Research Article

Open Access

Nanocatalysts in Olefins and Dienes Polymerization Processes

Fuzuli A Nasirov*, Zakir Y Tagizade, Almaz M Tagiyeva

Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, AZ 1025, Baku, Azerbaijan

ABSTRACT

Sustainable development, the design of green and economically feasible processes to produce synthetic polymers is one of the major needs and biggest challenges. Catalysis of polymerization processes is among the most important applications within the field of nanoscience. Intensive research is being conducted and considerable success has been achieved in the heterogenization of various homogeneous catalysts on nano supports for polymerization of olefins and dienes. The large surface area of various nanomaterials qualifies them quite naturally to act either as a heterogeneous promoter for catalytic reactions or as a support for the heterogenization of homogeneous catalysts. To the polymerization of olefins and dienes by using nanocatalysts are devoted significant numbers of published papers, but to elucidate the possible effect of both the type and properties of nano supports and their sizes and amounts on the activity and stereoselectivity of heterogenized catalysts and the properties of the obtained polymers are needed more detailed studies.

This review attempted to collect some published research materials in the field of the nanocatalysis of olefins and dienes polymerization processes and our main aim is to assess the critical points and to indicate the future perspectives and possible strategies in this area of research.

We are confident that this review will be a helpful companion and deliver key hints to those, in academia and in the industry, who decide to move their research interest in this direction.

*Corresponding author

Fuzuli A Nasirov, Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, AZ 1025, Baku, Azerbaijan; E-mail: fizuli_nasirov@yahoo.com

Introduction

Olefins (especially, ethylene and propylene) and conjugated dienes (especially, butadiene and isoprene) represent the most widely monomers for the producing of polymers. Methods for their polymerization have been known for a long time, but no method known before 1954 allowed one to obtain polymers with a high stereo regularity of structure from the most common monomers. A true breakthrough in the development of polyolefin and diene rubbers took place after the discovery of stereospecific polymerization with transition metal-based coordination catalysts. From the late 1950s, rapid developments of industrial polymerization processes with Ziegler-Natta type catalysts were observed. It is worth noting that no other method of polymerization of olefins and conjugated dienes so far known shows the high degree of chemo- and stereoselectivity of coordination catalysts [1-6].

Polyethylene and polypropylene have been used to make different kinds of daily used products, so it is seen as one of the great innovations of the last century. It is very important to discover and synthesize an effective catalyst for ethylene polymerization. Because of their interesting catalytic behaviors towards ethylene and the easily controlled polyethylene produced the late transition catalysts have drawn more attention. However, this kind of catalyst has the same disadvantages as other homogeneous catalysts, such as a short lifetime of active sites and the limitations of use in large scale processes. Instability of the catalyst is the most important disadvantage of homogeneous catalysis. A deactivation mechanism of catalyst through the loss of ligands is unique for homogeneous catalysis. This may happen by dissociation or the reaction of some external reagents with the ligands: a) inhibition by the solvent; b) inadvertent admission of air or moisture; c) inhibition by the buildup of reaction products; d) inappropriate substrate functionality, from undesired substrate reactions, or by deposition of bulk metal [1-4]. To pass those challenges and develop suitable systems for most of the industrial processes (slurry or gas-phase reactors), both early and late transition metals catalysts were immobilized on inorganic supports. There are strong correlations between the nature of the supporting material and the size, diameter, and distribution of the pores with the polymerization activity of supported catalysts.

Heterogenization of the homogeneous catalyst for industrial processes is very important, because heterogenization offers many advantages such as ease separation and catalyst reusability. The discovery of very high-activity supported Ziegler-Natta catalysts has promoted the polyolefin industry. Higher catalyst activities

mean lower production costs owing to possibilities of eliminating some operations from the production technology or introducing new cheap production technologies (e.g., gas-phase processes). A gas phase process is lower in cost and energy consumption in comparison with a solution process. In gas phase polymerization solvents are not used, and at the same time, after polymerization, a ready-made commercial polymer is obtained, which excludes energy-consuming and ecologically dangerous stages from the technological scheme of production [7-9]. The polymer product can inherit the morphology of solid-supported catalysts, and these solid supports with controlled particle sizes and narrow particle size distributions can easily be prepared. Moreover, the heterogenized catalysts require a smaller amount of cocatalyst than soluble systems to achieve high activity for the polymerization of olefins.

Polybutadiene rubber (BR) is the second largest produced synthetic rubber next to styrene butadiene rubber (SBR). Following extensive work carried out over the last decades and continuing up to present, a vast number of catalysts based on the combination of transition metal compounds of groups IV to VIII of the periodic system or of the lanthanide or actinide series with aluminum alkyls or hydrides, and thus they fit the definition of Ziegler-Natta type catalysts. Derived from Ti-, Co-, Ni- and Nd- based precursors and organometallic or metal hydride activators these catalysts are at present the most important with regard to both activity and stereo regularity, and they are the only ones now used for the industrial manufacture of conjugated diene (butadiene and isoprene) polymers [10,11].

As most of the existing olefin`s polymerization plants run a slurry- and gas-phase process with heterogeneous catalysts, the homogeneous catalysts for dienes polymerization also must be heterogenized on a support in order to be applied in those processes [12,13]. In addition, the heterogenization of the dienes polymerization catalysts is necessary to avoid reactor fouling with finely dispersed polymer particles, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology [14,15]. In the gas phase polymerization of dienes, the formation of gel is particularly important, because the monomer conversion in the individual polymer granules can be remarkably high, especially when diffusion of monomer becomes the rate determining step. In addition, a local overshoot of temperature can easily occur especially at the start of the polymerization when the polymer granules are small and their respective heat capacities are still low [16-18].

As is known only a small percentage of the metal atoms in the non-supported catalysis (typically less than 1% in the first-generation catalysts) were active for alkenes and dienes polymerization [19]. It was realized that much of the pro-catalyst mass acted simply as a support for the active sites formed by activation, and the significant improvement could be made by depositing the active metal species on a support, whose residues would be inert and not detrimental to the properties of the polymer. It is evident that higher catalyst activities will be achieved using transition metal compounds supported on appropriate matrices. Thus, for the industrial ethylene and propylene polymerization processes a wide range of supported catalysts have been successfully developed and used. For this purpose have been applied as catalyst supports various metal oxides, chlorides, oxychlorides and alkoxides, such as Al2O3, SiO2, Al2O3•SiO2, MgO, ZnO, ZrO2, TiO2, ThO, Mg(OH)Cl, Mg(OEt)2 and MgCl2. The functions of the catalyst support may also be played by organic polymers [8].

The catalyst particle size significantly influences the polymerization rate, and it is possible that both chemical and physical differences exist between the larger and smaller particles in each batch of catalyst. With the catalyst, the smaller the catalyst particles are, the higher the yield is for one hour of reaction, and faster the activation/deactivation are. The literature materials show that Ziegler-Natta type catalytic systems, heterogenized on nanosized supports, are highly active in the gas phase polymerization of olefins and dienes and in their presence the catalysts productivity and polymers main properties can be regulated in very wide range [20-23].

As known, the great factors which influence the catalytic activity of the homogeneous systems are the electronic density and the bulkiness around metal center provided by the ligands. When the homogeneous catalyst immobilized on nanomaterials through non-covalent or covalent interaction, there should be a strong interaction between the homogeneous compound and the nanosupport. This naturally influences the electron properties of the metal loaded onto the support and have an influence on the catalytic activity. It`s also known, that the steric hindrance around the metal center is one of the important factors influencing the catalytic reaction. The heterogeneous catalysts have a direct interaction between the active center and the nanosupport. The nanomaterials are the huge group compared to the organic species and can be considered as "macro-ligands", are then introduced into the polymerization process. During the polymerization a great influence to monomer insertion and chain walking stages has the large bulkiness of these "macro-ligands". By this way, the presence of the nanosupport plays an important role in the catalytic activity, stereo selectivity and as well as on polymer characteristic (molecular weight and MWD) [20-23].

One reason to consider nanomaterials as suitable supports for metallocomplexe catalysts is the high surface to volume ratio. High surface areas and a well-developed porosity are essential for achieving large metal dispersions, which usually results in a high catalytic activity. On the other hand, the surface areas and porosity offer the possibility to absorb the olefin or diene monomer gas via π-π-interaction. These unique properties of the nano support increase the rate of monomer insertion on the surface of the nanosupport material and increase the effectiveness of the catalyst [20-23]. Below we will consider a review of literature materials in the field of nanocatalysis of olefins and dienes polymerization process using catalysts heterogenized on various nano supports.

Nanocatalysis in Olefins Polymerization Processes
No doubt that how important is the catalyst for a chemical reaction, the finding of an effective catalyst is also the key step for the polymerization. As already stated, heterogeneous catalysts supported on inorganic support have been reported and some of them have been successfully used in the industrial processes. It is worth mentioning that nano supports have the key properties, similar to the inorganic support used, such as large surface area, high thermal conductivity, porosity, etc. Moreover, nano supports are much more stable to the pH, temperature, and oxygen, therefore, they have the potential possibility to support the homogeneous catalysts for applications in polymerization processes. Nano support heterogenized catalysts for the polymerization have been studied and various publications reported different kinds of polymerization processes for a wide variety of monomers, such as ethylene, propylene, norbornene, styrene, caprolactone, etc. [21-24]. Among them, the catalysts for the ethylene polymerization represent the most important part.

Ethylene polymerization

In the last decade, some of the classic homogeneous catalysts have been anchored to nanosupports and then investigated in the ethylene polymerization reaction. It is reported that the presence of the nanosupports can affect the activity and has a great influence on the properties of produced polymer. Carbon nanotubes (CNTs) are well known as long and slender fibres with superior mechanical, thermal and electrical properties. Some hydroxyl and carboxylic groups contained on the surface of the purified CNTs can make the metallocomplexe catalysts stabilized on its surface [25-31]. Supported on the capped-ended and open-ended CNTs the Cp2ZrCl2 catalyst have high polymerization activities (106 kg PE/mol Zr·h). It is seen from SEM investigation that on the morphology of resulting PE has a significant effect the structure of the CNTs. The catalyst is mainly adsorbed on the surface of pristine CNTs and polyethylene form fibrous morphology, encapsulated on the surface of CNTs. The capped ends of CNTs are opened partly after treatment with nitric acid. The catalyst can disperse into the pore of the CNTs, so the hydraulic pressure of ethylene in polymerization makes the CNTs break up into fragments and the resultant PE has fractional morphology [32,33].
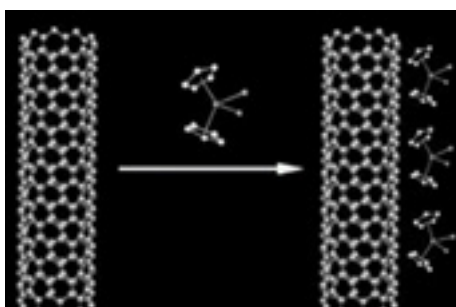

**Figure 1:** Preparation of Cp2ZrCl2-MWCNT catalyst

New catalytic systems, where CNTs are coated by the Ziegler-Natta catalyst through MgCl$_2$/nOH were synthesized and investigated as polymerization catalysts [35]. Ethylene polymerized on the surface of the SWCNTs and between the SWCNTs and PE a crosslink have formed. It was obviously that in situ polymerized PE layer played an important role as an interfacial modifier [35].

In the article is reported that for production of Ultra High Molecular Weight Polyethylene (UHMWPE) synthesised and used mono- and bi-supported Ziegler–Natta type catalysts using magnesium ethoxide (Mg(OEt)$_2$) and graphene oxide (GO) as catalyst support [36]. The activity of TiCl$_4$/Mg(OEt)$_2$, TiCl$_4$/Mg(OEt)$_2$-GO and TiCl4/GO catalysts in terms of g PE/mmol Ti·h was experimentally obtained for catalysts with different ratios of co-catalyst (tri-isobutylaluminium) to TiCl$_4$ and the TiCl$_4$/Mg(OEt)$_2$-GO catalyst has highest activity than TiCl$_4$/GO [36].

High active and selective late transition metal catalysts can also be grafted on nanocarbons and be investigated in the ethylene polymerization reaction. These catalysts can be supported on nanocarbons through non-covalent or covalent approaches depending on which kind of group is used to anchor onto the nanocarbon. A series of nickel com plex with the amino group have been synthesized and grafted on carbon nanotubes by Kemp et al. [37]. Both supported and unsupported catalysts showed good activity, but the supported catalysts was more active.
Supported on SWCNTs the nickel (II) carborane complex ([closo-1-Ni(PPh$_3$)2-2-Me-3-((CH2)$_4$NH-)-ή5-2,3-C$_2$B$_9$H$_9$][OEt])

$_n$(SWCNT) (3) has been synthesized (Scheme 1) [37]. By the reaction of closo-1-Me-1,2-C$_2$B$_{10}$H$_{11}$ (4) with n-butyl lithium followed by treatment with 1-bromopentane received closo-1-Me-2-pentyl-1,2-C$_2$B$_{10}$H$_{10}$ (5), after decapitation which with sodium hydroxide in refluxing ethanol has been obtained the salt Na[nido-7-Me-8-pentyl-7,8-C$_2$B$_9$H$_{10}$] (6). For the comparison of catalytic activity, homogeneous analogue closo-1-Ni(PPh3)2-2-Me-3-Pentyl-ή5-2,3-C$_2$B$_9$H$_9$ (7) has been prepared from its nido-precursor (6). The above synthesized nickel complexes (3) and (7) have been tested as moderately active catalysts for olefins (ethylene, vinyl chloride, etc.) polymerization in the presence of the MAO co-catalyst [37].
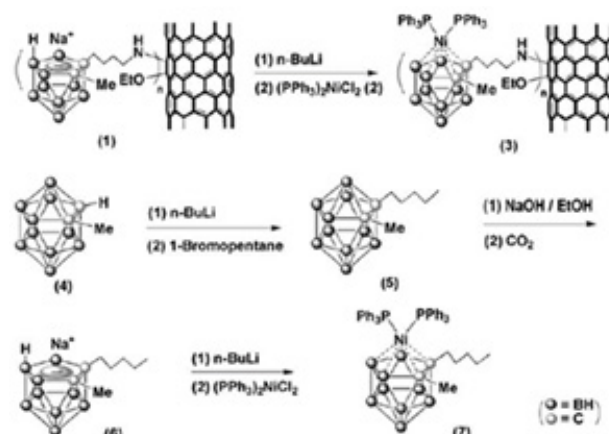
**Scheme 1:** Synthesis of carborane nickel (II) complexes

In another work ethylene polymerization was carried out with Cp$_2$ZrCl$_2$ catalyst supported on Multiwall Carbon Nanotubes (MWCNTs). Under optimum polymerization conditions (T=50°C, [Al]/[Zr]=1000), the fibres of the original MWCNTs could be replicated by polyethylene to obtain nano polyethylene fibres [38]. The diameters of the nano-fibres are 80–130 nm. With the increase of polymerization temperature and the [Al]/[Zr] molar ratio, the "overload" of polyethylene on the surface of CNTs made the polyethylene fibres disappear. The morphology of the resultant polyethylene can be controlled easily depending on the polymerization conditions.

The dimethylsilyl (N-tert-butylamido)(tetramethylcyclopentadienyl) titanium dichloride was synthesized and immobilized on the modified with MAO nano porous silica support and then used as catalyst for ethylene polymerization [39]. The influence of some critical parameters such as silica type and immobilization conditions including temperature and time of immobilization on catalyst performance was studied.

Calcination of support at 350oC and 600oC was performed and the results revealed that calcinations at higher temperature led to systems with higher activity. Synthesis of heterogeneous catalysts was investigated, and the synthesized catalyst showed the highest activity at 60oC for ethylene polymerization. The time of immobilization of catalyst was evaluated and higher activity was obtained at 18 hours. The catalyst synthesis and polymerization were at different temperatures, and the results showed that the optimum temperature for the polymerization of these systems was 75oC. With changing the molar ratio of [Al]/[Ti] from 190 to 1160 the activity of catalyst systems changed from 37 to 1042 kg polymer/mol Ti·h·bar. The specific morphology of the polymer particles is amorphous with a crystallinity of about 44-66% [39].

Cp_2ZrCl_2/MAO catalyst were supported on the nano-sized and micro-sized silica particles and used in ethylene polymerization [40]. Nano-sized catalyst exhibited much better polymerization activity than micro-sized catalyst. Due to the better active site dispersion, the absence of internal diffusion resistance, and the large specific external surface area the nano-sized catalyst's activity was 4.35 times higher than micro-sized catalyst's activity at the optimum temperature of 60oC. SEM analysis indicated that the resulting polymer morphology contained discrete tiny particles and thin long fibrous interlamellar links (Figure 2).
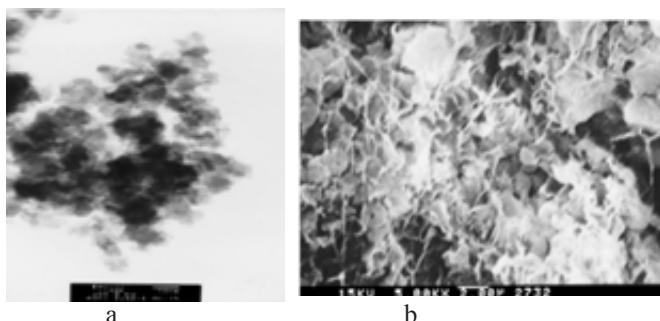
Figure 2: TEM micrograph of nano-sized silica supported Cp2ZrCl2/MAO catalyst (a) and SEM micrograph of polyethylene produced with this catalyst (b).

The same catalyst Cp_2ZrCl_2/MAO was supported on a nano-sized silica with the length of 10 nm and a width of 4 nm and used in the catalysis of the copolymerization of ethylene/1-hexene and ethylene/1-octene to produce linear low-density polyethylene (LLDPE) [41]. Exhibited more than 1.7-2.7 times higher polymerization activity under identical reaction conditions the nano-sized catalyst allow to produce the copolymer with greater molecular weight and lower polydispersity index than a micro-sized catalyst, which has the much lower internal diffusion resistance. With the increasing of polymerization temperature due to the decreasing of reactivity ratio and ethylene solubility the copolymer density decreased. Increasing of co-monomer concentration leads to a rapidly increasing in polymerization activity of the nano-sized catalyst. Ethylene/1-octene exhibited higher polymerization activity and had a stronger co-monomer effect than ethylene/1-hexene [41].

Nano-sized (diameter of 2-6 nm) and micro-sized (particle size of around 100 μm) silica particles were used to support a zirconocene catalyst [racemic-dimethylsilylene-bis(1-indenyl) zirconium dichloride], with methylaluminoxane as a cocatalyst (Figure 3) [42]. The resulting catalyst was used in the polymerization of ethylene in the temperature range of 40-70oC, and observed that nano-sized catalyst is more active than micro-sized catalyst. At the optimum temperature of 60oC, nano-sized catalyst's activity was two times higher than micro-sized catalyst's activity. Polymers obtained with nano-sized catalyst had higher molecular weight and higher crystallinity than those obtained with micro-sized catalyst. The better performances of nano-sized catalyst were attributed to its large external surface area and its absence of internal diffusion resistance [42].
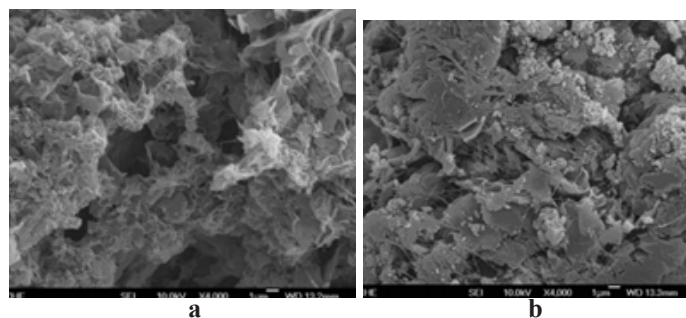
Figure 3: SEM micrograph of polyethylene produced with: nano-sized catalyst (a) and micro-sized catalyst (b) at 70oC.

The metallocene catalyst $(nBuCp)_2ZrCl_2$ supported on the synthetic hybrid layered (HLSNP) and tube-like (TLSNP) silica nano particles observed significant catalytic activities, comparable to a homogeneous analogue [43]. For the study of the catalyst loading effect and particle surface on catalytic behaviour and polymer properties the different amounts of zirconium were directly supported on the nano particles either with or without methylaluminoxane (MAO) treatment. With the increasing the amount of zirconium on the support the catalytic activity of the metallocene catalyst, supported on MAO-treated nano particles, also increased and the molecular weights of the polyethylene synthesized using both supported systems were higher than those from homogeneous analogue [43].

Supported catalyst consisted one Cp_2ZrCl_2 molecule and 1-2 MAO molecules inside super cage of NaY zeolite prepared and used in ethylene polymerization [44]. This catalyst showed low activity without any additional MAO co-catalyst and the activity was dependent on the kind of aluminium alkyl. With long activation time in situ generation of active site between NaY/MAO and homogeneous Cp_2ZrCl_2 showed low activity, which could be regarded as the diffusion effect of Cp_2ZrCl_2 inside the super cage of NaY. NaY/Cp_2ZrCl^2 and homogeneous MAO system showed the characteristic ethylene polymerization with homogeneous catalyst, indicating that active site was not generated inside the super cage of NaY. Activity of these catalysts was 22-1180 kg-PE/(mol Zr·h·atm) [44].

The preparation of dealuminated (DEAL) ZSM-2 zeolite nano crystals for use as an active metallocene polymerization catalyst support is presented in the work [45]. Metallocene catalyst was directly supported on the zeolite and used in the polymerization of ethylene using methylaluminoxane (MAO) or an alkylaluminum co-catalysts. Due to the activator effect of extra framework aluminum species with strong Lewis acidity existing in the DEAL-ZSM-2 zeolite structure the supported metallocene catalyst exhibited high activity. High external surface area of the nano-sized zeolite also contributes to reduce the diffusion effects commonly observed in micro-sized zeolite supports. The results demonstrate that DEAL-ZSM-2 zeolite support does not necessitate to be treated with MAO previous fixation of the metallocene catalyst, and that polymerization activity can be also achieved using a trialkyaluminum as cocatalyst. Using of DEAL-ZSM-2 zeolite as metallocene support could contribute to reduce the amount of MAO required for ethylene polymerization [45].

Nano-sized catalysts for the synthesis of micro fine ultra-high molecular weight polyethylene (UHMWPE) particles a catalytic approach was proposed. In a simple preparation step a Ziegler-Natta-type MgO/MgCl$_2$/TiCl$_4$ core-shell catalyst with the particle size in a nano-range scale by utilizing MgO nano particles as a

core material was prepared [46].

With different molar ratios of Mg/Ti the MCM-41 and SiO2 supported $TiCl_4$ and $TiCl_4/MgCl_2$ catalysts were synthesized and used for ethylene polymerization under atmospheric pressure [47]. The active sites formed inside the nano channels of MCM-41, which serve as nano scale polymerization reactor. Ethylene monomer diffused into the channels and growing polyethylene chains were extruded to form nano fibres, which were observed

in SEM micrographs of resulting polyethylene (Figure 4). MCM-41 showed higher activity than SiO2 supported catalysts and at polymerization conditions: Al:Ti= 30, P= 1 atm, T = 50oC and τ = 30 min catalyst productivity was $(1.6-4.7)\cdot10^4$ g PE/mole Ti·hour. MgCl2 has enhanced the catalytic activities of both supports. The resulting PE prepared by MCM-41 supported catalysts has higher melting points, more crystallinity, and molecular weights than that of SiO2 supported catalysts.


| a | b | c | d |
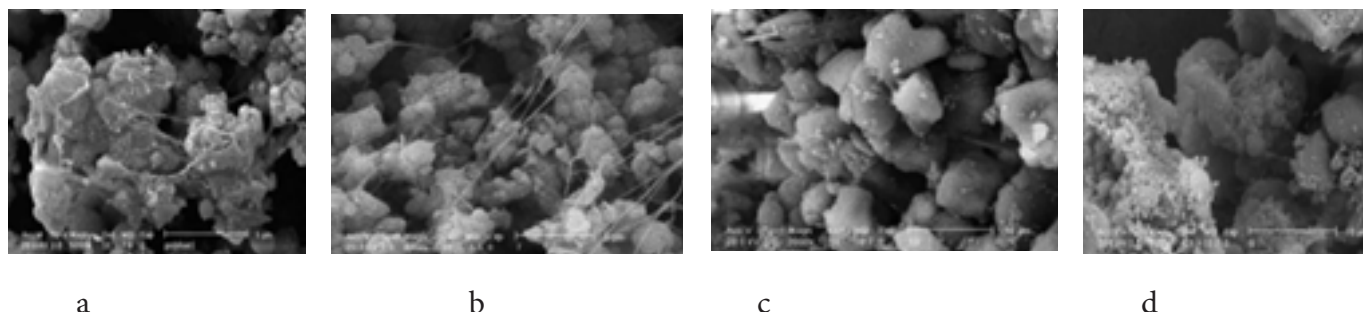
Figure 4: SEM micrograph of the polyethylene prepared by catalysts: A) $MCM-41/TiCl_4$ (a) and $MCM-41/MgCl_2/TiCl_4$ (Mg:Ti=2) (b) and B) $SiO_2/TiCl_4$ (c) and $SiO_2/MgCl_2/TiCl_4$ (Mg:Ti=2) (d)

Only work was found by us devoted to the heterogenization of olefin polymerization catalyst on an organic nanosupport. Nano-sized PS beads functionalized with polyethylene oxide (PEO) or polypropylene oxide (PPO) were prepared by miniemulsion polymerization and used as support in heterogeneous ethylene polymerization [48, 49]. The monomers used are styrene, divinylbenzene as crosslinker and PEO-b-PS (polyethylene oxide-block-polystyrene) or PPO-b-PS (polypropylene oxide-block-polystyrene) copolymers as surfactants (Scheme 2).
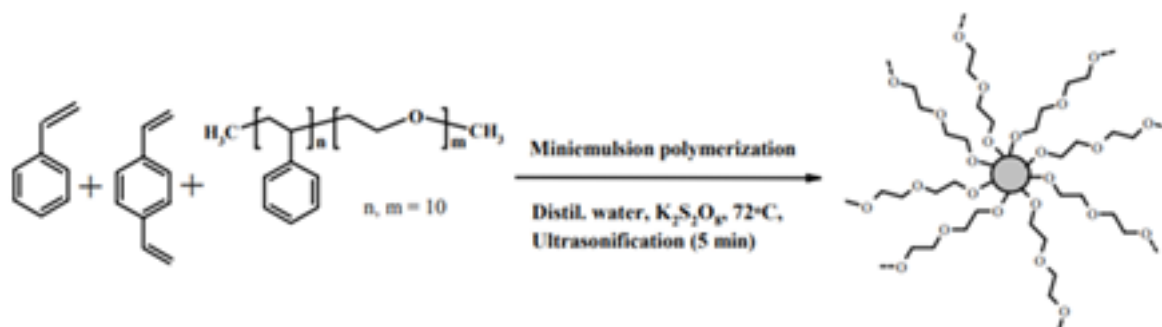
**Scheme 2:** The preparation of nano-sized PS beads functionalized with polyethylene oxide (PEO)

For immobilizing the metallocene catalyst on the nano-sized PS beads functionalized with PEO (Scheme 3), the PS beads were first mixed with a solution of methylalumoxane (MAO) in toluene to remove traces of water. Independently, the $Me_2Si(2MeBenzInd)_2ZrCl_2$ metallocene catalyst and MAO were mixed in toluene and stirred until completely dissolved. From this preformed metallocene/MAO complex, the calculated amount needed for the support immobilization was added to the suspension of the nano-sized PS beads and MAO in toluene. Additional stirring for half an hour was needed for complete binding of the catalyst to the support. Stirring the mixture for 1 hour it was washed with dry toluene/hexane (50/50 vol %) mixture, the extra, i.e. non-supported metallocene/MAO solution was removed from the supported catalyst via a cannula. The supported catalyst was washed two more times and then the remaining solid was dried in vacuum.
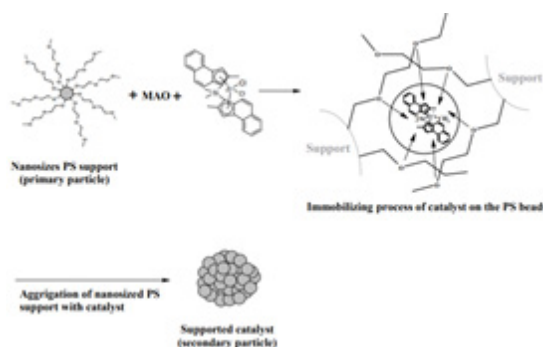
Scheme 3: Preparation of catalyst supported on the nano-sized PS beads functionalized with PEO

As the PEO shell of the nano-sized particles consists of very nucleophilic ether groups, the immobilization via a non-covalent bonding of the MAO/metallocene

complexes can be achieved and the aggregation of the nano-sized PS beads takes place. SEM pictures presented in Figure 5 show the morphology of the supported catalyst on the nano-sized PS beads.
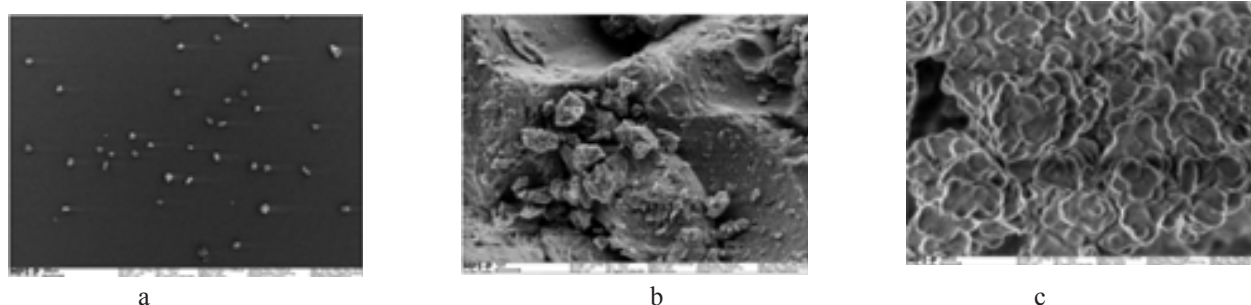
Figure 5: SEM images of the supported catalyst on the nanosized PS beads functionalized with PEO: scale bar – 200 μm (a), 1 μm (b), 200 nm (c)

The obtained supported catalyst particles are normally spherical and their size is about 50-100 micrometre (is about 1000 times larger than that of the nanosized PS beads) due to the aggregation of the PS beads induced by the interaction between PEO chains on PS beads and the active metal sites. The SEM image of the supported catalyst particle in Fig.3 (b) and (c) show exactly the formation of the conglomerates of the nanosized PS beads (primary particles) through the interaction between PEO chains of the nanosized PS beads and MAO/zirconocene complexes in Scheme 2. By using these nanosized PS beads, different supported catalysts were prepared, and ethylene polymerizations were carried out at 70oC polymerization temperature and 40 bar ethylene pressure in 400 ml iso-butane as solvent. In this heterogeneous ethylene polymerization 40 μmol/g metallocene activation and 350 MAO/Zr mol ratio were used. This catalyst exhibits an activity of about 1000-3460 kg PE/mol Zr·hour·bar. The PE molecular weights (Mw) are about 1150000-1310000 and the MDW is about 2.3-2.6 [48,49].

Propylene Polymerization

In 1985 Kaminski et al. obtained highly isotactic polypropylene (PP) by using a chiral zirconocene (rac-$(C_2H_5)(Ind)_2ZrCl_2$) catalyst combined with methylaluminoxane (MAO) as cocatalyst [50]. Metallocene-based catalytic systems are dramatically different from Ziegler–Natta type catalysts, because they have much higher activity and lower polydispersity [51]. To solve the problems (such as the difficulty in controlling the polymer morphology, the very large amount of MAO needed, and the reactor-fouling problem) observed with the soluble homogeneous catalysts, heterogenization of the metallocene is crucial for industrial application [7,52-58]. Development of supported metallocene catalysts enables their use in gas- and slurry-phase processes and prevents reactor-fouling problems. It also enables the controlling of the polymer morphology with the formation of uniform particles with narrow size distribution and high bulk density. Supported systems need a much smaller [Al]/[Zr] ratio than homogeneous systems. To obtain the maximum activity, [Al]/[Zr] ratio was decreased from 3000-100000 for the homogeneous catalysts to 100-500 for the heterogeneous catalysts, probably because MAO had the lower deactivation rate when one side is blocked by the support [58].

Nanosized silica particles were used as the support for metallocene/MAO catalyst and was found that the nanosized catalytic system exhibited significantly better propylene polymerization activity than the microsized system under identical reaction conditions and received polymer`s particles has good morphological features. To immobilize metallocene catalyst on silica there are three methods were commonly used [8, 58-61]: (a) adsorption of metallocene onto a MAO-pre-treated silica support; (b) reacting silica with a mixture of metallocene with MAO; (c) reacting with MAO after supporting the metallocene [8]. The most used industrial method is firstly treating the support with MAO and then adsorb the metallocene on it (i.e., method a).

Authors of the work investigated nanosized silica supported $(C_2H_5)(Ind)_2ZrCl_2$/MAO catalyst, containing 1.09 wt% Zr and with [Al]/[Zr]=17, which has been prepared by impregnation of metallocene on an MAO-modified silica support [62]. At the optimum temperature of 50oC and with [Al]/[Zr]=570, the nanosized catalyst had polymerization productivity of 3824 kg PP/mol Zr·h, which was 1.64 times more than obtained with the microsized catalyst (polymerization productivity was 2325 kg PP/mol Zr·h) [62]. However, the molecular weight and isotacticity of PP produced by the nanosized silica supported (C2H5)(Ind)2ZrCl2/MAO catalyst were not high enough, probably because of the smaller rigidity of the ethylidene bridge in $(C_2H_5)(Ind)_2ZrCl_2$MAO [63].

Nanosized silica supported $[(CH_3)_2Si(Ind)_2ZrCl_2$ catalyst (Figure 6, a) also has better activity (polymer yield of 80%) at the temperature of 55oC, which allow producing a polypropylene with a higher melting point, a greater molecular weight, a narrower MWD, iso-tacticity, and melting point in comparison to that produced with the nanosized silica supported $(C2H_5)(Ind)_2ZrCl_2$/MAO catalyst and microsized analogy [64].
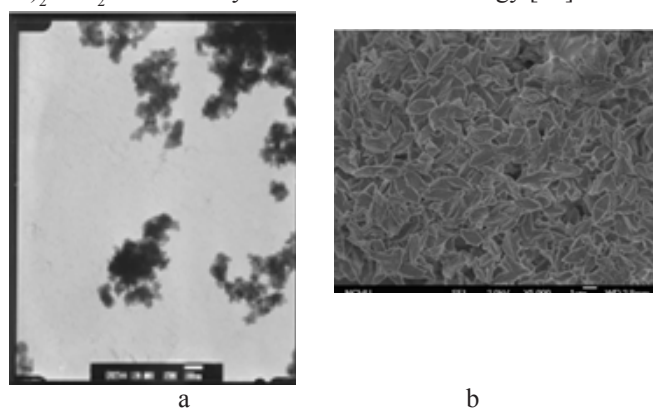

Figure 6: TEM micrograph of the nanosized silica supported $Me_2Si(Ind)_2ZrCl_2$ catalyst (a) and SEM micrograph of PP particles produced with the nanosized catalyst (polymerization time = 2 h)

The nanosized catalyst's activity was attributed to its larger surface area and to the higher monomer concentration at its

external active sites (which were free from internal diffusion resistance). On the contrary, the microsized catalyst's internal active centres had strong internal diffusion resistance, which resulted in the lower monomer concentration and inferior performances. Each nanosized catalyst particle had uniform polymerization activity and produced polymer particles of similar sizes and shapes, which is obviously from electron microscopy results [64].

The MAO-treated rice husk ash (RHA) contained 120 nm spherical silica particles, was used to support Me2Si(Ind)2ZrCl2 and $C_2H_4(Ind)_2ZrCl_2$ catalysts [65]. In contrast to commercial microsized silica supported catalyst this nanocatalyst exhibited higher polymerization activity and allow receiving polypropylene particles with uniform size and shape. Polypropylene with much greater molecular weight (and longer chain length) but with much smaller number (than in the case of $C_2H_4(Ind)_2ZrCl_2$) produced in the presence of $Me_2Si(Ind)_2ZrCl^2$, which resulted in the difference in the size and shape of polymer assembly. The increase of reaction temperature decreased polymer molecular weight and stereoregularity, which resulted in the change of the shape or the decrease of the size of polymer assembly (Scheme 4) [65].
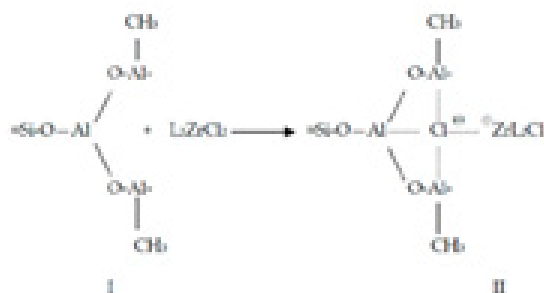

Scheme 4: The reaction of MAO-modified silica (species I) with metallocene and formation of species II.

Formation of nanoscale structures during the interaction of components of the catalytic systems $Ni(acac)_2/PPh_3/AlR_2Cl$, $Ni(acac)_2/AlR_2Cl$ (R= Et, i-Bu) and $Ni(acac)_2/AlEt_3$ was shown using TEM, EPR and UV spectroscopy. The publication also presents the results to justify the participation of nanoparticles Ni-coll. in stabilizing the catalytically active nickel centres in the oligomerization of propylene [66].

Nanocatalysis in Dienes Polymerization Processes
**Butadiene Polymerization**
Mesoporous silica nanoparticles (MSNs) are suitable for studying the effects of the catalyst carriers, especially the size effect of the carrier, because MSNs are chemically and thermally stable, and have high surface area, well-defined, and controllable particle size, morphology, and porosity [67]. Compared with the mesoporous silica bulky materials, such as MCM-41 and SBA-15, the MSNs have shorter channels. So, the reactant molecules could avoid a long journey through the channels and possible obstruction, which can improve molecule transport in the channels.

Authors of work [67] have synthesized a series of nano catalysts with different sizes (50–200 nm) by immobilizing salicylaldimine cobalt complexes on the mesoporous silica nano particles (MSNs) for polymerization of 1,3-butadiene (Scheme 5).
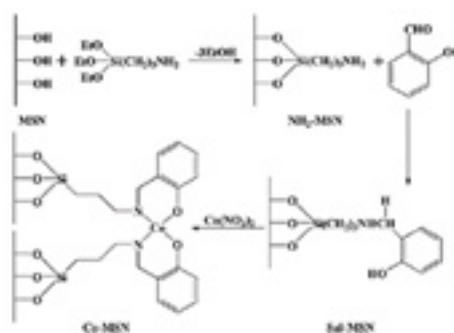

Scheme 5: The synthesis of the MSN-supported salicylaldimine cobalt complex

The SEM images (Figure 7, A) of MSNs show that they all consist of spherical nanoparticles. After immobilization with the organic groups and an complexation, the shape of the carrier is retained. On the morphology of all the MSNs the nature of the complex does not significant impact and nanoparticles are highly monodisperse. The TEM images (Figure 7, B) show that all of these nanocatalysts are mesoporous materials. From the adsorption branches of N2 adsorption-desorption isotherms, based on the BJH model, the pore size distributions were calculated.
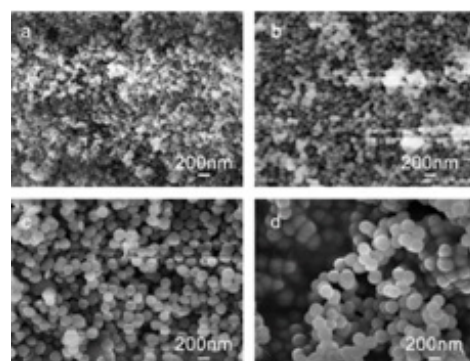

a
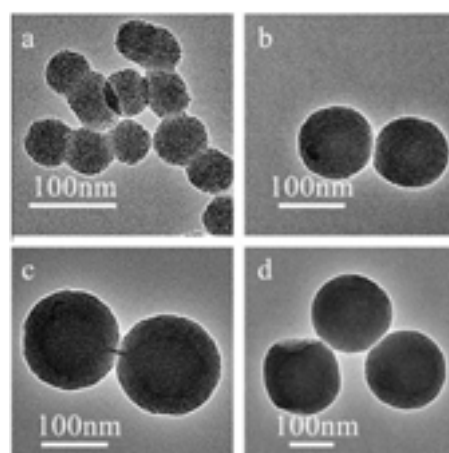
b

Figure 7: SEM (A) and TEM (B) micrographs of a nanocatalysts, heterogenized on mesoporous silica gel: Co-MSN-50 (a), Co-MSN-100 (b), Co-MSN-150 (c) and Co-MSN-200.

The results also show that MSN (150 nm) has the BET surface area of 738 m^2/g and a pore volume (Vp) of 0.29 (cm3/g). The

average pore diameter is calculated to be 27.1 Å. The TG curve of the nanocatalysts shows a major weight loss of 23 % (wt) in the temperature range of 200-600°C, which can be corresponded to the loss of the organics. The nanocatalysts in combination with methylalumoxane (MAO) show excellent catalytic efficiency in the polymerization of 1,3-butadiene to 1.4-cis-polybutadiene (the content of 1.4-cis-units 86-95%). As it seems from the results these nanocatalysts also show higher activity than the same catalyst on bulky mesoporous silica supporting materials and the homogeneous analogue of cobalt complex. The received yield of 60-100% and the molecular weight of 130000-490000 with the MDW of 1.75-2.65 of polybutadiene depend on the particle size of the catalyst nano support [67].

A heterogeneous cobalt-nickel (oxide) bimetallic catalyst for the polymerization of butadiene was subjected to calcination at different temperatures, which results in the formation of different phases with multiple oxidation states [68,69]. SEM micrographs of the fresh samples, calcined at different temperatures, are presented in Figure 8 (a, c, e). No open pore structures can be seen on fresh samples calcined at 673K and 873K, but calcined at 1173K sample has irregular pore structure. The packing order seen on these samples could be due to geometrically well-defined channels of the oxide formed and such structures are fairly stable. The SEM analysis performed on the spent catalysts (Figures 8, b, d, f) supports authors argument that the particle size, characteristics, and the nature of the catalytic active sites changes appreciably. The polymerization process takes different interaction routes on different types of active sites, due to different oxidation states. The best activity was achieved on the catalyst sample calcined at 1173 K and the received product contains polybutadiene, terminated by OH group, and aliphatic and aromatic carbonyl compounds. The GPC and LLS studies indicate that the polydispersity of high molecular weight products is in the narrow range. In products selectivity are mainly responsible the catalytic reaction conditions, the calcinations temperatures, which control the oxidation state, phase and stability of the catalyst. No effect of pressure and temperature were observed on the product distribution [68,69].

a

b

c

d

e

f
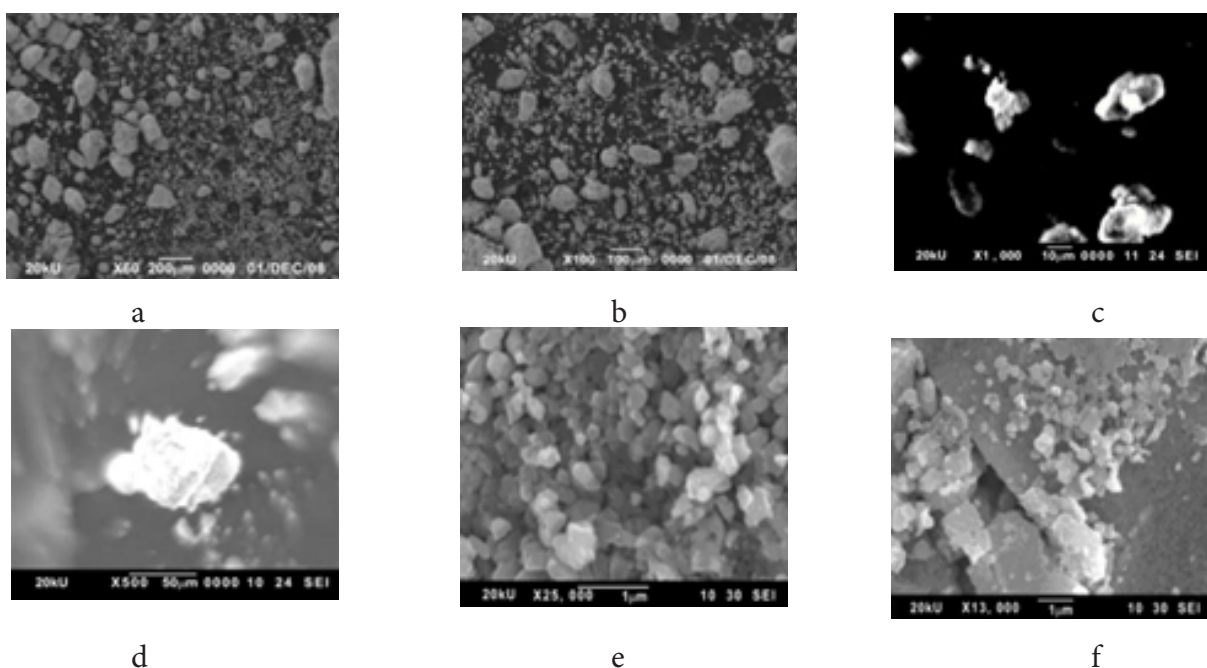
A new family of titanium–magnesium nanocatalysts (TMNCs), which are suitable for the trans-polymerization of conjugated dienes (butadiene, isoprene), were developed in the works [70, 71]. In the presence of TMNCs combined with tri-iso-butyl aluminum the suspension polymerization of butadiene was studied, which have demonstrated that they are active catalysts and enable the production of trans-polybutadiene with content of trans1,4-units up to 98.5%. The kinetic parameters of the process and the properties of received trans-1,4-polybutadiene were investigated (Table 1). With respect to the monomer and catalyst the reaction is of the first order. Variation in concentrations of Ti and monomer has no effect on the microstructure of trans-polybutadiene. Increasing in Al:Ti and the temperature of the process, decrease the content of trans-1,4-units. A hypothesis that the size of TMNC particles affects the nascent packing of trans-polybutadiene macromolecules in the crystal lattice was made [70].

Nano-sized neodymium chloride (NdCl$_3$) was prepared through the dissolution of anhydrous NdCl3 in THF (ca. 1.5 THF molecules were coordinated), after which the THF was slowly replaced with the addition of a cyclohexane and pale blue nuclei, nanosized below 200 nm, was formed [71]. The structural studies for NdCl3·xTHF using X-ray powder diffraction (XRD) and SEM microscope indicate that highly ordered crystallinity is decreased with reduced particle size from trigonal prismatic to porous sphere structure (Fig. 9). Nano NdCl$_3$, obtained as colloidal state in cyclohexane, was activated with Al(i-Bu)3 and Al(i-Bu)2H at room temperature and employed for 1,3-butadiene solution polymerization. Comparable to the ternary neodymium catalyst Nd(neodecanoate)3/AlEt$_2$Cl/Al(i-Bu)3 the nanosized Nd catalysts showed 15 times high activity (1.0~1.3·10^5 g/Nd mol·h), and received polybutadiene has microstructures: cis-, trans-, and vinyl-contents, about 96.0, 3.5, and 0.5%, respectively [71].

A new highly activity and stereo selectivity heterogenized bifunctional cobalt-containing catalytic dithiosystems for butadiene

gas phase polymerization has been developed at work [72]. Based on organic dithiocompounds of cobalt (Co-DTC) (O,O-dithiophosphates, N,N-dithiocarbamates) in combination with aluminum organic compounds (AOC) (DEAC, TEA, MAO) bifunctional cobalt-containing catalytic dithiosystems has been heterogenized on silica gel (commonly used and nanosized) by the methods of "direct deposit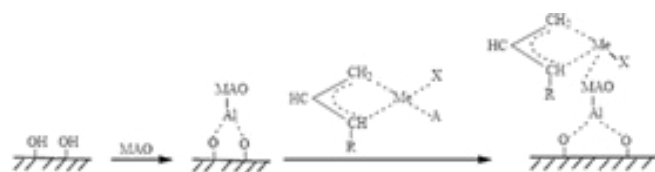ion" or "covalent binding with pre-alumination". The received data demonstrate that the "covalent binding with pre-alumination" method of immobilization of bifunctional cobalt-containing catalytic dithiosystems shows an extremely high activity in a gas phase polymerization of butadiene (Scheme 6).

Table 1: The effect of conditions of butadiene polymerization catalyzed by TMNCs on the initial rate of the process and the microstructure of trans-polybutadiene.

Experi-ments	$CTi \cdot 10^3$, mol/l	Al:Ti, mol/mol	Cm, mol/l	T,°C	W0, mol/l·min	Microstructure, %		
						trans-1,4	cis-1,4	1,2-
1	1.0	2	1.0	30	$8.0 \cdot 10^{-5}$	-	-	-
2	1.0	5	1.0	30	$1.0 \cdot 10^{-4}$	-	-	-
3	1.0	10	1.0	30	0.02	98.5	0.5	1.0
4	1.0	20	1.0	30	0.67	98.5	0.5	1.0
5	1.0	30	1.0	30	0.15	96.0	3.0	1.0
6	1.0	40	1.0	30	0.09	92.5	5.5	2.0
7	1.0	50	1.0	30	0.09	86.0	12.0	2.0
8	1.0	20	1.0	30	0.81	98.5	0.5	1.0
9	1.0	20	1.0	40	0.81	94.5	4.5	1.0
10	1.0	20	1.0	50	0.81	84.0	13.0	3.0
11	1.0	20	1.0	60	0.81	63.0	33.0	4.0
12	1.0	20	1.0	30	0.67	98.5	0.5	1.0
13	0.5	20	1.0	30	0.26	98.5	0.5	1.0
14	0.25	20	1.0	30	0.15	98.0	1.0	1.0
15	0.1	20	1.0	30	0.06	98.5	0.5	1.0
16	0.25	20	0.5	30	0.075	98.0	1.0	1.0
17	0.25	20	1.0	30	0.15	99.0	1.0	0
18	0.25	20	1.5	30	0.27	98.0	0.5	1.5
19	0.25	20	2.0	30	0.31	98.0	0.5	1.5
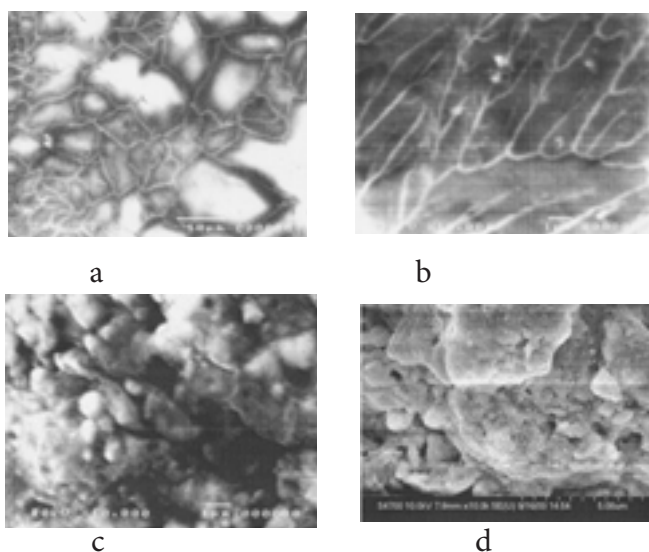
Figure 9: The SEM micrographs of NdCl3 particles: 1720 nm (a), 197 nm (b), 92 nm (c) and bulk image of 92 nm (d)


Scheme 6: Heterogenization of a homogeneous metal-complex catalyst by "covalent binding with pre-alumination" (Me-Cobalt, MAO – methylaluminoxane, A – aluminumorganic compound molecule)

The heterogenized catalyst has prepared as follows: to the nano-sized silica gel, dehydrated at 650ºC, was added the toluene solution of MAO at 25ºC and stirred for 2 hours, the slurry filtered, the solid product sometimes washed with toluene and in inert atmosphere dried under vacuum. The toluene solution of catalytic complex Co-DTC+AOC+BD added to the pre-aluminated nano silica gel and stirred for 60 min. The slurry filtered, the remaining solid product sometimes washed with toluene and dried under vacuum in an inert atmosphere. These catalysts provide the preparation of high molecular mass 1.4-cis- (91.0-97.0%) or 1.4-cis+1.2-(1.4-cis- 62.0-65.0% and 1.2- 32.0-35.0%) polybutadienes with productivity - 500.0-2500.0 kg PBD/g Co·h. The received results are significantly higher than the yield in the solution process (by using the same homogeneous catalysts

- 57.0 kg PBD/g Co·h.) and the known gas-phase process (by using the heterogenized neodymium-catalysts - 500.0 kg PBD/mole Nd·h.). The results obtained open up new opportunities for the development of principally new ecologically favorable and economically benefited technology of butadiene gas phase polymerization process by using heterogenized bifunctional cobalt-containing catalytic dithiosystems [72].

Dithiophosphorylated nano halloysite (NHS-DTPh) was synthesized by the direct phosphorosuphurization reaction of active OH-groups on a nano support surface with P2S5 (DTPh - dithiophosphate group) and on their basis the Ni, Co, and Nd-containing complexes (NHS-DTPh-Me) have been prepared [73, 74]. The assumed route of reactions in a simplified version is presented in Scheme 7.
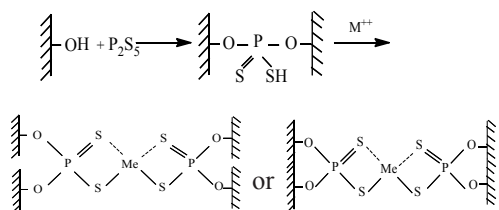
Scheme 7: Synthesis of heterogeneous dithiophosphorylated component of nanocatalyst (where, M= Ni, Co, or Nd).

The preliminarily dried NHS was placed into a glass reactor equipped with a mixer, reflux condenser, gas outlet line and a neutralizer of H_2S. To the NHS emulsion in m-xylene was added by drop wise the crushed P2S5 and stirred, which is accompanied by the intensive isolation of H_2S. After entering all quantities of P_2S_5 the temperature was raised to 135-140°C and the process was carried out to complete isolation of H_2S, which was caught by aqueous $CdCl_2$. On the quantity of formed precipitate CdS a quantity of isolated H2S was calculated. For complete removal of H2S the process was carried out under small vacuum and on finished of reaction the reaction mixture was blown by nitrogen for 2 hours, then washed 2-3 times by warm ethanol and dried under vacuum at 80°C. As a result, has been prepared NHS-DTPh with content of 3.65% phosphor and 1.69% sulfur.

For preparation of metal containing compounds the NHS-DTPh, as suspension in ethanol, was placed in the above-mentioned reactor and at T=80-90°C the alcohol solution of the corresponding metal chloride (or nitrate, sulfate, etc.) added in stirring for 4-5 hours. After cooling, the reaction product was filtered, washed hot ethanol, and dried under vacuum at 70°C. Initial NHS, synthesized NHS-DTPh and NHS-DTPh-Me were identified by the methods of SEM, IR and DTA.

The heterogenized catalysts have been used as a component of catalysts in the butadiene polymerization process in gas phase and liquid phase in suspension of catalyst. These NHS-DTPh-Me+DEAC catalysts under comparable conditions on productivity in solution (110-500 kg PBD/g Me·h) and gas phase (800-2500 kg PBD/g Me·h.) considerably exceed both their homogeneous (27-70 kg PBD/g Me·h.) and heterogeneous (500 kg PBD/mole Me·h.) analogues, respectively [73,74].

Isoprene Polymerization
The polymerization of isoprene on titanium-magnesium nanocatalysts (TMNCs) modified with electron donor (ED) compounds based on organic phosphine and sulphide have been studied [75, 76]. The isoprene polymerization on TMC combined with TIBA was carried out at 30-50°C, the titanium concentration in the reaction zone ranged from 10^{-4} to 10^{-3} mol/L and molar ratio Al:Ti = (20-100):1; the concentration of isoprene in the reaction medium was 1-2 mol/L. It was shown that the variation in polymerization parameters over a wide range had no effect on the relative amount of trans-1,4 units in polyisoprene, thus indicating the stability of trans-controlling active centres in TMC (Table 2).

Table 2: Polymerization of isoprene on TMC in the presence of TIBA (reaction time is 1 h, T = 30°C)

Isoprene concentration, mol/l	[Ti]·103, mol/l	Al:Ti, mol/mol	Isoprene conversion, %	microstructure, %	
				trans-1,4	3,4-
1	1.0	30	95	97-98	2-3
	1.0	100	98	97	3
	0.5	30	74	96	4
2	0.5	20	70	98	2

In the case of a catalyst, modified with tri-butyl-phosphine, the effects of the P:Ti ratio on the polymerization kinetics, on the microstructure of 1,4-trans-polyisoprene, and on the molecular mass of the polymer has been estimated. Figure 10 shows X-ray patterns of nascent trans-polyisoprene which indicate that the polymer has the α-monoclinic crystal modification.

Figure 11 shows the DSC thermo grams of trans-polyisoprene. During the first heating, the melting temperature of the sample is close to 70°C, a result that is also indicative of the presence of the α-monoclinic crystal modification of the nascent polymer. Melting and the subsequent crystallization results in the formation of the β-crystalline modification (second heating) with a melting temperature of about 50°C [76].
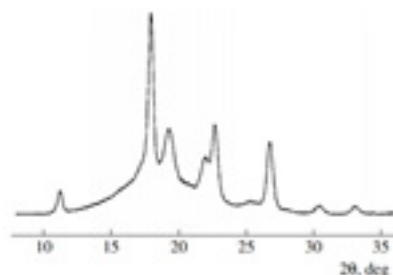
Figure 10: X-ray pattern of gutta-percha synthesized on TMC
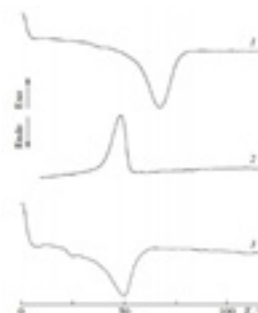
Figure 11: DSC curves for trans-polyisoprene: (1) the first heating (Tm = 68°C, α-monoclinic form), (2) cooling, and (3) the second heating (Tm = 52°C, β-form).

The study of isoprene polymerization on TMNCs/Bu3P showed that the presence of the electron donor leads to a reduced initial rate of polymerization, which becomes more pronounced with an increase in the content of the modifier in the TMNCs relative to the content of Ti (up to 50 mol/mol). At Bu3P:Ti=0.5-10 mol/mol, the catalyst activity does not diminish, the content of 1,4-trans-units increases from 83 to 97%, and Mw changes from 43000 up to 330000 with a simultaneous decrease in the polydispersity coefficient [77,78].

Conclusions

Due to their extraordinary properties, nanomaterials can provide excellent advantages in polymerization catalytic systems, such as, increase the catalytic activity, boost the reaction selectivity, and change the produced polymer's properties. One question that must come to our mind is: how the nanomaterials affect reaction activity? We must remember that the catalytic activity of the homogeneous systems influences the electronic density, and the bulkiness around the metal centre provided by the ligand.

It is obvious from publications dealing with nano catalysis, that to display high activity the homogeneous catalysts well dispersed on the nanomaterial are necessary. Nanomaterial supported catalysts display higher catalytic activity due to smaller particle sizes, more finely dispersed to optimize yields, decrease in reaction times, and are possible to run gas-slurry processes.

The size-dependence of catalysts can be attributed to geometrical and electronic effects because, with the decreasing particle size, the coordination environment of the surface atoms changes dramatically. Changing the particle size of a catalyst will also lead to the variation of its local electronic structure. Detailed studies evidenced a strong correlation between the polymerization activity of supported catalysts, and both the nature of the supporting material and the size, diameter, and distribution of the pores.

Perspectives

The homogeneous catalysts covalently or non-covalently supported on various nanomaterials (CNTs, nano oxides, nano clays, nano zeolites, etc.) show good, or excellent activities in olefin polymerization. Interestingly, the presence of the nanomaterials has a great influence on catalyst activities and properties of the resulting polymers. An important extension of this work would be to use these homogeneous and supported catalysts to synthesize other polymers or copolymers. Therefore, one of the further works could investigate the polymerization behavior of nanomaterial supported catalysts in those kinds of polymerization and copolymerization.

The selection of the best nano support is also a promising issue. According to the results of the works described here, the nature of the nanomaterials has a significant effect on catalytic activity and polymer properties can be controlled by the chemical composition of supported catalysts. Therefore, it is suggested that various nanomaterials with different sizes and diameters are used to support homogeneous catalysts and investigated in polymerization processes.

Concerning the polydienes part, polymerization conditions should be further investigated to improve the selectivity between cis-1,4-, trans-1,4- and 1,2-polydienes. For those immobilized catalysts, data concerning the number of metals (Ni, Co, Nd, Ti, etc.) complexes that were effectively immobilized on the nano supports and their butadiene and isoprene gas phase polymerization activity should be investigated.

The resulting polymer morphology and the properties of the resulting polymer (mechanical, thermal conductivity, flexibility, etc.) are worth to be comprehensively studied.

Acknowledgments

References
1. W Kaminsky (2006) Olefin Polymerization, Wiley New York 500 p.
2. Z Guan (2009) Metal Catalysts in Olefin Polymerization, Springer-Verlag Berlin Heidelberg 260 p .
3. Eds R Hoff and RT Mathers (2010) Handbook of Transition Metal Polymerization Catalysts Wiley 575 p.
4. RH Crabtree (2015) Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance, and Cure, Chemical Reviews 115: 127-150.
5. WM Saltman (1977) The Stereo Rubbers Wiley-Interscience New York 211 p.
6. G Ricci and G Leone (2014) Recent advances in the polymerization of butadiene over the last decade, Polyolefins Journal 1: 43-60.
7. MR Ribeiro, AA Deffieux and MF Portela (1997) Supported Metallocene Complexes for Ethylene and Propylene Polymerizations: Preparation and Activity, Ind. Eng. Chem. Res. 36: 1224-1237.
8. GG Hlatky (2000) Heterogeneous Single-Site Catalysts for Olefin Polymerization, Chem. Rev 100: 1347-1376.
9. M Smit (2005) Heterogenization on Silica of Metallocene Catalysts for Olefin Polymerization, PhD Thesis Technical University of Eindhoven 141 p.
10. G Ricci, A Sommazzi, F Masi, MM Ricci, A Boglia and G Leone (2010) Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization, Coordination Chemistry Reviews 254: 661-676.
11. R Taube and G Sylvester (1996) Stereospecific polymerization of butadiene or isoprene, In: Applied homogeneous catalysis with organometallic compounds, Eds B. Cornils and W. A. Herrmann VCH Weinheim 280 p.
12. C Eberstein, B Garmatter, KH Reichert and G Sylvester (1996) Gasphasen polymerization von butadien, Chemie Ingenieur Technik 68: 820-823.
13. G Sylvester (1996) Gasphasen Polymerization von Butadien, Gummi Asbest Kunststoffe 49: 60.
14. J Sun, C Eberstein and KH Reichert (1997) Particle growth modeling of gas phase polymerization of butadiene, J.App. Polym.Sci. 64: 203.
15. S Zhiguan, L Weishi and Z Yifeng (2000) Kinetic model of gas phase polymerization of 1,3-butadiene catalyzed by supported rare earth coordination system, Science China Chemistry 43: 477-484.
16. K Zoellner and KH Reichert (2000) Experimentelle untersuchungen der gasphasen polymerization von butadiene imlaborreaktor, Chemie Ingenieur Technik 4: 396-400.
17. K Zoellner and KH Reichert (2001) Gas phase polymerization of butadiene – kinetics, particle size distribution, modeling, Chemical Engineering Science 56: 4099-4106.
18. M Bartke, A Wartmann and KH Reichert (2003) Gas-Phase Polymerization of Butadiene. Data Acquisition using Minireactor Technology and Particle Modeling, Journal of

Applied Polymer Science 87: 270-279.

19. P. Munnik, P. E. de Jongh and K. P. de Jong, Recent Developments in the Synthesis of Supported Catalysts, Chemical Reviews, 115 (14), 6687-6718 (2015).

20. L Zhang (2014) Immobilization on nanomaterials the molecular catalysts of olefins polymerization, PhD Thesis Institute of National Polytechnique de Toulouse 263 p.

21. S Bredeau, L Boggioni, F Bertini, I Tritto, F Monteverde, et al. (2007) Ethylene–Norbornene Copolymerization by Carbon Nanotube-Supported Metallocene Catalysis: Generation of High-Performance Polyolefin Nanocomposites, Macromol. Rapid Commun. 28: 822-827.

22. K Wiemann, W Kaminsky, FH Gojny and K Schulte (2005) Synthesis and Properties of Syndiotactic Poly(propylene)/ Carbon Nanofiber and Nanotube Composites Prepared by in situ Polymerization with Metallocene/MAO Catalysts, Macromolecular Chemistry and Physics 206, 15: 1472-1478.

23. W Kaminsky, A Funck and C Klinke (2008) In-situ Polymerization of Olefins on Nanoparticles or Fibers by Metallocene Catalysts, Topics in Catalysis, 48: 84-90.

24. L Qu, LM Veca, Y Lin, A Kitaygorodskiy, B Chen, et al. (2005) Soluble Nylon-Functionalized Carbon Nanotubes rom Anionic Ring-Opening Polymerization from Nanotube Surface, Macromolecules 38: 10328-10331.

25. J Chen, MA Hamon, H Hu, Y Chen, AM Rao, et al. (1998) Solution Properties of Single-Walled Carbon Nanotubes, Science 282: 95-98.

26. S Banerjee and SS Wong (2002) Synthesis and Characterization of Carbon Nanotube−Nanocrystal Heterostructures, Nano Lett 2: 195-200.

27. X Wang, H Liu and L. Qiu, Cationic polymerization of tetrahydrofuran from multiple-walled carbon nanotubes: Preparation and glass transition kinetics, Mater. Lett. 61 (11-12), 2350-2353 (2007). https:/doi.org/10.1016/j.matlet.2006.09.015.

28. M Salavati-Niasari and M Bazarganipour (2009) Synthesis, characterization and catalytic oxidation properties of multi-wall carbon nanotubes with a covalently attached copper (II) salen complex, Appl. Surf. Sci 255: 7610-7617.

29. Y Liu and A Adronov (2004) Preparation and Utilization of Catalyst-Functionalized Single-Walled Carbon Nanotubes for Ring-Opening Metathesis Polymerization, Macromolecules 37: 4755-4760.

30. AA Koval'chuk, AN Shchegolikhin, VG Shevchenko, PM Nedorezova, AN Klyamkina, et al. (2008) Synthesis and Properties of Polypropylene/Multiwall Carbon Nanotube Composites, Macromolecules 41: 3149-3156.

31. A. Toti, G. Giambastiani, C. Bianchini, Meli, S. Bredeau, P. Dubois, D. Bonduel and M. Claes, Tandem Action of Early-Late Transition Metal Catalysts for the Surface Coating of Multiwalled Carbon Nanotubes with Linear Low-Density Polyethylene, Chem. Mater. 20, 3092-3098 (2008). https:/doi.org/10.1021/cm7035184.

32. X Dong, L Wang, T Sun, J Zhou and Q Yang (2006) Study on ethylene polymerization catalyzed by Cp2ZrCl2/carbon nanotube system. J. Mol. Catal. Chem 255: 10-15.

33. X Dong, L Wang, L Deng, J Li and J Huo (2007) Preparation of nano-polyethylene fibres using Cp2ZrCl2/carbon nanotube catalytic system, Mater. Lett. 61: 3111-3115.

34. S Park, SW Yoon, KB Lee, DJ Kim, YH Jung, et al. (2006) Carbon Nanotubes as a Ligand in Cp2ZrCl2-Based Ethylene Polymerization, Macromol. Rapid Commun. 27: 47-50.

35. X Tong, C Liu, HM Cheng, H Zhao, F Yang and X Zhang (2004) Surface modification of single-walled carbon nanotubes with polyethylene via in situ Ziegler–Natta polymerization, J. Appl. Polym. Sci. 92: 3697-3700.

36. A Kheradmand, ASA Ramazani, F Khorasheh, M Baghalha and H Bahrami (2015) Effects of Nanographene Oxide as Support on the Product Properties and Performance of Ziegler-Natta Catalyst in Production of UHMWPE, Polym. Adv. Technol 26: 315-321.

37. Z Yinghuai, SLP Sia, K Carpenter, F Kooli and RA Kemp (2006) Syntheses and catalytic activities of single-wall carbon nanotubes-supported nickel (II) metallacarboranes for olefin polymerization, Journal of Physics and Chemistry of Solids 67: 1218-1222.

38. X Dong, L Wang, L Deng, J Li and J Huo (2007) Preparation of nano-polyethylene fibres using Cp2ZrCl2/carbon nanotube catalytic system, Materials Letters 61: 3111-3115.

39. F Azimfar, A Badiei, SM Ghafelebashi, M Daftari-Besheli and AR Shirin-Abadi (2018) Effect of MAO-modified nonporous silica supports with single-site titanocene catalyst on ethylene polymerization, Korean Journal of Chemical Engineering 35: 1026-1032.

40. Li KT, Dai CL, Kuo CW (2007) Ethylene polymerization over a nano-sized silica supported Cp2ZrCl2/MAO catalyst, Catal. Commun 8: 1209-1213.

41. Li KT, Dai CL, Li CY (2010) Synthesis of linear low-density polyethylene with a nano-sized silica supported Cp2ZrCl2/MAO catalyst, Polym. Bull 64: 749-759.

42. Li KT, Li CY (2012) Nano-Sized Silica Supported Me2Si(Ind)2ZrCl2/MAO Catalyst for Ethylene Polymerization, Journal of Applied Polymer Science 123: 1169-1175..

43. P Zapata, RR Quijada, R Benavente, I Lieberwirth, H Palza (2011) Synthetic layered and tube-like silica nanoparticles as novel supports for metallocene catalysts in ethylene polymerization, Applied Catalysis A 407 2: 181-187.

44. YS Ko, SI Woo (2003) Generation of active site confined inside super cage of NaY zeolite on a nanoscale and its ethylene polymerization, European Polymer Journal 39: 1553-1557.

45. C Covarrubias, R Quijada, R Rojas (2008) Ethylene polymerization using dealuminated ZSM-2 zeolite nanocrystals as an active metallocene catalyst support, Applied Catalysis A: General 347: 223-233.

46. P Chammingkwan, Y Bando, M Terano, T Taniike (2018) Nano-dispersed Ziegler-Natta catalysts for 1 μm-sized ultra-high molecular weight polyethylene particles, Front. Chem 6: 524-544.

47. MA Semsarzadeh, A Aghili (2008) Novel Preparation of Polyethylene from Nano-extrusion Polymerization Inside the Nanochannels of MCM-41/MgCl2/TiCl4 Catalysts, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 45: 680-686.

48. YJ Jang, N Nenov, M Klapper, K Müllen (2003) Organic Nanoparticles with Polypropyleneoxide Chains as Support for Metallocene Catalysts: Influence of the Concentration of PPO chains on the Surface of Nanoparticles on the Catalyst Activity in Ethylene Polymerization, Polymer Bulletin 50: 351-358.

49. YJ Jang, M Klapper, K Müllen, G Fink (2005) Fragmentation Study of Metallocene Catalyst Supported on Nanosized Organic Particles in Ethylene Polymerization, e-Polymers 13.

50. W Kaminsky, K Kuelper, HH Brintzinger, FRWP Wild (1985) Polymerization of propene and butene with a chiral

zirconocene and methylaluminoxane as co-catalyst, Angew. Chem. Int. Ed. Engl 24: 507-508.

51. W Kaminsky (2004) The discovery of metallocene catalysts and their present state of the art, J. Polym. Sci., Part A: Polym. Chem 16: 3911-3921.

52. HG Alt, A Koppl (2000) Effect of the Nature of Metallocene Complexes of Group IV Metals on Their Performance in Catalytic Ethylene and Propylene Polymerization, Chem. Rev. 100: 1205-1221.

53. S Hakim, M Nekoomanesh, A Shahrokhinia (2015) The effect of mixed and individual silane external donors on the stereo-defect distribution, active sites and properties of polypropylene synthesized with fourth generation Ziegler—Natta catalyst, Polymer Science Series A 57: 573-580.

54. F Zaccaria, A Vittoria, A Correa, C Ehm, PH M Budzelaar, et al. (2018) Internal Donors in Ziegler–Natta Systems: is Reduction by AlR3 a Requirement for Donor Clean-Up? Chem. Cat. Chem 10: 863-863.

55. X Dang, Q Li, H Li, Y Yang, L Zhang, et al. (2014) Ziegler-Natta catalysts with novel internal electron donors for propylene polymerization, Journal of Polymer Research 21: 619-627.

56. Y Weng, B Jiang, Z Fu, Z Fan (2018) Mechanism of internal and external electron donor effects on propylene polymerization with MgCl2-supported Ziegler–Natta catalyst: New evidences based on active center counting, Journal of Applied Polymer Science 135: 1-10.

57. MR Ribeiro, A Deffieux, MF Portela (1997) Supported Metallocene Complexes for Ethylene and Propylene Polymerizations: Preparation and Activity, Ind. Eng. Chem Res 36: 1224-1237.

58. G Fink, B Steinmetz, J Zechlin, C Przybyla, B Tesche (2000) Propene Polymerization with Silica-Supported Metallocene/MAO Catalysts, Chem Rev 100: 1377-1390.

59. W Kaminsky, H Winkelbach (1999) Influence of supported metallocene catalysts on polymer tacticity, Top Catal 7: 61-67.

60. M Smit, X Zheng, J Loos, JC Chadwick and CE Koning (2005) Effects of methylaluminoxane immobilization on silica on the performance of zirconocene catalysts in propylene polymerization. J. Polym. Sci., Part A: Polym. Chem 43: 2734-2748.

61. W Kaminsky, F Renner (1993) High melting polypropenes by silica-supported zirconocene catalysts. Makromol. Rapid. Commun 14: 239-243.

62. KT Li and YT Kao (2006) Nanosized silica-supported metallocene/MAO catalyst for propylene polymerization, J.Appl.Polym.Sci 101: 2573-2580.

63. B Wang (2006) Ansa-metallocene polymerization catalysts: Effects of the bridges on the catalytic activities, Coord. Chem. Rev 250: 242-258.

64. KT Li and F Sh Ko (2008) Dimethylsilyl-bis(1-indenyl) Zirconium Dichloride/ Methylaluminoxane Catalyst Supported on Nanosized Silica for Propylene Polymerization, Journal of Applied Polymer Science 107: 1387-1394.

65. KT Li and CN Yang (2019) Propylene Polymerization Catalyzed by Metallocene/Methylaluminoxane Systems on Rice Husk Ash, Molecules 24: 1467-1480.

66. VS Tkach, DS Suslov, OV Gubaidulina, MV Bykov and VA Umanets (2013) Nanosized Structures based on Bis(Acetylacetonat)Nickel and Aluminium Alkylhalides as Support for Complexes Active in Propene Oligomerization. Qquestions of the History of Natural Sciences and Technology 34: 104-112.

67. D Tang, L Zhang, Y Zhang, ZA Qiao, Y Liu and Q Huo (2012) Mesoporous silica nanoparticles immobilized salicylaldimine cobalt complexes as highly efficient catalysts for polymerization of 1,3-butadiene, Journal of Colloid and Interface Science 369: 338-343.

68. ST Hussain, R Naheed, A Badshah, M Saddique, MS Saleem Khalid (2010) Heterogeneous Supported Catalysts for Butadiene Polymerization: The Effect of Calcination Temperature and Solvent, The Open Catalysis Journal 3: 1-13.

69. ST Hussain, RN Naheed, A Badshah and T Mehmood (2019) Design and synthesis of nano heterogeneous supported catalysts for olefin polymerization, African Journal of Chemistry 6: 4391-3199.

70. OV Smetannikov, MS Chinova, EA Mushina, VI Kleiner, GN Bondarenko and BF Shklyaruk (2012) Polymerization of Butadiene with Titanium-Magnesium Nanocatalysts, Polymer Science, Ser. B 54: 215-222.

71. G Kwag, D Kim, S Lee, C Bae (2005) Morphology and Activity of Nanosized NdCl3 Catalyst for 1,3-Butadiene Polymerization, Journal of Applied Polymer Science 97: 1279-1283.

72. SS Salmanov, ZY Tagizadeh, AM Tagiyeva and FA Nasirov (2019) Heterogenization of Bifunctional Cobalt Containing Catalytic Dithiosystems for Gas Phase Polymerization of Butadiene. Processes of Petrochemistry and Oil Refining 20: 85-98.

73. Z Tagizade (2019) Ecologically Favourable Process of Dienes Polymerization by Cobalt-Containing Catalytic Dithiosystems, Heterogenized on Nano Supports, Int. Journal of Nano Materials and Chemistry 5: 27-35.

74. Z Tagizade (2020) Synthesis of Dithiophosphates of Nickel, Cobalt and Neodymium on Nano Halloysite and use of Heterogenized Catalyst in Polymerization of Butadiene, Processes of Petrochemistry and Oil Refining 21: 138-14.

75. IE Nifant'ev, OV Smetannikov, AN Tavtorkina, MS Chinova, PV Ivchenko (2016) Titanium–Magnesium Nanocatalysts of Polymerization (Review). Petroleum Chemistry 56: 480-490.

76. OV Smetannikov, EA Mushina, MS Chinova, VM Frolov, Yu Ya, et al. (2006) Isoprene Polymerization on Titanium–Magnesium Catalysts, Polymer Science, Ser. A 48: 793-798.

77. OV Smetannikov, AN Tavtorkin, IE Nifant'ev, MS Chinova, IF Gavrilenko (2013) Modified Titanium-Magnesium Nanocatalysts in the Polymerization of Isoprene. Polymer Science, Ser. B 55: 453-459.

78. OV Smetannikov, MS Chinova, IE Nifant'ev, AN Tavtorkin, AV Ivanyuk (2015) Influence of the Synthesis Conditions on the Structure and Composition of the Titanium–Magnesium Nanocatalyst and on Its Activity in Isoprene Polymerization. Russian Journal of Applied Chemistry 88: 1808-1815.