

Metal Complex Catalysts Immobilized in Polymer Gels

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SUMMARY: A number of polymer gels have been prepared using tertiary ethylene-propylene-ethylidenenorbornene copolymer as a rubber base with grafted poly-4-vinylpyridine, polymethacrylic acid and polymethacrylamide ligand chains. The grafted copolymers were crosslinked and complexes of nickel, zirconium and titanium were immobilized in the formed crosslinked copolymers. After treatment with organoaluminium compounds the obtained catalysts demonstrate high catalytic activity in the reactions of dimerization of lower olefins. Structures of the complexes and the catalytic activity of the gel immobilized catalysts have been investigated.

Introduction

Complexes of transition metals with polymer ligands combine the advantages of heterogeneous catalysts such as simplicity of separation from the reaction media and high stability with high activity and selectivity of homogeneous catalysts¹⁾.

Metal complexes immobilized in polymer gels able to swell in hydrocarbon substrate are of special interest. These are two phase systems, wherein nonpolar rubber base is dispersion medium containing domains of graft chains of macromolecular ligands. The dispersion is crosslinked, treated with metal compounds and complexes are formed in sites of macromolecular ligands. Due to rubber base the catalysts swell in hydrocarbons forming a gel easily accessible for reagents. The immobilized complexes act as homogeneous catalysts because the rate of diffusion in highly swollen polymers is comparable with that in liquids. On the other hand, they can be easily separated from the reaction media like heterogeneous catalysts.

The term "gel immobilized metal complex catalysts" was introduced by Prof.Dr.V.A.Kabanov and Prof.Dr.V.I.Smetanyuk^{2,3)}, and then research continued in

laboratory of Prof.Dr.V.I.Smetanyuk in cooperation with laboratory of the author of the present paper.

This paper summarises the results on synthesis, investigation and use of nickel, zirconium and titanium complexes immobilized in rubber base with grafted macromolecular ligands⁴⁻⁶.

Results and Discussion

We have synthesized a number of polymer gels using tertiary ethylene-propylene-ethylidene norbornene copolymer (CEP) as a rubber base with grafted poly-4-vinylpyridine (PVP), polymethacrylic acid (PMA) and polymethacrylamide (PMAA) ligand chains^{4,5}. The above mentioned monomers were added to the solution of tertiary copolymer in n-heptane together with 1-2% of azobis-isobutironitrile and heated at 75-80° for 6-10 hours. The grafted copolymers were crosslinked by adding 2-4 mass % of benzoperoxide to the solution. The crosslinked graft-copolymers were precipitated from the reaction medium in a form of swollen gels which were dried and granulated.

The crosslinked graft-copolymers were contacted with hydrocarbon solvent (n-heptane, toluene) and in swollen form were treated with salts of nickel (nickel chloride, nickel acetylacetonate), titanium (dibutoxititanium dichloride) or zirconium (dibutoxi-zirconium dichloride).

The resulted gel complexes were repeatedly washed with toluene-methanol mixture and n-heptane to remove the excess of the metal salt until the washing gave a negative test for metal and then treated with organoaluminium compound (OAC). Diisobutylaluminium chloride (DIBAC), ethylaluminium dichloride (EADC), diethylaluminium chloride (DEAC), sesquichloride ethylaluminium (SCEA) and triisobutylaluminium (TIBA) have been chosen for such treatment. Swelling capacity of the obtained gel immobilized catalysts in n-heptane was in the range of 600-800 vol.%.

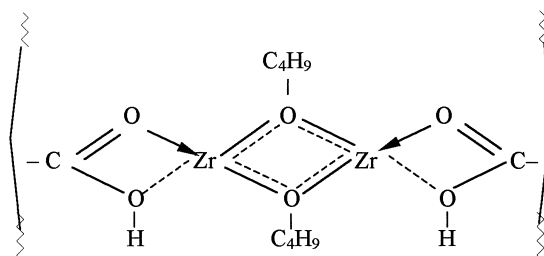
Comparison of IR-spectra of CEP and CEP-PVP shows that bands at 1620, 950 and 930 cm⁻¹ characterizing non-saturation of CEP disappear after grafting of PVP and band at 1600 cm⁻¹ associated with pyridine ring appears. After treatment of CEP-PVP

with dibutoxyzirconiumdichloride bands at 1640 cm^{-1} , 1600 cm^{-1} , and 1500 cm^{-1} with shoulder at 1529 cm^{-1} appear. Similar picture can be also observed in the case of treatment of CEP-PVP with dibutoxytitaniumdichloride. One could assume that in these cases coordination with zirconium and titanium takes place not only with nitrogen atom but also with π -electron system of pyridine ring, i.e. arene complex is formed.

In IR-spectrum of CEP-PMAA there is a band in the region of $3320\text{--}3400\text{ cm}^{-1}$ characterizing N-H bond of amide group. After treatment with nickel chloride this band is shifted to long-wave region. On the other hand, a band associated with C=O bond of amide group does not change. One might assume that coordination of nickel takes place only with N-H groups.

In IR-spectrum of nickel complexes of CEP-PVP we observe a band at 1640 cm^{-1} which characterizes complexation of nitrogen atom and decrease of intensity of the band at 1600 cm^{-1} which characterizes free pyridine ring. It might be assumed that in case of nickel coordination takes place only with nitrogen atom.

In IR-spectrum of CEP-PMA there is a band at 1720 cm^{-1} characterizing C=O group. After treatment of CEP-PMA with dibutoxyzirconium dichloride this band is shifted to long-wave region. From these data it might be assumed that both CO and OH-groups take part in coordination with metal. In spectrum of zirconium complex with CEP-PMA bands at 1100 cm^{-1} and 570 cm^{-1} characterizing C=O and Zr-O bonds are observed and bands characterizing Zr-Cl bonds are absent. On the base of these data the structure of zirconium complexes with CEP-PMA might be illustrated as follows:



Similarly, the structure of complexes of CEP-PMA with titanium can be represented.

After treatment of the complexes with OAC active gel-immobilized catalysts are formed. Catalytic activity of the obtained catalysts was studied in the reactions of dimerization of ethylene and propylene.

It is known that on dimerization of ethylene in the presence of homogeneous nickel complexes initially butene-1 is formed, its major part being isomerized into *cis*-butene-2. The latter, in turn, is isomerized into *trans*-butene-2 which is more stable compound in terms of thermodynamics.

Equilibrium mixture resulting from dimerization of ethylene in the presence of homogeneous nickel complexes has the following composition⁷⁾:

butene-1	3 % mass
<i>cis</i> -butene-2	27 % mass
<i>trans</i> -butene-2	70 % mass

Meanwhile, it is well known that butene-1 has more practical applications.

Dimerization of ethylene in the presence of homogeneous titanium and zirconium complexes proceeds with mass selectivity up to 98-98% with respect to butene-1 but one always observes at least 0,5 - 1% mass of polymer formation which creates problems when scaling up.

We carried out dimerization of ethylene in the presence of the obtained gel immobilized complexes of nickel, titanium and zirconium. The reaction was carried out in 0,5-litre thermostatted stainless steel reactor fitted with stirrer and manometer¹¹⁾. n-Heptane was used as a solvent. Temperature range was 293-353 K; pressure range 0,2-4 Mpa; molar ratio Al/Me varied in the range of 3 - 10.

The catalytic activity of the catalysts was evaluated according to decrease of pressure in the reactor. Gas-liquid chromatography method was used for analysis of the reaction products.

Results of dimerization of ethylene at different temperatures in the presence of CEP-PVP-Ni (ac.ac.)₂-DEAC are given in Fig. 1.

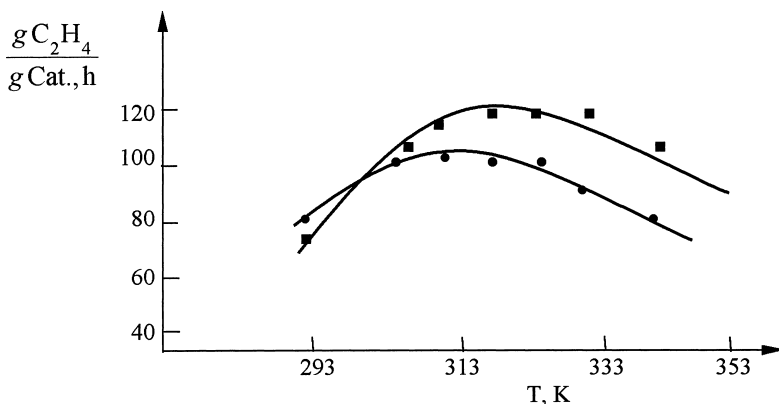


Fig. 1: Dimerization of ethylene at various temperatures: catalysts: CEP-PVP-Ni (ac.ac.)₂, ■ = EADC; ● = DEAC; pressure – 0,2 MPa; molar ratio Al/Ni – 10.

It is seen that optimum temperature range is within 313-333 K. It is known that homogeneous nickel complexes are not stable at temperatures higher than 293 K¹⁴). The process of dimerization is exothermic one and to prevent overheating at large scale complicated system of heat tapping is required. Gel immobilized nickel complexes remain active for a long time period at higher temperatures, up to 353 K.

In Fig.2 dependence of dimerization of ethylene in the presence of CEP-PVP-Ni (ac.ac.)₂ – DEAC on pressure is shown.

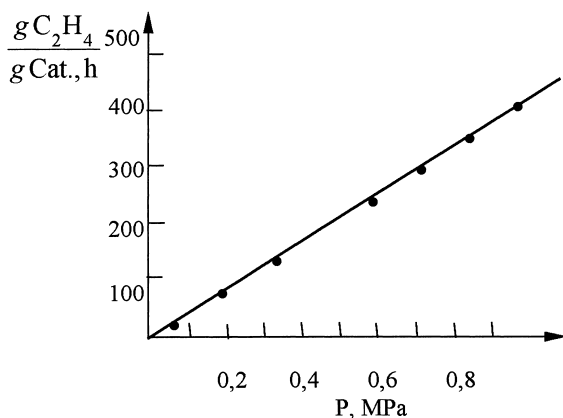


Fig.2: Dimerization of ethylene at different pressures: catalyst – CEP-PVP-Ni (ac.ac.)₂ – DEAC; temperature – 313 K; molar ratio Al/Ni = 10.

As we see from the Fig.2 the rate of dimerization increases linearly in the pressure range 0,1 - 1,0 MPa.

Results of dimerization of ethylene using the same catalysts at various molar ratios Al/Ni are presented in Fig.3.

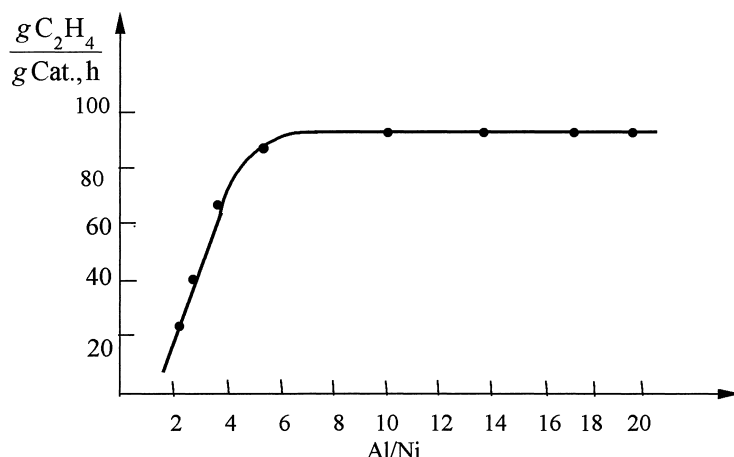


Fig. 3: Dimerization of ethylene at different molar ratios of Al/Ni: catalyst - CEP-PVP-Ni (ac.ac.)₂-DEAC; pressure – 0,2 MPa; temperature – 313 K.

As it could be seen from the Fig.3 maximum catalytic activity is achieved with molar ratio 10. Further increase of molar ratio does not lead to increase of catalytic activity. It is known that homogeneous nickel complexes might be usually used when molar ratio Al/Ni is 50 - 100.

Thus, it can be seen from above mentioned data that gel immobilized nickel complexes have significant advantages comparing to homogeneous nickel complexes, as they can be used at elevated temperatures and at much lower molar ratio Al/Ni.

The results of dimerization of ethylene in the presence of the obtained nickel, titanium and zirconium complexes with different macroligands and OAC are given in Table 1. Temperature in all the experiments was 313 K; pressure 0,2 MPa; molar ratio of OAC/Ni 10 and OAC/Ti or Zr was 4.

Table 1. Dimerization of ethylene in the presence of gel immobilized complex catalysts

Catalyst	Composition of the reaction products, % mass		
	Butene-1	<i>trans</i> -Butene-2	<i>cis</i> -Butene-2
CEP-PMAA-NiCl ₂ -SCEA	86,0	11,0	3,0
CEP-PVP-Ti (OC ₄ H ₉) ₂ Cl ₂ -TIBA	99,9	traces	traces
CEP-PMA-Ti (OC ₄ H ₉) ₂ Cl ₂ -TIBA	67,0	33,0	traces
CEP-PMAA-Ti (OC ₄ H ₉) ₂ Cl ₂ -TIBA	99,9	traces	traces
CEP-PVP-Zr (OC ₄ H ₉) ₂ Cl ₂ -TIBA	99,9	traces	traces
CEP-PMA-Zr (OC ₄ H ₉) ₂ Cl ₂ -TIBA	99,9	traces	traces
CEP-PMAA-Zr (OC ₄ H ₉) ₂ Cl ₂ -TIBA	99,9	traces	traces

It can be seen from the Table that when using gel immobilized complexes of titanium and zirconium we can achieve very high selectivity with respect to butene-1, up to 99.9 % mass practically without any formation of polymer. Besides, homogeneous complexes are not stable enough and lose their activity after a few hours, whereas gel immobilized complex catalysts remain active for hundred hours and more.

It can be also seen from the Table that nickel complexes with PMAA macroligands demonstrate 86% selectivity with respect to butene-1, whereas in case of homogeneous nickel complexes as it was already mentioned selectivity does not exceed 3 %.

We also studied dimerization of propylene in the presence of gel immobilized nickel complexes. It is known that on dimerization of propylene with homogeneous nickel complexes a mixture of dimers containing 4-methylpentene-1, 4-methylpentene-2, 2-methylpentene-2, 2,3-dimethylbutene-2, hexene and other compounds is formed, and the content of 4-methylpentene-1 does not exceed 8% mass¹⁴⁾. It is also known that 4-methylpentene-1 has more practical application as its polymer is widely used in electric power engineering, electronics, medicine etc.

The reaction was carried out using the same unit as with dimerization of ethylene. The conditions of the reaction were: pressure - 0,2 MPa; temperature - 313 K; molar ratio Al/Ni - 10. CEP-PMAA-NiCl₂•6H₂O-SCEA was used as a catalyst. Analysis of the reaction products has shown that there was 46.0% mass of 4-methylpentene-1; 41,0% mass of 4-methylpentene-2 and 13,0% mass of other isomers in the mixture.

Thus, using gel immobilized nickel complexes one can significantly increase the yield of 4-methylpentene-1 on dimerization of propylene.

Conclusion

Obtained results show that immobilization of metal complexes in polymer gels leads to an essential increase in activity, selectivity and stability of the prepared catalysts in the reactions of dimerization of lower olefins. The immobilization of the complexes opens new possibilities of macromolecular design of the catalysts with desired structural organization and will contribute to the development of general principles of synthesis of highly efficient, environmentally friendly catalytic systems for liquid phase processes.

Acknowledgement

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