



Production and use of elastomers complex catalysts of the Polymerization process

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Abstract

Research results of the capacity of foam polymer sorbents on the basis of multicomponent polymer mixtures for heavy metals, experimental data on the establishment of the effect of the ratio of polymer components, temperature, and pH of the medium on the regularity of the change in the sorption capacity have been presented. The real possibility of the chemical modification of the foam polymer sorbents has been shown with the aim of achieving high results in increasing the sorption capacity for a number of heavy metals.

Keywords: immobilization, polyaminoacids, poly amide – amines, acrylonitrile, transition metals compounds

Introduction

Experts in field of catalysis were searched the ways creation of catalysts by now type, combining the merits of homogen and heterogen metal-complex catalysts.

These catalyst it is proposed to call “Hybrid phase”, but the essence of phenomenon is more accurately expressed by term “immobilized catalysts” [1,2].

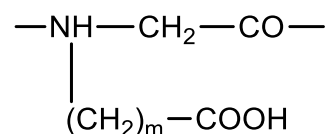
Immobilization in use of metal-complex catalysts includes limitation transition metals compounds by means of reaction with functional groups of polymer reagents.

Creation of immobilized catalyst pursue an aim important not only in partical but also in theoretical aspects.

Personally, receive of stable catalysts with good reproduction activity, selectivity, which easily are separated from products of reaction.

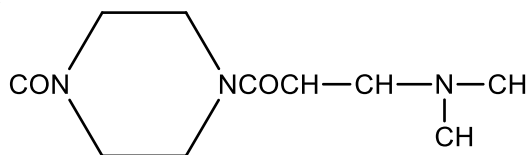
The initiated radical polymerization and copolymerization of 2 – oxyethyl methacrylate are enough studied [3]. The polymer carriers on base of acryl and metacryl acids ethers in form of macropore swelling granules find many – sided use. To that type it is follow to attribute the products of cation copolymerization of vinyl and acryl ethers copolymers of vinyl acetate and glycidyl alcohol, containing epoxy groups [4,5].

The polyaminoacids by total formula



Have a great significance in reactions of immobilization, from which the polyglutamine acid where (m=2), poly – L – cizin, poly – L – gistyline are often used.

By authors of works a new type of polymer carriers – poly (amide–amines)



have been synthesized.

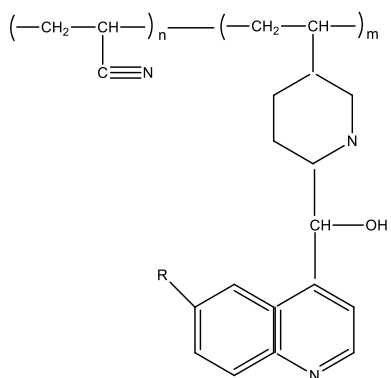
Series of polyfunctional carriers are shown at the table.

Table1: Some O- and N- containing polyfunctional carriers

Carrier	Structure	Literature
Copolymer based on hydroxypropyl methacrylamide	$\left[\begin{array}{c} \text{—CH}_2\text{—C(CH}_3\text{)—} \\ \\ \text{O=CNHCH}_2\text{CH(CH}_3\text{)OH} \end{array} \right]_n \text{---} \left[\begin{array}{c} \text{—CH}_2\text{—C(CH}_3\text{)—} \\ \\ \text{C(O)R} \end{array} \right]_m$ <p style="text-align: center;">R=OH, H, NH, CH₃, COOH, CH₂, C₆H₅</p>	[8]
Copolymer of methacrylate with N,N'-dimethylhexymethylenediacrylamide	$\left(\text{—CH}_2\text{—CH—} \right)_n \quad \left(\text{—CH—CH}_2\text{—} \right)_m$	[9]

Copolymer of N-ethyl-N'-(2-methacryloyloyletyl)-n-phenylenediamine with 2-hydroxyethyl methacrylate	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C} \\ \\ \text{O}=\text{COCH}_2\text{CH}_2\text{OH} \end{array} \right]_m$	[10]
Copolymer of N-phenylacryloyl hydroxamate, 1-vinyl of 2-methyl-imidazole and acrylamide	$\left(\begin{array}{c} \text{O}=\text{C} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{N}(\text{OH})-\text{C}_6\text{H}_5 \end{array} \right)_n \left(\begin{array}{c} \text{CH} \\ // \\ \text{N} \\ \\ \text{CH} \end{array} \right)_m \left(\begin{array}{c} \text{C}=\text{O} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{NH}_2 \end{array} \right)_t$	[11]
Copolymer of N-methyl-N-(n-vinylbenzyl)formamide and styrene	$\left(\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)\text{CHO} \end{array} \right)_n \text{-----} \left(\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array} \right)_m$	[12]
Copolymer of N-vinylphthalimide with vinyl acetate	$\left(\begin{array}{c} \text{O}=\text{C} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{N} \\ \\ \text{C}=\text{O} \\ \\ \text{C}_6\text{H}_4 \end{array} \right)_n \left(\begin{array}{c} \text{O} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} \right)_m$	[13]
Copolymer of 1-vinylimidazole (or 1-vinyl-2-methylimidazole) with 1-vinylpyrrolidone-2	$\left(\begin{array}{c} \text{N} \\ // \\ \text{CH} \\ \\ \text{R} \end{array} \right)_n \left(\begin{array}{c} \text{O} \\ \\ \text{N} \\ \\ \text{CH}_2 \end{array} \right)_m$ <p style="text-align: center;">R=H, CH₃</p>	[14]
Copolymer of ethylene glycol dimethacrylate, 4-vinylpyridine and 2-ethylheximethacrylate	$\left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{CH}_2-\text{CH}_2-\text{O} \end{array} \right)_n \left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}- \\ \\ \text{C}=\text{O} \end{array} \right)_m \left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{C}=\text{O} \\ \\ \text{O}-\text{C}_6\text{H}_{17} \end{array} \right)_t$ <p style="text-align: center;">-----CH₂-----</p> <p style="text-align: center;">\left(\begin{array}{c} -\text{CH}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_5 \end{array} \right)_t</p>	[15]

The interesting polymer carriers are also the products of radical copolymerization of alkaloids of quinine bark with acrylonitrile chloroform



where R=H, CH₃O.

Distribution of ion metals on carrier is studied, the peculiarity immobilization of heterocycles are revealed [18]. On example copolymerization of ethylene display of these effects in catalyst was considered. The base distinctive features of polymerization processes under influence of metals are discussed. It has been shown that stability of immobilized catalytic systems in base connect with braking of coordinated processes of disintegration in coordination sphere of transition metal. On initial stage of the works by fixing of complexes the tendency to immobilization of complexes, being the catalysts in solutions was displayed.

The Wilkinson catalysts (PPh₃)₃ PhCl and hydroformylation catalysts PhH(CO)(Ph₃)₂, which may be heterohemized by use of surface phosphine ligands [19] are on example.

But as far as development of works it became more obvious that the base direction in research of catalysts, containing the

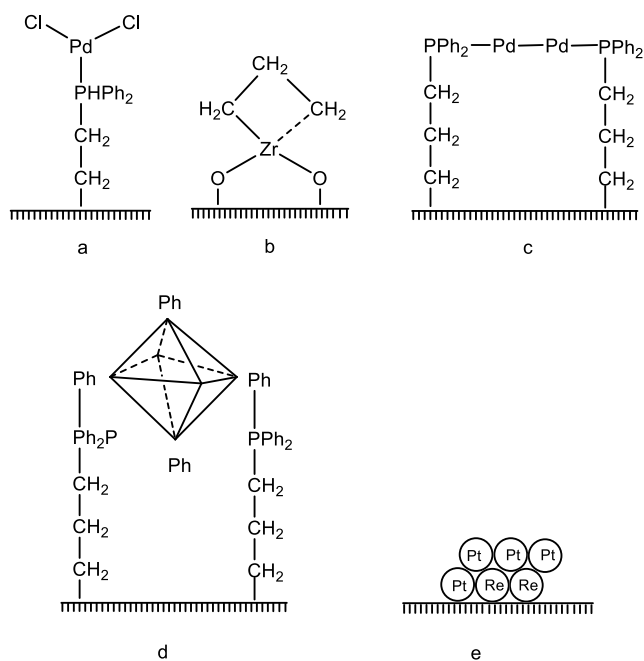
complexes at carriers is goal - directed synthesis of surface compounds, composition of which don't have the direct analogs among known solved catalytic systems.

One more advantage of catalysts, containing fixed complexes – its big “accuracy” by comparison with traditional heterogen systems.

In principle, concentration of active centers in it may be equal concentration of transition metal which give an additional possibilities for research of catalytic reactions mechanism by use of physical methods.

Complexity of fixed complexes composition create the continuous series by transition from catalysts – mononuclear complexes to traditional catalysts [20].

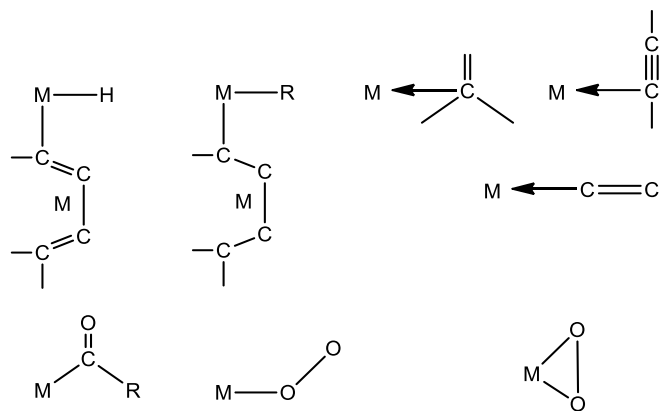
The following scheme illustrates this approach:



- fixed monomolecular complex;
- fixed binuclear complex;
- fixed cluster complex with appointed number of metal atoms;
- fixed cluster with unappointed number of metal atoms;
- Disperse particles of active component.

Synthesis and catalytic use of fixed mononuclear complexes (look scheme a) is the most well developed field of new direction in catalysis. The catalysts of that type give an additional possibilities for classification of catalytic reactions mechanism study of ligands influence on catalytic properties, conducting of complicated reactions on centers of different functionality.

Mechanism of reactions, catalized by mononuclear complexes may include formation of different intermediate compounds, the analogs of which are well known among stable complexes [20].



By achievement of high concentration of active centres by fixing of complexes it is a success to trace for its conversions on surface in reaction conditions and by that to reveal a mechanism. It is known that as binuclear fixed complex the centres, in which two atoms of metals connect between each other directly over bridge ligands in presence of solved cluster glue complexes are implied (look scheme b). It may be expected, that these complexes by comparison with mononuclear are able to conduct reactions by more complicated mechanisms on account of simultaneous activation of different parts of reacting molecule.

Moreover, unlike form mononuclear complexes, on catalytic activity of which on the whole the thermodynamical factors influence, an activity of binuclear complexes must depend from its structure.

However the amount of possible intermediate formations is insufficient for proceeding of reaction series. Some reactions, which are easily realized on metal catalysts weren't discovered in presence of solved complexes of compounds. To it, for example, the catalytic hydration of carbon oxide, hydrohenolysis of C – C bond, disproportionation of cyclohexane in benzene and cyclohexane are related.

According to Muetertize [21] by interaction of reagents with clusters it can be expect the same intermediate formations, which can arise also by adsorbition of cluster complexes on metals surface. The series of possible analogues between cluster complexes and metal particles is registered.

In presence of cluster complexes (look scheme c) it is be a success to realize a whole series reactions [22]: hydrogenation of the butylenes, omorins and carbon oxide, oligomerization of acetylenes and butadiens, but in spite of variety reactions, it is necessary to notice that catalysis by cluster glue complexes in solution have significant limitations.

By fixing of metalorganic compounds on lowvalent surface ions of IV – VII groups elements with following decomposition of surface formations it is possible to receive super dispers particles, containing unappointed number of metals atoms (look scheme d). These are an active centers of high-temperature catalytic conversion of hydrocarbons [22, 23] synthesis of that kind particles allow to receive centres of different composition and to study the reasons action of so

called modifying additions on properties of VII group metals in different conversion of hydrocarbons. In result development of different methods synthesis of surface formations as the centres proceeding of catalytic reactions the limits between separate types of catalysts on carriers became unstable. For example, it is difficulty to clearly delimit the catalysts containing fixed glues, which include from several atoms up to some dozens atoms, receiving over surface metal organic compounds.

Catalysts- compounds of dispers particles of active component may be (look scheme e) prepared by decomposition of surface fixed complexes. That kind catalysts are close to systems, received by traditional methods, although may have the more homogenous composition and more high activity. By using of that kind catalyst, it is a success to increase the field study of influence of particles size up to 10 \AA^0 and less on catalytic properties.

At the last time the series of untraditional methods immobilization of metal complexes have been developed. It are characterized by reduction of stoges number, composing the fixing process, for example by combination for the stage synthesis of polymer and immobilization of transition metals compounds, receive of metal complexes simnetaneously with its immobilization and etc. At present time the research in these directions are intensively developed.

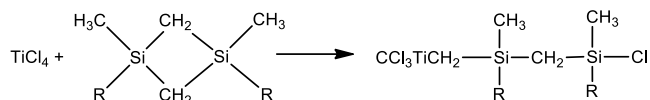
The structure, phase composition and temperature conduct of polybutadions samples, synthesized on binuclear metal complex systems and immobilized on solid carrier. It have been determined that the samples of polybutadion with structure present itself the mixture of 1,4-trans-and 1,4-cis-homopolymers, whereas 1,2-links are distributed in macromolecules of 1,4-transpolymer by accidental law. It have been shown, that structure ^[13] 1,4-trans-polybutadion is in principle three phase and contain crystal, amorf and low molecular form of mezomorf phase component.

Comparatively not long ago at the first time the successful synthesis of polybutadien on piled on silica gel titanium magnesium catalysts (TMC) and on the same catalysts, modified by metal organic compounds of Ni or Ir (TMC-1). These catalysts are characterized by essentially more high activity by comparison with usually used in polymerization processes:

The cinetic of ethylene polymerization in medium of n-heptane, toluene and ethyl chloride in presence of benzyl derivatives of titanium $(\text{C}_6\text{H}_5, \text{CH}_3)_n \text{ Ti X}_m$, where X-are groups $\text{C}_6\text{H}_5, \text{Cl}$ and OC_2H_5 ; $n=2-4$, $m=1-2$ and polymerization of ethylene and propylene under action of silicon titanium organic catalysts, 2,2 4,4-tetramethyl-4-chlor-2,4-decilbutyltitaniumtrichloride.

The high stability of silicon titanium containing catalyst is noted, which don't lose activity during some month by keeping of it in inert atmosphere by room temperature. Activity of these catalysts is importantly increased by processing of them by diethyl aluminium chloride ^[24].

The catalysts 2,2,4,4-tetramethyl-4-chlor-2,4-desil butyl titanium chloride (1) and 2,4-dimethyl-2,4-diethyl-4-chlor-2,4-dicsilbutyl titanium trichloride (2) have been received with yield >90% by reaction



Where $\text{R}=\text{CH}_3$ (1) and $\text{R}=(\text{C}_2\text{H}_5)$ (2).

The influence of transition metal nature of piled titanium and vanadium magnesium catalysts on molecular-mass characteristics of ethylene co-polymers with branched α L-olefine, containing tertiary carbon atom in L- position to double bond, which have been received in conditions of ion-coordination polymerization in suspension regime.

Copolymers, containing up to 5% mol links of co-monomers are characterized by linear structure with branching conditioned only by alkyl substituent of L-olefine.

Tye polymerization of isobutylvinyl ester and L-methylstyrene under action of SuCl_4 , absorbed on polystyrene and coordinated by methyl ethyl ketone have been studied. It have been shown, that polymerization proceed by cation mechanism.

By data of IR- and UF-spectroscopy, SuCl_4 is coordinated on phenyl rings of polystyrene and is complexed with methyl ethyl ketone by carbonyl group. The mechanism initiation of polymerization under catalyst action have been considered.

At the last decade by combined condensation of metals vapour and organic compounds the colloid solution of metals series, for example Au, Ag, Cu, Pb, Al, Iu ^[25] have been received. The received results shown that the catalytic propertics of colloid metals are comparative or exceed the catalytic properties of known glue catflysts.

Information about catalytic activity of similar systems are limited by individual works ^[26, 28], where catalystis is fixed on example of reactions.

Known for corresponding metals, in compact state, although there are data that colloid metals, prepared by traditional way may be active in polymerization reaction.

The catalytic properties of received colloid systems have been studied on example of reaction addition of carbone tetrachloride to hexen-1.

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