Int. J. Nano. Chem. **5**, No. 2, 27-35 (2019)

International Journal of Nano Materials and Chemistry

http://dx.doi.org/10.18576/ijnc/050202

Ecologically Favourable Process of Dienes Polymerisation by Cobalt-Containing Catalytic Dithiosystems, Heterogenized on Nano Supports

Zakir Tagizade[*]

Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences, Baku, Azerbaijan, Khojaly av., 30.

Received: 3 Feb. 2019, Revised: 2 Apr. 2019, Accepted: 3 Apr. 2019

Abstract: Bifunctional cobalt and nickel containing catalytic dithiosystems, heterogenized on nano supports (Montmorillonite, Halloysite, Al2O3, Silica gel) by pre-alumination method, were studied in the gas phase polymerization of butadiene. The effect of various parameters (catalyst amount, Al:Co ratio, reaction temperature and time, butadiene pressure) on activity and stereo selectivity of heterogenized catalysts was investigated and established the optimal catalyst (Co-DCDTPh+DEAC+BD catalytic system, heterogenized on nano-Hylloysite) and optimal reaction conditions([Me]=1.0●10-7 mol/g support; Al:Co=100:1; T=30oC; τ= 90 min; PBD=1,0 MPa). At optimal conditions were reached the catalyst productivity – 1250-6000 kg PBD/g Co●hour, polybutadiene molecular mass – 95000-1100000 and MWD – 1.20-4.15.

Smaller particle sizes more finely dispersed to optimize yields, decrease in reaction times, possibility to run gas-slurry processes of dienes, are reasons why nanomaterials supported catalysts have received attention and they are known to offer the possibility to display higher catalytic activity and stereo selectivity.

Keywords: heterogenized bifunctional catalysts-stabilizers, cobalt, nickel, butadiene, gas phase polymerization, catalyst productivity, molecular mass control.

1 Introduction

The wide introduction of polymer materials into various areas of human activity has posed several important problems, including the problem of environmental protection. The importance of solving environmental problems has led to stringent requirements for polymers and technologies for their production: the production of polymers must be ecologically favourable or at least have a minimal impact on the environment; polymers should be technologically processed after the end of their operation or biodegradable [1-7].

As known, polydienes, polybutadiene and polyisoprene, have been used to make rubber and tyre products, so they are one of the great innovation of the last century. Industrial processes to produce polydienes in solution are based on the use of coordination-ion systems containing metals of variable valence (titanium, cobalt, and nickel). The technological design of these processes includes the following main stages: 1) purification of the monomer and solvent; 2) preparation of a mixture of butadiene with a solvent; 3) polymerization; 4) deactivation of the catalyst and adding of the antioxidant; 5) washing of polymer solution from catalyst residues; 6) separation of the polymer from the solution; 7) drying and packaging of rubber. All these stages of polymerization create specific environmental problems [8-10].

In addition, in the most modern manufactures of stereo regular polydiene rubbers, catalyst residues remain in the polymer, and subsequently, even after thorough washing accelerate the processes of its thermal and photo-oxidative aging during storage and processing. The stage of aqueous washing and decontamination of the polymer complicates the technological scheme of the process and significantly worsens the environmental situation around the production, leading to significant energy and labour costs, the appearance of large amounts of waste water containing

---

[*] Corresponding author E-mail: tagiyeva1962@mail.ru

harmful metal ions [11].

This problem is successfully solved with the use of new types of bifunctional catalysts possessing, in addition to high polymerization activity, also thermal and photo stabilizing efficiency. The remains of such a bifunctional catalyst not only do not accelerate the aging process of the polymer, but, on the contrary, protect it from photo- and thermo-oxidative aging [12, 13]. However, these kinds of catalysts have the same disadvantages as other homogeneous catalysts, such as a short life time of active sites and the limitations of use in large scale processes. In order to pass those challenges and develop suitable systems for most of the industrial processes (slurry or gas-phase reactors), the immobilization of such catalysts on supports is required [14-19].

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 [20, 21].

As most of the existing olefin`s polymerization plants run a s the homogeneous catalysts for dienes polymerization also must be heterogenized on a support in order to be applied in those processes [22, 23]. In addition, the heterogenization of the 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 [24-27]. 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 very 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 reactor granules are small and their respective heat capacities are still low [24-27].

In 1992-1993 Bayer recognized the potential of Nd catalysis for the gas-phase polymerization of BD [28, 29]. The first patent in this field claims the use of supported Nd catalyst systems for the gas-phase polymerization of dienes [28]. Soon after, gas-phase polymerization of BD is mentioned in a patent filed by UCC [30]. Finally, Goodyear [31] and Ube [32] joined Bayer and UCC in their efforts to establish gas-phase technology for BR production.

Various inorganic materials, such as silica gel, MgCl2, Al2O3, MgO, polymers, etc., have been used as support to immobilize homogeneous polyolefins and polydienes synthesis catalysts [20, 33-39]. But, nanomaterials (nano carbons, nano clays – nano-Montmorillonite, nano-Halloysite; nano-Aluminum oxide, nano-Silica gel, etc.) are attractive candidates as support to immobilize homogeneous dienes polymerization catalysts. Moreover, nanomaterials, due to their outstanding and unique mechanical, thermal and electronic properties, are hoped to have a positive influence on the catalytic activity and produce advanced products [40-45].

As the cobalt-containing bifunctional catalytic complexes display high activity and stereo selectivity in solution [12, 13] and gas phase polymerization of butadiene (after supporting on common used supports) [46-49], in these paper we have investigated the cobalt-containing bifunctional catalysts-stabilizers, supported on various nano supports.

2 Experimental

2.1 Materials - Co-dicresyldithiophosphate and Ni-diphenyldithiophosphate Complexex were Synthesized According to [12].

Halloysite nanotube (HNTs) was kindly obtained from Eczacıbaşı Esan, Turkey. HNTs are a kind of natural clay from earth with hollow tubular structure and alumina-silicate groups on their surface. Nano Montmorillonite (NMMT) received from FLUKA. NMMT is the main constituent of the clay stone bentonite, named after a clay deposit near Montmorillon in southern France. Nano-Aluminium oxide (Al_2O_3) and nano-Silica gel were received from Sigma-Aldrich.

Freshly dried Toluene of Merk, n-Hexane Analytical Grade of Merk along with Butadiene gas of purity of 99.95 were used in the study.

2.2 Catalyst Heterogenization Methods

The heterogenization routes reported in the literature for supported catalysts can be described as follow: 1) Pre-alumination method: immobilization of the co-catalyst, like methylaluminoxane (MAO) (or triethyl aluminum (TEA), for in situ synthesis of MAO) on the support, followed by reaction with the metallocomplexe; 2) Direct impregnation of metal complex on the support, which is the most widely used method; 3) Immobilization of the ligands on the support, then reaction with a metal salt [20].

Moreover, using different preparation routes for supported homogeneous catalysts can have great influences on the catalytic activity and received polymer properties.

2.3 The Catalyst Characterization

The morphologies of the support, the synthesized catalysts were examined by Phillips scanning electron microscope (SEM) XL-30ESEM FEG, equipped with an energy dispersive X-ray spectrometer (EDX). The thermal decomposition behaviours of the samples were studied by Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) on a Mettler TGA/SDTA 851 in oxygen environment. The Infrared (IR) spectra of the catalysts and product were obtained on Bio-Red Excalibur FTIR Model 3000 MX as KBr pellet and as NaCl cell, respectively. The 1H and 13C-NMR spectra of polymer were recorded on a Bruker 400 MHz instrument, using deuterated chloroform ($CDCl_3$) as solvent. The GPC analysis was performed using Perkin Elmer Injector Detector L3350 equipped with RI Monitor. Laser Light Scattering (LLS) of the products were performed using a commercial light scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-t digital time correlator).

2.4 Butadiene Gas Phase and Slurry Polymerizations

For each experiment 0.5-25.0 g of catalyst (with [Me]=1.0●10-7 mol/g support; Al:Me = 100:1) was loaded inside the micro reactor using n-hexane and toluene in two different experiments for catalyst heterogenization and slurry polymerization of butadiene. The system was flushed with argon to ensure complete removal of air from the micro reactor and then butadiene at 50~60 psig (pounds per square inch) pressure at a flow rate of 40–50 mls/min was injected into the micro reactor with continuous stirring.

The temperature of the reaction was raised to 10-120oC and was maintained at this temperature for 15-150 min. When the product becomes stabilized, the reaction was stopped and the resultant mixture was analysed using 1H-NMR and 13CNMR along with GC/MS, FTIR, GPC and LLS (Laser Light Scattering) methods.

2.5 Characterization of Product

The microstructure of received polybutadiene product was determined by IR spectroscopy. The following peaks were used for quantitative determination of polymer structure: 723~760 cm-1 is due to long chain band. The vinyl loop for (cis-R-CH=CR-H) 1,4-cis- ~0.192), 912 cm-1 (R-CH=CH-H), 1,2- ~1.0), 965 cm-1 (trans-R-CH=CR-H), 1,4-trans- ~0.769). The aromatic absorption band is present in 1580~1600 cm-1. The polymeric H-The bonding is found in 3400~3441 cm-1, The absorption at 3150 cm-1 is due to stretching of =CH. The characteristic carbonyl peak is present at 1730 cm-1 [50]

Polybutadiene, which is predominantly of 1,4-microstructure, show two major signals of 13C at 27.2~27.4 and 32.5~32.7 ppm corresponding to cis- and trans-methylene carbons next to 1,4-units, respectively. A high vinyl contents, a methylene carbon line at 30.97 ppm has been assigned. The peaks assigned at 42.03~44.51 ppm is for 1,4-v-1,4 CH [51, 52].

3 Results and Discussion

3.1 Nano Supports Characterization

Halloysite nanotubes (HNTs) are the kind of natural clay from earth with hollow tubular structure and alumina-silicate groups on their surface and have large L/D ratio (dimensions of up to 10 μm in length, the inner diameter in order of 10-30 nm, and the outer diameter in order of 30-100 nm). The chemical formula of HNTs is Al2[Si2O5(OH)4] ●2H2O. It is similar with kaolinite structure; however HNTs differ from kaolinite with intermolecular water. The tubular structure of HNTs is like multi-walled carbon nanotubes (MWCNTs), but HNTs are cheaper than MWCNTs. The chemical analysis of HNTs was made and the results found as: 43.3% SiO2, 38.4% Al2O3, 0.7% Fe2O3, 0.1% TiO2, 0.08% CaO, 0.12% MgO, 0.27% Na2O and 0.12% K20.

Nano Montmorillonite (NMMTs) is the main constituent of the clay stone bentonite, named after a clay deposit near Montmorillon in southern France. Bentonites are formed by degradation of mica minerals and as a new formation from weathering products, in particular volcanic tuffs and ashes. The chemical formula of NMMTs is (Al,Mg)2(OH)2[Si4O10] ●nH2O. Chemical components of NMMT are (% mass.): SiO_2 – 35.95-53.95, MgO – 0.23-25.98, Al2O3 – 0.14-29.90, H_2O – 11.96-26.00, Fe_2O_3 – 0.03-29.00. In the structure also presents FeO, Cr2O3, CaO, NiO, CO, Na_2O, K_2O, ZnO. Crystallites size of naturel NMMTs are in the area of from 3 to 300 nm.

Nano-Al2O3 (NAO) - nearly spherical nanoparticles with purity – 99.0, 30-60 nm particle size (TEM), surface area – 115-150 m2/g (BET), linear formula Al2O3, molecular weight – 102, density – 1.06 g/cm3 at 25oC.

Nano-Silica gel (NSG)- Spherical powder nanoparticloes with purity – 99.0, 3-30 nm particle size (TEM), linear formula SiO2, atomic weight – 28, surface area - ~230-350 m2/g; density - 1.2 g/cm3 at 25 °C, melting point – 1410oC

3.2 Catalytic Activity

It`s known that nanomaterials have a large surface area, which serves as the support, to form supported catalysts. Moreover, nanomaterials have other exceptional physical and chemical properties, like small size, electron mobility, relatively stabilities to high temperature, oxidation, basic and acid action, making them useful support material for heterogeneous catalysis. For those reasons, the presence of nanosupport material can be expected to increase the catalytic activity, enhance the catalytic life time and reduce the reaction time.

Especially, HNTs as support matrix for polymerization either by intercalation or by immobilization are more reproducible. HNTs used as catalytic support in different polymerization processes because of following reasons: 1) HNTs improve the catalytic activity of different molecular species; 2) HNTs not only enhances the separation of catalyst but also improve the recovery of catalyst from reaction media; 3) HNTs due to their ionic interaction, facilitate the recycling as well as improve the disposal of catalyst; 4) HNTs has pre-defined tubular diameter which allows the entrance of molecules with specific sizes. This caters the shape and size selectivity to the catalyst; 5) Compare to other clay minerals, HNTs show higher reactivity and higher cationic exchange capacity.

These characteristics of HNTs make them an attractive candidate to be used for support matrix for immobilization of catalysts in polymerization reactions.

Immobilization of homogeneous catalysts on the surface of a solid support, usually results in a significant loss of the catalytic activity of catalyst, but HNTs, because of their nanometer size and regular shape, may reduce these drawbacks of immobilization.

Considering these advantages, Cobalt dicresyldithiphosphate+diethyl aluminum chloride (Co-DCDTPh+DEAC) and Nickel diphenyldithiophosphate+diethyl aluminum chloride (Ni-DPhDTPh+DEAC) catalytic dithio systems were heterogenized on nano supports (NMMT, HNT, NAO, NSG) by the pre-alunmination method: immobilization of the co-catalysts – diethyl aluminum chloride (DEAC) (or methylaluminoxane - MAO) on the support, followed by reaction with the metallo complexe of transition metal Co or Ni (Me-DTC+AOC+BD) (Figure 1).

Results of the catalytic activity and stereo selectivity of heterogenized cobalt- and nickel-containing catalytic dithiosystems in comparison with common used supports (Al2O3 and Silica gel) and homogeneous catalyst of IPCP ANAS in slurry and gas-phase polymerisation of butadiene are shown in table 1.

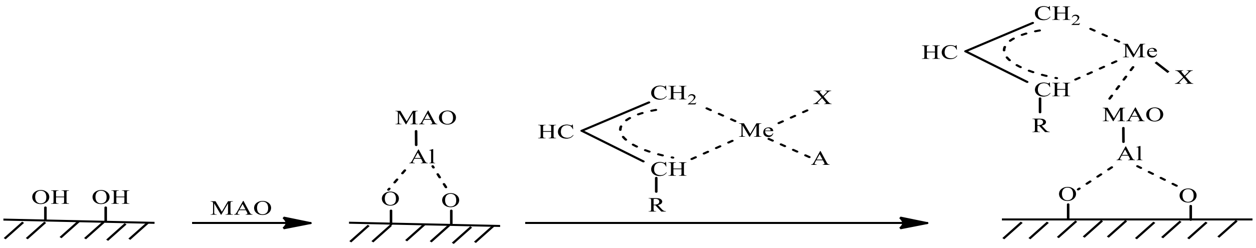

Fig. 1: Immobilization of Co-DCDTPh+DEAC or Ni-DPhDTPh+DEAC metallocomplexe catalysts on support, pretreated with MAO.

Table 1: Supported on nano materials Co-DCDTPh+DEAC and Ni-DPhDTPh+DEAC catalyst`s activity and stereoselectivity in the polymerization of butadiene. [Me]=1.0●10^{-7} mol/g support; Al:Co=100:1; T=30ºC; τ= 90 min; P=1,0 MPa.

NN Exp.	**Support**	**Catalyst**	**Polymerization methods**	**Catalyst productivity, kg PM/g Me·hour**	**M_w● 10^{-3}**	**M_w/M_n (MWD)**	**Microstructure, %**		
							1,4-cis	**1,4-trans**	**1,2-**
1	Nano-MMT	Co	Gas-phase	3800	830	1.5	97	2	1
2	Nano-MMT	Ni	Slurry	850	15	1.8	82	13	5
3	Nano-Hylloysite	Co	Gas-phase	4500	790	1.7	98	1	1
4	Nano-Hylloysite	Ni	Slurry	1000	20	2.0	85	12	3
5	Nano-Al_2O_3	Co	Gas-phase	2200	720	1.8	95	4	1
6	Nano-Al_2O_3	Ni	Slurry	650	10	2.2	78	20	2
7	Nano-Silica gel	Co	Gas-phase	3200	750	2.0	96	3	1
8	Nano-Silica gel	Ni	Slurry	830	15	2.5	80	15	5
9	Al_2O_3	Co	Gas-phase	1100	640	1,8	94	4	2
10	Al_2O_3	Ni	Slurry	350	13	2.0	77	17	6
11	Silica gel	Co	Gas-phase	1500	700	2,0	95	3	2
12	Silica gel	Ni	Slurry	460	18	2.4	82	14	4
13*	-	Co	Homogen.	40	450	2.5	94	4	2
14*	-	Ni	Homogen.	10	10	2.2	75	19	6

Note: *) Homogeneous Co-DCDTPh+DEAC and Ni DPhDTPh+DEAC catalytic systems: [Me]= 1.0●10^{-4} mol/l, [M]=3.0 mol/l, Al:Me= 100:1, T= 30ºC, τ= 60 min., solvent – toluene.

According to our investigations (table 1), the presence of the nanosupport materials affords the possibility to increase the catalytic activity 2-4 times (650-1000 kg PBD/g Ni●hour for nickel and 1100-1500 kg PBD/g Co●hour for cobalt-containing catalyst), more than common used supports (350-460 kg PBD/g Ni●hour for nickel and 2200-4500 kg PBD/g Co●hour for cobalt-containing catalyst), much more than homogeneous catalysts (10 kg PBD/g Ni●hour for nickel and 40 kg PBD/g Co●hour for cobalt-containing catalyst) and improve the reaction selectivity (table 1, exp.1-8). This is partly since, in a supported catalytic system, the significance of using the nano materials as support are to increase the dispersion of the active phases and have an influence on the catalytic active centres. Smaller particle sizes, more finely dispersed to optimize yields, decrease in reaction times, possibility to run gas-slurry processes, are reasons why nanomaterials supported catalysts have received attention and they are known to offer the possibility to display higher catalytic activity.

Among the studied heterogenized catalysts very hig activity and stereo selectivity was shown by Co-DCDTPh+DEAC catalytic dithiosystem, heterogenized on HNTs (catalyst productivity – 4500 kg PBD/g Co●hour, molecular mass – 790000, MMD – 1.7 and 1,4-cis content – 98%). Based on this study, Co-DCDTPh+DEAC catalytic system, heterogenized on HNTs, was used as optimal catalyst. All further investigations studying the effect of various parameters, such as amount of heterogeneous catalyst, Al:Co ratio, reaction temperature, reaction time and butadiene pressure on the catalyst productivity, selectivity and the main properties of end polymer, were conducted using this catalyst and received results are shown in tables 2-6.

As seen from the table 2, by increasing the amount of heterogeneous catalyst from 0.5 till 25 g (the concentration of Co on support 1.0●10-7 mol/g) decreases the catalyst productivity from 4750 till 2200 kg PBD/g Co●hour and molecular mass from 930000 till 95000, with increasing of MMD from 1.6 till 3.0.

Table 2: Effect of catalyst amount on gas phase polymerization of butadiene.[Me]=$1.0\bullet 10^{-7}$ mol/g support; Al:Co=100:1; T=30°C; τ= 90 min; P=1,0 MPa.

Catalyst content, g	Catalytic efficiency, (kg PBD/g Co●hour)	$M_w\bullet 10^{-3}$	MWD
0.5	4750	930	1.6
1.0	4500	790	1.7
2.5	3900	640	2.0
5.0	3500	380	2.3
10.0	3000	150	2.6
25.0	2200	95	3.0

The increasing of Al:Co ratio in the interval (25-200):1 allow to increase the catalyst productivity in the interval 2000-6000 kg PBD/g Co●hour and MWD in the interval 1.20-3.50 and decreasing of the molecular mass in the interval 970000-150000 (table 3).

As is known, dienes polymerization is a highly exothermic reaction and the formation of hot spot in the reaction mixture is generally not beneficial to the stability of the supported catalytic active species. This means that the reaction temperature could locally increase during the reaction and then accelerate the active species decay. Nanomaterials supported catalysts can slow down the decay of catalysts and increase the lifetime of the catalytic active species due to the high thermal conductivity property of nanosupport materials.

Table 3: Effect of Al:Co (in catalytic complex preparation) on gas phase polymerization of butadiene. [Me]= $1.0\bullet 10^{-7}$ mol/g support; T= 30°C; τ= 90 min; P= 1.0 MPa.

Al/Co (mol. ratio)	Catalytic efficiency, (kg PBD/g Co●hour)	$M_w\bullet 10^{-3}$	MWD
25	2000	970	1.20
50	2250	950	1.30
75	3000	900	1.50
100	4500	790	1.70
120	5000	700	2.30
150	5750	500	3.00
200	6000	150	3.50

With the increasing of reaction temperature from 10 to 60oC (table 4) we can regulate the increasing of catalyst productivity from 3000 till 4900 kg PBD/g Co●hour, molecular mass from 710000 till 790000 and MWD from 1.5 till 2.3. The further increasing of tempera-ture till 120oC the catalyst productivity decreases till 4000 with the decreasing of molecular mass of polymer till 400000. At this time the MWD is increased from 1.50 till 4.15.

Table 4: Effect of reaction temperature on gas phase polymerization of butadiene. [Me]= $1.0\bullet 10^{-7}$ mol/g support; Al:Co= 100:1; ; τ= 90 min; P= 1,0 MPa.

Temperature, °C	Catalytic efficiency, (kg PBD/g Co●hour)	$M_w\bullet 10^{-3}$	MWD
10	3000	710	1.50
30	4500	790	1.70
40	4800	850	1.95
50	4880	860	2.30
60	4900	790	2.80
80	4750	800	3.50
100	4400	620	3.90
120	4000	400	4.15

By increasing the reaction time in the interval 15-150 min the polymerization can reach the maximum productivity of catalyst after 60 min (table 5). In this interval were increased: the catalyst productivity 2200-4750 kg PBD/g Co●hour, the polymer molecular mass 660000-860000. After it till 150 min were decreased the catalyst productivity till 2950 and molecular mass till 660000. In the period of 15-150 min the MWD of received polymer was increased from 1.30 till 1.82.

Table 5: Effect of reaction time on gas phase polymerization of butadiene. [Me]= 1.0●10^{-7} mol/g support; Al:Co= 100:1; ; T= 30°C; P= 1,0 MPa.

Reaction time, min	Catalytic efficiency, (kg PBD/g Co●hour)	$M_w \cdot 10^{-3}$	MWD
15	2200	660	1.30
30	3960	800	1.40
45	4500	850	1.50
60	4750	860	1.63
90	4500	790	1.70
120	4000	700	1.80
150	2950	660	1.82

The pressure of butadiene at reaction zone during of gas phase polymerization of butadiene also affects the catalyst productivity and polymer properties. Thus, the increasing of butadiene pressure in the interval 0.1-10.0 MPa increase the catalyst productivity (from 2000 till 7000 kg PBD/g Co●hour), the polymers molecular mass (from 700000 till 1100000) and MWD (from 1.40 till 2.50) (table 6).

Table 6: Effect of butadiene pressure on gas phase polymerization of butadiene. [Me]= 1.0●10^{-7} mol/g support; Al:Co= 100:1; T= 30°C; τ = 90 min.

Butadiene pressure, MPa	Catalytic efficiency, (kg PBD/g Co·hour)	$M_w \cdot 10^{-3}$	MWD
0.1	2000	700	1.40
0.5	3500	750	1.60
1.0	4500	790	1.70
2.5	5250	875	1.90
5.0	6200	1000	2.30
10.0	7000	1100	2.50

The received results show, that catalytic dithiosystems, heterogenized on nano supports are very active in the gas phase polymerization of butadiene and in their presence the catalysts productivity and polymers main properties can be regulated in very wide range.

As known, the great factors which influence the catalytic activity of the homogeneous systems are the electronic density and the bulkiness around metal centre provided by the ligands. When the homogeneous catalyst anchored on nanomaterials through non-covalent or covalent interaction, there should be a strong interaction between the homogeneous compound and the nanosupport. This naturally has an effect on 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 of the metal centre is one of the important factors influencing the catalytic reaction. The heterogeneous catalysts have a direct interaction between the active centre and the nano support. The nano materials are the huge group compared to the organic species and can be considered as macro-ligands, are then introduced into the polymerization process. The large bulkiness of these macro-ligands has a great influence of the chain walking important role in the catalytic activity, stereo selectivity and Another reason to consider nanomaterials as suitable as and the monomer insertion during the polymerization. By this way, the presence of the nano support plays an well as on polymer molecular weight.

supports for metal catalyst 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 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.

Especially, solvents are not used in gas phase polymerization process, therefore there are no technological, economic, or ecological problems concerning cleaning and drying the solvents, washing off catalyst residues from the polymerizate, polymer degassing, polymer solubility, viscosity problem in reaction medium. From gas phase polymerization process also are excluded the complicate procedures of aggregation and separation of polymer from solution, which are needed in solution polymerization. These allow significantly reducing the construction-operation costs and environmental pollution problems in gas phase polymerization processes.

4 Conclusions

Bifunctional cobalt and nickel-containing catalyst-stabilizers- Me-DTD+AOC+BD were heterogenized on nano supports- NMMT, HNT, NAO, NSG, by the pre-alumination method, Heterogenization of these catalysts on the nano support materials affords the pos-sibility to increase the catalytic activity in gas phase polymerization of butadiene more 2-4 times (catalyst productivity - 650-1000 kg PBD/g Ni●hour for nickel and 1100-1500 kg PBD/g Co●hour for cobalt catalysts), than catalytic activity of commonly used supports (catalyst productivity 350-460 kg PBD/g Ni●hour for nickel and 2200-4500 kg PBD/g Co●hour for cobalt catalysts), and much more than homogeneous catalysts (10 kg PBD/g Ni●hour for nickel and 40 kg PBD/g Co●hour for cobalt catalysts) and improve the reaction selectivity (1,4-cis content 78-85% in nickel and 96-98% in cobalt nanocatalysts, against 78-82 in nickel and 94-95% in cobalt-containing catalysts, respectively), The optimal cobalt-containing catalytic dithiosystem (Co-DCDTPh+DEAC), heterogenized on HNTs, has very high activity and stereo selectivity (catalyst productivity – 4500 kg PBD/g Co●hour, molecular mass – 790000, MMD – 1.7 and 1,4-cis content – 98%) in the gas phase polymerization of butadiene, It was established, that by varying reaction parameters, such as amount of heterogeneous catalyst, Al:Co ratio, reaction temperature, reaction time and butadiene pressure, in the gas phase polymerization of butadiene the catalyst productivity and main properties of polybutadiene can be regulated in very wide range, High surface areas and a well-developed porosity of nanosupports are essential for achieving large metal dispersions, which usually results in a high catalytic activity. The sur-face areas and porosity also offer the possibility to absorb the diene monomer gas via π-π-interaction. These unique properties of the nano supports increase the rate of monomer inser-tion on the surface of the nanosupport material and increase the effectiveness of the catalyst and In gas phase polymerization process solvents are not used, therefore there are no technological, economic, or ecological problems concerning cleaning and drying the solvents, washing off catalyst residues from the polymerizate, polymer degassing, polymer solubility and viscosity problems in reaction medium. In this process also are excluded the complicate procedures of aggregation and separation of polymer from solution, which are needed in solution polymerization. These allow significantly reducing the construction-operation costs and environmental pollutions.

Symbols and Abbreviations

AOC = Aluminum organic compound
DEAC = Diethylaluminumchloride
DIBAC = Diizobutilaluminumchloride
MAO = methylaluminoxane
TEA = Triethylaluminum
PBD = Polybutadiene
DTPh = Dithiophosphate
DTD = Dithioderivative
DCDTPh-Co = Cobalt O,O'-di-4-methylphenyl dithiophosphate
GPC = Gel permeation chromatography
IR = Infra-Red Spectrophotometer
NMR- Nuclear Magnetic Resonance
HNTs =Halloysite nanotubes
NMMT = nano Montmorillonite
NAO = nano Aluminum oxide
NSG = nano Silica gel

References

[1] Anastas P.T., Warner J.C. Green Chemistry: Theory and Practice. Oxford University Press, 135 p,1998.

[2] Anastas P.T., Breen J.J. Design for the environment and Green Chemistry: the heart and soul of industrial ecology. J. Cleaner Production., **5(1–2)**, 97-102,1997.

[3] Anastas P.T., Beach E.S. Green chemistry: the emergence of a transformative framework: Original Article. Green Chemistry Let. Rev., **1(1)**, 9-24, 2007.

[4] Berthouex P.M., Brown L.C. Chemical Processes for Pollution Prevention and Control. CRC Press, Taylor & Francis Group, LLC, Boca Raton, London., 225, 2018.

[5] Thompson R.C., Moore C.J., vom Saal F.S., Swan S.H. Plastics, the environment and human health: current consensus and future trends- Review. Phil.Trans.R.Soc.B., **364**, 2153–2166, 2009.

[6] Singh B., Sharma N. Mechanistic implications of plastic degradation. Polymer Degradation and Stability, **93 (3)**, 561-584, 2008.

[7] Al-Salem S.M., Lettieri P., Baeyens J. Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Management., **29**, 2625–2643, 2009.

[8] Garmonov I.V. Synthetic Rubber. L.: Khimiya., 752 (rus.),1976.

[9] Saltman W.M. The Stereo Rubbers, Wiley-Interscience, New York., 211,1997.

[10] Kirpichnikov P.A. Album of technological schemes of the main production of the synthetic rubber industry., 225 c. (rus.),1986.

[11] Cole-Hamilton D.J. Homogeneous catalysis – new approaches to catalyst separation, recovery and recycling. Science., **299**, 1702-,2003.

[12] Nasirov F.A. Bifunctional Nickel- or Cobalt-containing Catalyst-stabilizers for Polybutadiene Production and Stabilization (Part I): Kinetic Study and Molecular Mass Stereoregularity Correlation. Iranian Polymer Journal., **12 (3)**, 217-235, 2003.

[13] Azizov A.H., Janıbayov N.F., Nasirov F.A., Novruzova F.M., Salmanov S.S., Quliyev N.A. Bifunctional catalysts for production and stabilization of stereoregular polybutadienes. In.: «Synthesis in the Field of Oil-Refining, Petrochemistry, Organometallic and Ionic-Liquid Catalysis» (Collected papers of İPCP ANAS), Baku, "Elm"., 395, 2009.

[14] Dolgoplosk B.A., Tinyakova Y.I. Metalloorganic catalysis in polymerization processes. M.: Nauka., 511,1982.

[15] Taube R., Sylvester G. Stereo specific polymerization of butadiene or isoprene//In: Cornils B., Herrmann W.A./Eds. Applied homogeneous catalysis with organometallic compounds. VCH, Weinheim., **1**, 280,1996.

[16] Zhang Z., Cui D., Wang B., Liu B., Yang Y. Polymerization of 1,3-Conjugated Dienes with Rare-Earth Metal Precursors. In: Molecular Catalysis of Rare-Earth Elements/Ed.: Roesky P.W., Springer-Verlag, XIII., 250, 2010.

[17] Ricci G., Sommazzi A., Masi F., Ricci M., Boglia A., Leone G. Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization. Coord. Chem.Rev., **254**, 661-676, 2010.

[18] Friebe L., Nuyken O., Obrecht W. Neodymium-based Ziegler/Natta catalysts and their application in diene

polymerization. Adv.Polym.Sci., **204**, 1-154, 2006.

[19] McNamara C.A., Dixon M.J., Bradley M. Recoverable catalysts and reagents using recyclable polystyrene-based supports. Chem.Rev., **102**, 3275-3300, 2002.

[20] Hlatky G.G. Heterogeneous single-site catalysts for olefin polymerization. Chem.Rev., **100**, 1347-1376, 2000.

[21] Smit M. Heterogenization on Silica of Metallocene Catalysts for Olefin Polymerization. Ph.D. Thesis, Eindhoven: Technische Universiteit Eindhoven., 141, 2005.

[22] Eberstein C., Garmatter B., Reichert K.-H., Sylvester G. Gasphasen polymerization von butadien. Chemie Ingenieur Technik., **68**, 820-823,1996.

[23] Sylvester G. Gasphasen polymerization von butadien. Gummi Asbest Kunststoffe, 49, 60,1996.

[24] Eberstein C. Gasphasen polymerization von butadiene. Kinetik, Partikelbildung und Modellierung. Ph.D. Thesis, TU Berlin, 1997.

[25] Zoellner K., Reichert K.-H. Gas phase polymerization of butadiene – kinetics, particle size distribution, modeling. Chemical Engineering Science., **56**, 4099-4106,2001.

[26] Sun J., Eberstein C., Reichert K.-H. Particle growth modeling of gas phase polymerization of butadiene. J.App.Polym.Sci., **64(13)**, 203,1997.

[27] Spiller C. Untersuhungenzum Stoff- und warmetransportbei der gasphasen polymerization von 1,3-Butadien. Ph.D. Thesis, TU Berlin, 1998.

[28] Sylvester G., Vernaleken H. Catalyst, its manufacture and its use in the gas-phase polymerisation of conjugated dienes. Eur. Patent, 647657/Bayer AG (DE)./Chem. Abstr., 123:229280,1995.

[29] Sylvester G., Vernaleken H. Method for the production of diene rubbers in the gas phase, Bayer AG, US Patent., **5(914)**, 377, 1999.

[30] Bernier R.J.N., Boysen R.L., Brown R.C., Scarola L.S., Williams G.H. Gas phase polymerization process, Eur. Patent 697421/ Union Carbide Chem.Plastic (US)/Chem. Abstr., **123**, 341350, 1996.

[31] Nissim C.J., Joel J.M., Castner H.A., Floyd K. US Patent 5859156/ Chem. Abstr., **130**, 96764, 1999.

[32] Tsujimoto N., Tsukahara M. Jap Patent 1060020/ Chem. Abstr., **128**, 180791,1998.

[33] Li K-T., Kao Y-T. Nanosized Silica-Supported Metallocene/MAO Catalyst for Propylene Polymerization. J.Applied Polymer Science., **101**, 2573–2580, 2006.

[34] Hussain S.T., Naheed R., Amin Badshah A., Tariq Mehmood T. Design and synthesis of nano heterogeneous supported catalysts for olefin polymerization. African Journal of Pure and Applied Chemistry., **3 (12)**, 247-261, 2009.

[35] Galvin M.E., Heffner S.A. Reaction of butadiene with a heterogeneous Ziegler-Natta catalyst in solid polymers and solutions. Macromolecules., **22**, 3307-3313,1989.

[36] Dong W., Masuda T. Homogeneous neodymium isopropoxide/modified methylaluminoxane catalyst for isoprene polymerization. Polymer.,**44**, 1561-1563, 2003.

[37] Barbotin F., Spitz R., Boisson C. Heterogeneous Ziegler-Natta catalyst based on neodymium for the stereospecific polymerization of butadiene. Makromol.Rapid.Commun., **22 (17)**, 1411–1414, 2001.

[38] Hussain S.T., Naheed R., Badshah A., Saddique M., Khalid M.S., Baig Z.I. Heterogeneous Supported Catalysts for Butadiene Polymerization: The Effect of Calcination Temperature and Solvent. The Open Catalysis Journal, **3**, 1-13, 2010.

[39] Yu G., Li Y., Qu Y., Li X. Synthesis and characterization of polymer-supported lanthanide complexes and butadiene polymerization based on them. Macromolecules., **126**, 6702-6707,1993.

[40] Fan J., Gao Y. Nanoparticle-supported catalysts and catalytic reactions – a mini-review. Journal of Experimental Nanoscience., **1(4)**, 457–475, 2006.

[41] Zhang L. Polymerization of diolefins by molecular catalysts, immobilized on nanomaterials. Ph.D. Thesis, Toulouse National Polytechnic Institute., 263, 2014.

[42] El-Shall M.S. Polymerization in the Gas Phase, in Clusters and on Nanoparticle Surfaces. Accounts of chemical Research, Vol. 41, No. 07, p. 783-792,2008.

[43] Jang Y-J. Nanosized Polymer Carriers for Metallocene Catalysts in Heterogeneous Olefin Polymerization. Ph.D Thesis, Johannes-Gutenberg-Universität zu Mainz., 206, 2005.

[44] Shin S-Y A., Simon L.C., Soares J.B., Scholz G., McKenna T.F.L. Gas-Phase Polymerization with Transition Metal Catalysts Supported on Montmorillonite – A Particle Morphological Study. Macromol.Symp., **285**, 64–73, 2009.

[45] Wan S., Cheng-Cheng Tian Ch-Ch., San-Xi Li S-X. Highly Active Fe(II) Catalyst Supported on Spherical MgCl2/Montmorillonite for Ethylene Polymerization. Joint International Conference on Materials Science and Engineering Application (ICMSEA) and International Conference on Mechanics, Civil Engineering and Building Materials (MCEBM)., 1-3, 2017.

[46] Pat. Azerb. № 2006 0065 Nasirov F.A, Novruzova F.M., Salmanov S.S.,Qasımzade E.Y., Janıbeyov N.F. Gas Phase Polymerization of Butadiene, 2006.

[47] Nasirov F.A., Novruzova F.M., Salmanov S.S., Azizov A.H., Janibayov N.F.. Gas Phase Polymerization of Butadiene on Heterogenized Cobalt-containing Catalytic Dithiosystems. Iranian Polymer Journal., **18 (7)**, 521-533, 2009.

[48] Nasirov F.A., S.S.Salmanov, N.F.Janıbayov. Novel Heterogenized Cobalt Containing Dithiosystems for Gas Phase polymerization of Butadiene. In.: «Additives in Polymers: Analysis and Applications/Eds.: A.A.Berlin, S.V.Rogovina, G.E.Zaikov. CRCnet BASF, Apple Academic Press.,

325, Chapter 8, 237-247, 2015.

[49] Nasirov F.A., Salmanov S.S. Novel Heterogenized Cobalt Containing Dithiosystems for Gas Phase polymerization of Butadiene. In.: «High-Performance Polymers for Engineering-Based Composites», App.Acad.Press and CRC Press, USA., 59-76, 2015.

[50] Haslam J., Willis H.A. Identification and analysis of Plastics, London, Iliffe Books, Princeton, New Jersey: D.Van Nostrand Co., 172-174, 1965.

[51] Brandolini A.J, Hills D.D. NMR Spectra of Polymers and Polymer Additives. Marcel Dekker, New York., 123-150, 2000.

[52] Krajewski-Bertrand M, Laupretre F. 13C NMR Investigation of the Size of the Moving Units in Polybutadienes of Various Microstructures, Macromolecules., **29**, 7616-7618,1996.