2^{2+}$	66	51	4	1
9	PDMAEM-WO$_2^{2+}$	35	16	10	8
10	PDMAEM-Co $^{2+}$	50	7	11	9
11	PDMAEM-Fe $^{3+}$	67	8	7	8
12	PDMAEM-Cu $^{2+}$	44	4	6	7

*- according data below TABLE 1

cyclohexene-1-one were considerably lower with molybdenum catalyst compared to vanadium one, despite that the degree of conversion of t-BHP was about the same-67% and 63%, respectively.

With Fe(III), Co(II) and Cu(II), the yields of cyclo hexene oxide, 2-cyclohexene-1-ol an 2-cyclohexene-1-one were significantly lower-within 3-8%. The conversion was much higher 45-78%. It means that these metals are not selective in the decomposition of the organic peroxide. Similar results were obtained by the use of manganese complexes with Schiff bases in cyclohexene oxidation reaction[45].

Experiments were carried out with the same complexes but with divinylbenzene 10%. The results are presented in (TABLE 2, rows 7-12). The higher content of cross-linking agent is supposed to impede the reagents diffusion to the catalytic centers and, as a result, the yields were expected to be lower. The analyses carried out, however, showed that both the yields and conversion were not quite different. This was probably due to the good swelling of the polymer matrix in toluene which is used as solvent for reactions of oxidation.

Part of the polymer metal complexes synthesized-Mo (VI), V(IV) and Fe(III) with degree of cross-linking 5% were used twice in the test reaction to assess the change of their catalytic activity. The experimental data did not show significant differences in both degree of conversion vs *t*-BHP and product yields. The yield of cyclohexene oxide when Mo was used was 54% while with vanadium it was 44%. This means that the metal ions were not washed away from the polymer carrier after one operation cycle. Similar results were obtained with molybdenum complexes of cross-linked copolymer of polyoxyethene and polyvinylpyridine [34] by epoxidation of styrene where it was established that the molybdenum catalyst did not lose its activity for 50h.

CONCLUSION

The analysis of the scientific literature available so far shows that the problems, associated with the preparation of new polymer-supported catalysts have been studied in detail. The choice of a suitable matrix-monomer couple and the method for conducting the grafting reactions make it possible to form a surface layer, containing active functional groups. The combination of the properties of the polymer support with the ability of ligand functional groups to form metal complexes provides long-term prospects for the development of heterogenized polymer catalysts.

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