

case of TMC-C than for the catalyst TMC-A. The PP obtained using catalyst TMC-C has a lower content of atactic fractions. This is probably due to the higher DBP/Ti ratio in TMC-C than in TMC-A after the treatment with AlEt_3 (Table 1, entries 4, 11).

Pretreatment of TMC-A and TMC-C catalysts with PTMS leads to a sharp activity decrease, by a factor of about 25 (Table 2, runs.1 and 2, 5 and 6). These data indicate that pretreatment of the catalyst with PTMS results in deactivation of active sites, probably by adsorption of PTMS to Ti ions. Our chemical analysis data show indeed that the high contents of PTMS and of total PTMS+DBP+Ti components can be explained only by an adsorption of PTMS on Ti centers of the catalyst (Table 1, runs.3, 10).

We carried out additional experiments, in which catalysts TMC-A and TMC-C were treated with PTMS directly in the reactor at 70°C for 1h, before starting the propylene polymerization (Table 2, entries 1 and 3, 5 and 7).

In this case, the activity of the catalysts was also found to be reduced, but to a lesser extent, while the fraction of atactic polypropene (APP) decreased approximately twice. This means that PTMS is absorbed mainly on non-stereospecific catalyst sites and deactivates them.

Further experiments were carried out with catalysts TMC-A and TMC-C under conditions typical for the stereospecific polymerization of propylene. In this case, a heptane solution of AlEt_3 and PTMS (molar ratio $\text{Al/Si} = 20$) was injected into the reactor before starting the polymerization (Table 2, entries 1 and 4, 5 and 8). The activity of both catalysts decreased slightly and the yield of atactic PP was greatly reduced in this case.

Thus, the conditions of interaction of an external donor (PTMS) with TMCs significantly affect the composition of these catalyst systems and their properties in propylene polymerization. The presence of the AlEt_3 cocatalyst in the reaction system is the most important factor controlling the interaction of a TMC with the external donor (PTMS). If the AlEt_3 cocatalyst is absent in the reaction system, the external donor PTMS partially replaces DBP on the surface of MgCl_2 and is mainly adsorbed on coordinatively unsaturated Ti ions; this leads to deactivation of active sites and,

hence, to a great decrease in activity. In the presence of AlEt_3 , however, reaction between AlEt_3 and an ID such as DBP results in freeing LAS on the surface of MgCl_2 . As a consequence, the external donor PTMS is mainly adsorbed onto free acidic sites of MgCl_2 and on coordinatively unsaturated Ti ions, predominantly on non-stereospecific active sites, thus resulting in some decrease of activity and in a marked increase in stereospecificity.

So polymerization data show:

- The activity of both catalysts was found to decrease sharply (5-6 fold) after a pretreatment with PTMS. Probably, PTMS is firmly adsorbed on the titanium ions, leading to a sharp decrease in the activity;
- When treated only with the cocatalyst AlEt_3 , the catalysts showed high activity and low stereospecificity. Reduced stereospecificity is in this case related to the removal of DBP from the catalysts;
- Their activity decreases only slightly if polymerization proceeds with a mixture $\text{AlEt}_3/\text{PTMS}$, but in this case the amount of atactic PP decreases;
- The differences in activity and stereospecificity of the TMC-A and TMC-C catalysts are probably due to different ratios of the individual components (Ti, DBP, PTMS, Al) in the initial state of these catalysts and after the reaction with a mixture of $\text{AlEt}_3/\text{PTMS}$.

CONCLUSION

Three types of TMC were used in this study. Catalysts TMC-A and TMC-B were prepared using an MgCl_2 carrier obtained by reacting Mg with BuCl in heptane in the absence of electron donor compounds, and consecutive treatment of this MgCl_2 carrier with DBP and TiCl_4 and with $(\text{DBP}\cdot\text{TiCl}_4)$ complex, respectively. Catalyst TMC-C was synthesized by reacting TiCl_4 and DBP with $\text{Mg}(\text{OEt})_2$ in chlorobenzene. The interaction of TMCs prepared by different procedures with the external donor PTMS, AlEt_3 and a mixture of $\text{PTMS}/\text{AlEt}_3$ was studied by chemical analysis and infrared diffuse reflectance spectroscopy (DRIFTS).

It was found the amount of DBP and TiCl_4 removed from the catalysts after a treatment with PTMS or a mixture $\text{PTMS}/\text{AlEt}_3$ depended on: (i) a method of the catalyst preparation; (ii) a chemical composition and

textural parameters of the initial TMC; (iii) a presence of AlEt_3 at the interaction of TMC with an external donor.

DRIFTS and chemical composition data showed that PTMS could substitute both TiCl_4 and DBP. DRIFTS data evidenced also selective substitution of DBP by PTMS. One type of adsorbed DBP remained mainly after treatment of TMC with PTMS/ AlEt_3 mixture.

The presence of AlEt_3 in the PTMS/ AlEt_3 mixture played a key role on the chemical composition of the catalysts (content and DBP/ TiCl_4 ratio). The treatment of the catalysts with PTMS alone before polymerization led to a sharp decrease of activity due to its adsorption on titanium species, while the interaction of the catalysts with the PTMS/ AlEt_3 mixture led only to a slight decrease of activity, probably due to a deactivation of non-stereospecific active species.

ACKNOWLEDGEMENT:

We thank Prof. Brintzinger (Universität Konstanz) for helpful discussions. The work was partially supported by the Ministry of Education and Science of Russian Federation and Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V 44.2).

REFERENCES

1. Soga K, Shiono T, Doi Y (1988) Influence of internal and external donors on activity and stereospecificity of Ziegler-Natta catalysts. *Makromol Chem* 189: 1531-1541
2. Yang CB, Hsu CC, Park YS, Shurvell HF (1994) Infrared characterization of MgCl_2 supported Ziegler-Natta catalysts with monoester and diester as a modifier. *Eur Polym J* 30(2): 205-214
3. Arzoumanidis GG, Karayannis NW (1991) Infrared spectral characterization of supported propene polymerization catalysts. A link to catalyst performance. *Appl Catal* 76: 221-231
4. Panchenko VN, Goryachev AN, Vorontsova LV, Paukshtis EA, Zakharov VA (2014) Basicity of stereoregulating electron-donor compounds in Ziegler-Natta catalysts: A study by infrared spectroscopy and chemical exchange reactions. *J Phys Chem C* 118: 28572–28579
5. Potapov AG, Bukatov GD, Zakharov VA (2009) DRIFTS study of the interaction of the AlEt_3 cocatalyst with the internal donor ethyl benzoate in supported Ziegler-Natta catalysts. *J Mol Catal A-Chem* 301: 18–23
6. Makwana U, Naik DG, Singh G, Patel V, Patil HR, Gupta VK (2009) Nature of phthalates as internal donors in high performance MgCl_2 supported titanium catalysts. *Catal Lett* 131: 624–631
7. Shen X-R, Fu Z-S, Hu J, Wang Q, Fan Z-Q (2013) Mechanism of propylene polymerization with MgCl_2 -supported Ziegler-Natta catalysts based on counting of active centers: The role of external electron donor. *J Phys Chem C* 117: 15174–15182
8. Terano M, Kataoka T, Keii T (1990) Analytical and kinetic approaches for the basic type of MgCl_2 -supported high yield catalysts. *J Polym Sci Pol Chem* 28: 2035-2048
9. Cheruvathur AV, Langner EHG, Niemantsverdriet JWH, Thüne PC (2012) In situ ATR-FTIR studies on MgCl_2 -diisobutyl phthalate interactions in thin film Ziegler-Natta catalysts. *Langmuir* 28: 2643-2651
10. Chadwick JC (2001) advances in propene polymerization using MgCl_2 -supported catalysts. Fundamental aspects and the role of electron donors. *Macromol Symp* 173: 21–35
11. Credendino R, Liguori D, Morini G, Cavallo L (2014) Investigating phthalate and 1,3-diether coverage and dynamics on the (104) and (110) surfaces of MgCl_2 supported Ziegler-Natta catalysts. *J Phys Chem C* 118: 8050-8058
12. Stukalov DV, Zilberberg IL, Zakharov VA (2009) Surface species of titanium(IV) and titanium(III) in MgCl_2 -supported Ziegler-Natta catalysts. A periodic density functional theory study. *Macromolecules* 42: 8165–8171
13. Stukalov DV, Zakharov VA, Potapov AG, Bukatov GD (2009) Supported Ziegler-Natta catalysts for propylene polymerization. Study of surface species formed at interaction of electron donors and TiCl_4 with activated MgCl_2 . *J Catal*

- 266: 39-49
14. Bazhenov AS, Denifl P, Leinonen T, Pakkanen A, Linnolahti M, Pakkanen TA (2014) Modeling coadsorption of titanium tetrachloride and bidentate electron donors on magnesium dichloride support surfaces. *J Phys Chem C* 118: 27878-27883
 15. Busico V, Causa M, Cipullo R, Credendino R, Cutillo F, Friederichs N, Lamanna R, Segre A, Van Axel Castelli V (2008) Periodic DFT and high-resolution magic-angle-spinning (HR-MAS) ¹H NMR investigation of the active surfaces of MgCl₂-supported Ziegler-Natta catalysts. The MgCl₂ matrix. *J Phys Chem C* 112(4): 1081-1089
 16. Liu B, Nitta T, Nakatani H, Terano M (2004) Precise arguments on the distribution of stereospecific active sites on MgCl₂-supported Ziegler-Natta catalysts. *Macromol Symp* 213: 7-18
 17. Noristi L, Barbe' PC, Baruzzi G (1991) Effect of the internal-external donor pair in high-yield catalysts for propylene polymerization. 1. Catalyst-cocatalyst interactions. *Makromol Chem* 192: 1115-1127
 18. Seppälä JK, Harkonen M, Luciani L (1989) Effect of the structure of external alkoxy silane donors on the polymerization of propene with high activity Ziegler-Natta catalysts. *Makromol Chem* 190: 2535-2550
 19. Proto A, Oliva L, Pellicchia C, Sivak AJ, Cullo LA (1990) Isotactic-specific polymerization of propene with supported catalysts in the presence of different modifiers. *Macromolecules* 23: 2904-2907
 20. Pakkanen TT, Vahasarja E, Pakkanen TA, Iiskola E (1990) Modification of olefin polymerization catalysts. III. A ¹³C CP-MAS NMR study of adsorption of silyl ethers on MgCl₂-supported Ziegler-Natta catalysts. *J Catal* 121: 248-261
 21. Chumachenko NN, Zakharov VA, Bukatov GD, Sergeev SA (2014) A study of the formation process of titanium-magnesium catalyst for propylene polymerization. *Appl Catal A-Gen* 469: 512- 516
 22. Makhtarulin SI, Moroz EM, Vermel EE, Zakharov VA (1978) Influence of the substructure of supported titanium-magnesium catalysts on their activity in olefin polymerization. *React Kinet Catal Lett* 9(3): 269-274
 23. Boero M, Parrinello M, Weiss H, Hulffer S (2001) A first principles exploration of a variety of active surfaces and catalytic sites in Ziegler-Natta heterogeneous catalysis. *J Phys Chem A* 105: 5096-5105
 24. Chumachenko NN, Bukatov GD, Sergeev SA, Zakharov VA (2011) State of titanium in supported titanium-magnesium catalysts for propylene polymerization. *Kinet Catal+* 52: 234-241
 25. Potapov AG, Terskikh VV, Bukatov GD, Zakharov VA (2000) ²⁷Al MAS NMR study of the interaction of supported Ziegler-Natta catalysts with organoaluminium co-catalyst in the presence of donors. *J Mol Catal A-Chem* 158: 457-460
 26. Sacchi MC, Forlini F, Tritto I, Locatelli P (1996) Polymerization stereochemistry with Ziegler-Natta catalysts containing dialkylpropane diethers: A tool for understanding internal/external donor relationships. *Macromolecules* 29: 3341-3345.
 27. Sacchi MC, Tritto I, Shan C, Mendichi R, Noristi L (1991) Role of the pair of internal and external donors in MgCl₂-supported Ziegler-Natta catalysts. *Macromolecules* 24: 6823-6826
 28. Noristi L, Barbe PC, Baruzzi G (1991) Effect of the internal/external donor pair in high-yield catalysts for propylene polymerization, catalyst-cocatalyst interactions. *Makromol Chem* 192: 1115-1127
 29. Capone F, Rongo L, D'Amore M, Budzelaar PHM, Busico V (2013) Periodic hybrid DFT approach (including dispersion) to MgCl₂ supported Ziegler-Natta catalysts. 2. Model electron donor adsorption on MgCl₂ crystal surface. *J Phys Chem C* 117: 24345-24353