Applied Organometallic Chemistry (1990) 4 1–7

0268-2605/90/010001-07/$05.00

REVIEW

Soluble metal–polymer catalysts in the hydrogenation of organic compounds

E A Karakhanov, E B Neimerovets and A G Dedov
Chemistry Department, Moscow State University, 119899, GSP-3, Moscow, USSR

Received 6 August 1989 *Accepted 28 October 1989*

Literature describing the use of soluble metal–polymer catalysts in the molecular hydrogenation of alkenes, alkynes, aromatic and heterocyclic compounds has been reviewed. Special attention has been paid to coordinated metallic and organometallic catalytic systems and highly dispersed colloidal metals stabilized with polymers. The influence of metals, polymers and solvents on the structures of active sites is discussed. The prospects for the application of soluble metal–polymer catalysts in organic synthesis are also considered.

Keywords: Soluble metal–polymer catalysts, hydrogenation, metal complexes, highly dispersed metals

Polymers containing catalysts have been attracting attention for more than two decades, and this is shown in numerous publications, amongst which are many review articles,[1-9] in which different aspects of synthesis of heterogeneous metal–polymer catalysts and their employment in various reactions, involving hydrogenation, are discussed.

The main advantage of such catalytic systems is easy separation from the products of reaction and the possibility of using them repeatedly. At the same time they usually have an important drawback, namely a low catalytic activity as compared with homogeneous low-molecular-weight analogues in the majority of cases.

As a result, growing interest has been shown to work the creation and study of catalytic systems with soluble polymers[10]. Many publications are devoted to the use of (i) organometallic compounds in which one or more ligands are substituted by their macromolecular analogues, and (ii) colloidal metals, which are stabilized by the coordination of soluble polymers with different functional groups.

It is rather difficult to obtain relable data for the structure of active sites, the number of metal atoms, and the mechanism of their action. Consequently, in many cases it cannot be decided whether a metal complex or fine metal particles are active in the reaction.

Homogeneous metal–polymer catalysts are more active and have minimal diffusional limitations. At the same time, their separation from the reaction mixture is possible using a number of reliable, simple procedures, such as the addition of a precipitator, a change of pH or temperature, or filtration through different membranes.

Quite a number of examples of synthesis and employment of soluble metal–polymer catalysts in hydrogenation have been described. Soluble polystyrene, poly(ethylene glycol), poly(vinylpyrrolidone) and poly(vinyl chloride) have been used by one group[11] to obtain metal complexes with macroligands.

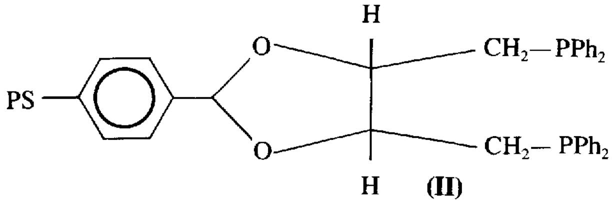
Polystyrene has been chloromethylated and treated with potassium diphenyl phosphide. Soluble polydiphenyl(styrylmethyl)phosphine was obtained which contained different amounts of chloride and phosphino groups (Scheme 1).

$$\mathrm{PS{-}CH_2Cl + KPPh_2 \rightarrow \underset{\textbf{I}}{PS{-}CH_2PPh_2} + KCl}$$

Ia 2.59% Cl, 0.45% P
Ib 0.05% Cl, 2.42% P
Ic 1.90% P

Scheme 1

Different complexes of platinum, palladium and rhodium, e.g. (**Ib**)$Rh(CO)_2Cl$, (**Ia**)$PdCl_2$, (**Ib**)$PdCl_2$, (**Ic**)Rh(CO)acac, were then obtained by ligand exchange or substitution. These complexes are highly active for hydrogenation and hydroformylation of pentene, the substrate:catalyst ratio being up to 200.



Scheme 2

The separation of catalyst from the products of the reaction was carried out by filtration through a polyamide membrane. The catalysts did not lose their activity when used six times repeatedly.

The use of linear polystyrene (PS) for the preparation of a catalyst for asymmetric hydrogenation with chiral diphosphine ligand (**II**), was described[12] (Scheme 2).

These homogeneous catalysts prepared from $[RhCl(C_2H_4)]_2$ and (**II**) *in situ* exhibit a smaller enantioselectivity, despite their higher activity for the hydrogenation of itaconic acid ($HOOCC(=CH_2)CH_2COOH$), than the analogous heterogeneous catalyst. The optical homogeneous yield of the main product R-($-\alpha$-methylsuccinic acid is 30.9%. For a heterogeneous catalysis the optical yield reaches 37.5% and for the catalyst which does not contain a macroligand it is 48.3%. In the authors' view[12], flexible polymer molecules lowered the catalytic activity by screening active sites.

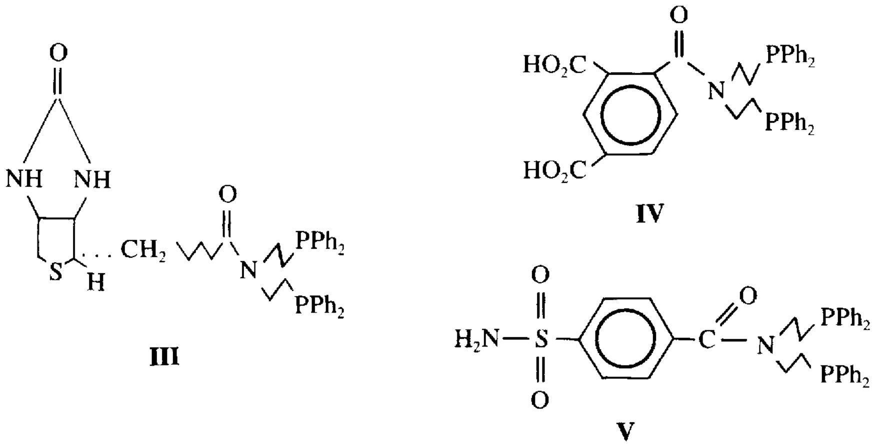
Another example of homogeneous asymmetric hydrogenations of amino acid precursors has been reported[13] in which a cationic rhodium catalyst was ligated by *N,N*-bis(2-diphenylphosphinoethyl)biotinamide (**III**) which had been irreversibly complexed to the protein avidin (Scheme 3). The best reported examples had turnover numbers in excess of 500. In this case the products of the reaction were separated from the catalyst by ultrafiltration.

The catalytic systems prepared using **IV**, **V** and avidin, carbonic anhydrase, α-chymotrypsin and serum albumin, similar to **III** in the reaction mentioned above, did not exhibit enantioselectivity[14]. The structure of the catalysts has not been discussed.

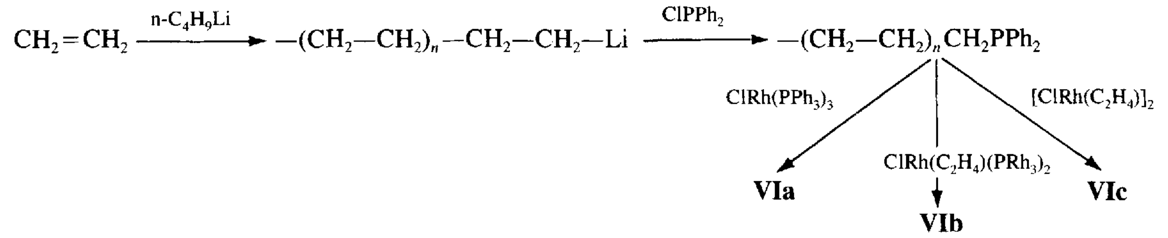
Ethylene oligomers can be used as macroligands. It was found that ethylene oligomers are easily soluble in hydrocarbon solvents at higher temperatures and are quantitatively precipitated when cooled or when a second solvent such as methanol is added. On this basis a number of catalysts have been synthesized for polymerization of dienes and their cyclodimerization using neodymium and nickel,[15–17] for hydrogenation of hydrocarbons.[18]

A homogeneous, easily recovered catalyst for hydrogenation was prepared by using phosphinated oligomers of polyethylene according to Schemes 4,[18] where **VI** is $[(-CH_2-CH_2)_n-CH_2CH_2(PPh_2)]_3RhCl$ and **VIa**, **VIb** and **VIc** are catalyst variants.

The activity of the catalysts prepared from various



Scheme 3



Scheme 4

complexes differed insignificantly. The catalysts were investigated by ^{31}P NMR in solution and in the solid state. It has been shown that none of them contained low-molecular-weight triphenylphospine (PPh_3), and the structure of the catalyst and its activity practically did not differ even after ten cycles of the reaction. The activity of such catalytic systems for the hydrogenation of olefins at atmospheric pressure of hydrogen reaches up to 80% of the activity of homogeneous $RhCl(PPh_3)_3$, which itself is ten times more active than a catalyst prepared by the immobilization of the $RhCl(PPh_3)_3$ complex on polystyrene cross-linked by divinylbenzene. The activity of such heterogeneous catalytic systems does not change after 18 cycles.

The homogeneity of the catalyst is proved by Crabtree's tests, in particular by the hydrogenation of dibenzocyclo-octatetraene and the 'triphase' test.[18]

Another approach to the synthesis of soluble metal–polymer catalysts was suggest in Ref. 19. Analogous to the low-molecular-weight acetate $Rh_2(CH_3COO)_4 \cdot 2H_2O$ they prepared a rhodium polyacrylic acid (PAA) complex with the metal:monomer unit ratio being metal:PAA = 1:400 to 1:200. The PAA–Rh—H complex was 120 times more active for the hydrogenation rhodium of olefins than its low-molecular-weight analogue under the same conditions.

The introduction of the macroligand into the complex was reported to change its selectivity in substantially in respect to substrates. Thus, the rhodium(II) acetate compound above, which is active in hydrogenation of alkenes, does not exhibit activity for the hydrogenation of internal *trans*-alkenes, e.g. *trans*-hex-2-ene, and dienes, e.g. hexa-1,5-diene. On the contrary, the polymer catalyst is active for the hydrogenation of such alkene types and dienes, but does not hydrogenate triple bonds.

The structure of the above polymer catalyst has been studied by IR spectroscopy. Its spectrum practically coincides with the spectrum of rhodium(II) acetate monomer and it does not change during the reaction. However, it should be noted that such data do not give us a clear distinction between the structures of the monomeric polymeric complexes.

The use of polymers for the stabilization of colloidal dispersions of metals is an effective way to create catalysts which exhibit high activity and selectivity. Corresponding salts of these metals may be reduced in the presence of polymers, with fine metal particles of practically the same size being formed. The size range of such metal particles does not exceed 50Å (5 nm), and their size can be controlled by changing the conditions of the preparation. There is scarcely any interaction between the metal particles themselves because they are quite closely connected with macromolecules which cover practically the whole surface of the metallic aggregates. Besides, such catalytic systems containing polynuclear metallic aggregates could be expected to exhibit high catalytic activity and stability (as compared with metal complexes), especially for hydrogenation of aromatic hydrocarbons and heterocycles. This makes it possible to use them widely in organic synthesis.

Synthetic polymers have been used for the stabilization of colloidal dispersions of platinum, palladium and rhodium since the 1940s.[20–22] The colloids, obtained by reduction with molecular hydrogen in an alkali medium, are active catalysts for hydrogenation of organic compounds, e.g. olefins, dienes, arenes, heterocycles and nitro- and cyano-groups.

A change of conditions of preparation for catalysts — i.e. alkaline alcohol rather than reduction by molecular hydrogen — leads to the preparation of catalysts with smaller metal particles.[23–30] Poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP) and poly(methyl vinyl ether) (PMVE) are effective stabilizing agents. At the same time the employment of poly(ethylene glycol) (PEG) or poly(ethyleneimine) (PEI) for this purpose is not effective. The use of PEI along with poly(acrylic acid) for the synthesis of a palladium-containing catalytic system exhibiting high selectivity and low activity for hydrogenation of dienes

$$\mathrm{RhCl_3} \xrightarrow{\mathrm{PVA}} \mathrm{Rh(III)\text{–}PVA} \xrightarrow{\text{methanol}} \text{small particles (8 Å)} \longrightarrow \text{large particles (40 Å)}$$

Scheme 5

has been discussed.[23] These authors explain the properties of the catalyst by substrate transport limitations through a double layer of polymer to the active sites.

Analogously, catalytic systems based on palladium, rhodium, platinum, iridium and osmium with poly (vinyl alcohol) (PVA) were obtained, the average diameter of metal particles being 53, 40, 27, 14 and less and 10 Å, respectively.

For PVA and rhodium(III) the course of formation of the catalyst has been discussed (Scheme 5).[24,27]

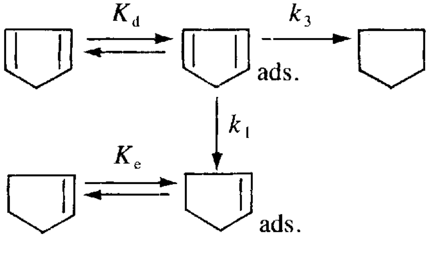
Rhodium(III) chloride is transformed into a large rhodium particle via the rhodium(III)–PVA complex and a small particle (8 Å), containing up to 20 atoms of rhodium. With the reduction of rhodium(III) chloride to rhodium(0), methanol is oxidized to formaldehyde.

According to the authors,[23–30] the synthetic polymer in colloidal dispersion suppresses the reduction rate of the metal ion due to coordination with the functional groups of the polymer and, on the other hand, prevents the small particles of metal from aggregating. They may act as a protective colloid in the manner where the hydrophobic parts of the main carbon chain interact with the suface of the metallic particles and the hydrophillic groups, directed outwards, make the colloidal metal particles hydrophillic.

The stabilizing ability of poly(vinylpyrrolidone) (PVP) is ascribed to the coordination of a number of carbonyl groups of a macromolecule with palladium atoms on the surface of the metal particles. Depending on the method of preparation, the size of the particles varies from 9 to 18 Å when methanol is used for reduction, up to 140 Å when *n*-butanol is used.[25]

These catalytic systems are effective for hydrogenation of olefins and dienes, and palladium–PVP hydrogenates cyclopentadiene to cyclopentene with high selectivity (the selectivity is more than 90% at practically complete conversion).

In the authors' view, the role of the polymer is not only in the stabilization of fine metal particles, but in increasing the selectivity of hydrogenation by weakening the adsorption of the formed olefin on the surface.



Scheme 6

The reaction mechanism can be presented as shown in Scheme 6.

The ratio of the initial hydrogenation rate of cyclopentadiene to (i) cyclopentane (k_3) and (ii) cyclopentene (k_1) in the presence of palladium–PVP–MeOH/NaOH is estimated to be 0.001:1; the ratio of the adsorption equilbrium constant K_d to K_e is 2000:1. For palladium on carbon (Pd/C) (5%) these figures are 0.03:1 and 20:1 respectively.

The valence state of the metal was concluded only from the spectrophotometric data.

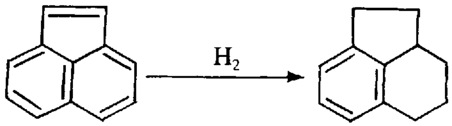
An effective method of synthesis of a highly active catalyst for the hydrogenation of olefins was proposed by Hirai and his group.[31] Colloidal rhodium particles, protected by a copolymer of methyl acrylate (MA) and *N*-vinyl-2-pyrrolidone, is treated with polyacrylamide (PAA) gel resulting in immobilization of the rhodium particles in the gel, due to the interaction of ether groups of the soluble copolymer at pH 4–9. The character of the metal particles according to their size, their diameter and high activity remains unchanged on incorporation into the polymer.

The employment of polyethyleneimine (PEI) for the synthesis of soluble hydrogenation catalysts is described by Frolov *et al.*[32,33] Water-soluble complexes of rhodium, nickel, and palladium treated by sodium tetrahydroborate ($NaBH_4$) hydrogenate alkenes and dienes to the corresponding olefins selectively. The catalytic systems, containing 50 or more monomer units of PEI per single atom of metal, remained homogeneous during the hydrogenation. The yield of the corresponding olefin in the hydrogenation of cyclopentadiene is 99%, the conversion of substrate is 36% and the substrate:metal molecular ratio is nearly

12000:1 with the PEI–palladium catalyst. The high selectivity of the catalysts for monoene formation is discussed in terms of the selective adsorption of the diene on the catalytic site, similar to palladium–polyvinylpyrrolidone.[25] The structure of the above-mentioned polymer catalysts has not been studied.

The formation of nitrogen–metal bonds has only been observed for catalysts with a greater content of metal (about two monomer units for a single atom of metal). These links remain after the reduction with molecular hydrogen and $NaBH_4$.[35–38] Such catalysts are slightly soluble, but like homogeneous ones they exhibit high activity and selectivity in the hydrogenation of dienes and polyenes to olefins in mild conditions: the selectivity of cyclodiene formation in the hydrogenation of cyclo-octa-1,3-diene is 100% with complete substrate conversion. In this case the palladium catalysts exhibit the highest selectivity. It should also be noted that the polyethyleneimine-based heterogeneous systems catalysed disproportionation of cyclohexa-1,3-diene to benzene and cyclohexene.[37,38]

The catalytic systems produced on the basis of rhodium chloride and polyethyleneimine (PEI) reduced by vanadium(II) in acid medium was investigated by extended X-ray absorption fine structure EXAFS, X-ray photoelectron spectroscopy XPS and X-ray emission spectroscopy XES methods.[38] The metal is anchored on macromolecules as charged clusters stabilized by atoms of nitrogen and chloride ions, the main mass of rhodium being present in the oxidized form rhodium(III) and rhodium (I).



Scheme 7

Active samples of the catalysts of hydrogenation of acenaphthalene (Scheme 7) were prepared by precipitation of the metallic vapours in hydrocarbon solutions of polymers.[39] The metal particles of size about 20–50 Å were stabilized by adsorption on the surface of the polymer.

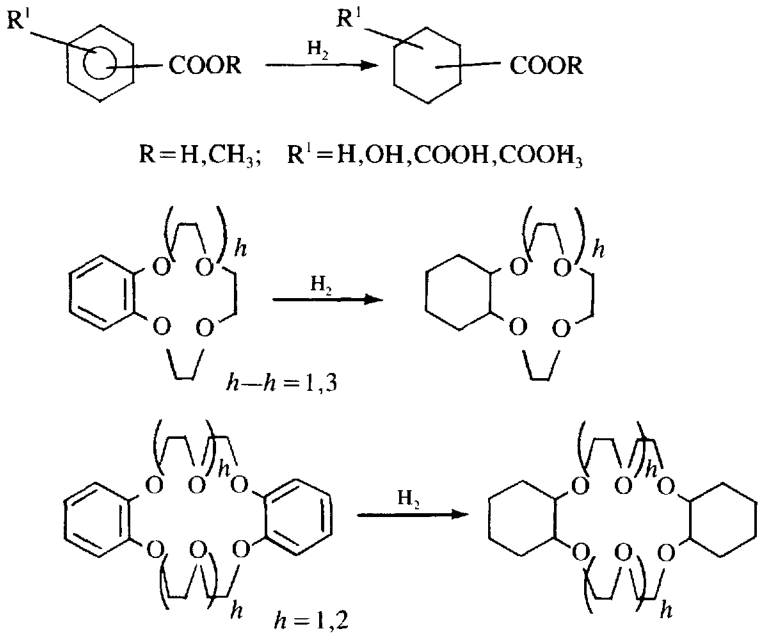
As catalysts the authors used systems containing soluble carboxyl functional group polymers and copolymers — PAA, PMAA, copolymers of maleic acid and styrene or methyl methacrylate — and salts of transition metals, e.g. $RhCl_3$, K_2PdCl_4 and K_2PtCl_4, all of which are reduced by $NaBH_4$ in an aqueous-alcohol medium. The polymer:metal ratio was one atom of metal per 5–20 monomer units.

The synthesized catalysts exhibited activity in the hydrogenation of different aromatic and heterocyclic compounds as atmospheric pressure of hydrogen (Table 1)[40–51] and at temperatures between 20–60°C. These metal–polymer catalysts were used for synthesis of saturated carbocyclic and heterocyclic compounds.

Table 1 The hydrogenation of organic compounds in the presence of the catalysts based on soluble carboxyl-containing polymers[40–46]

Substrate	Catalyst[a]	T(°C)	T_N[b] (h^{-1})	Reaction products (yield, %)
Hex-1-ene	PAA–Rh	25	289	Hexane (100)
Cyclohexene	MA–MMA–Rh	20	200	Cyclohexane (100)
Cyclo-octa-1,5-diene	ST–MA–Rh	30	179	Cyclo-octane (100)
Benzene	PAA–Rh	30	85	Cyclohexane (100)
Phenol	ST–MA–Rh	50	34	Cyclohexanol (100)
Furan	ST–MA–Rh	40	52	Tetrahydrofuran (100)
2-Methylfuran	ST–MA–Rh	30	117	2-Methyltetrahydrofuran (100)
Benzofuran	ST–MA–Pd	30	53	2,3-Dihydrobenzofuran (100)
1,7-Dioxy-4,7,8,9-tetrahydroindane	PAA–Pd	30	14	1,7-dioxyhexahydroindane (100)
1,4-Benzodioxan	PAA–Rh	30	7	Hexahydro-1,4,benzodioxan (32)
Furfural	ST–MA–Rh	25	262	Tetrahydrofuryl alcohol (98)
Furyl alcohol	MA–MMA–Rh	25	230	Tetrahydrofuryl alcohol (100)
Pyridine	PAA–Rh	40	38	Piperidine (100)
Pyrrole	PAA–Rh	35	263	Pyrrolidine (100)
N-Methylpyrrole	PAA–Rh	35	412	*N*-Methylpyrrolidine (100)

[a] Abbreviations: PAA, poly(acrylic acid); MA-MAA, copolymer of maleic acid and methylmethacrylate; ST-MA, copolymer of styrene and maleic acid; PMAA, poly(methacrylic acid). [b] T_n — turnover number.



Scheme 8

For example, the hydrogenation of aromatic acids and benzo-crown ethers gave the corresponding cyclohexano derivatives with high yield in mild conditions (Scheme 8).[42–45]

The kinetics were studied and the optimal conditions for the reactions with a number of substrates — pyridine, benzaldehyde, pyrrole and others — have been determined. The hydrogenation of such compounds as furfural, pyridine and benzaldehyde has been shown to be complicated by substrate inhibition, and in the case of pyrroles also by the reaction products.[50] At the same time, in the cases of phenol and benzoic acid, similar phenomena have not been detected.[43,44]

The structure of the metal–polymer catalysts has been studied for PAA–rhodium by XPS. UV spectroscopy, and electron microscopy. According to electron microscopy data, the size of the metal particle in the catalyst does not exceed 15 to 20 Å. XPS spectra show that the oxidation states of rhodium in the catalyst are (III) and (0) (with ratio 2:3) which does not vary during the reaction. Ultrafiltration showed that only 1–2% of the metal was not anchored to the polymer. Data from IR spectroscopy and potentiometric titration results have shown that the stabilization of metal in a fine, dispersed, state is due to interaction with the carboxyl groups of the polyacid. The macromolecules prevent complete reduction to Rh(0). Light scattering data testify to this intermolecular interaction. The average size of globules of PAA is 650 Å, while the size of the catalyst particles reaches 2400 Å.

Thus, the presented material has brought us to the conclusion that the employment of polymers for the stabilization of colloidal metals leads to the creation of catalytic systems with unique properties: on the one hand, high activity and selectivity for hydrogenation of various organic compounds in mild conditions; on the other, the stability and simplicity of the preparation. Moreover, the structure of the polymer used and the method of preparation influence the stability of the catalyst, as well as its selectivity in respect to different substrates.

REFERENCES

1. Chauvin, J, Commereuc, D and Dawans F *Progr. Polym. Sci.*, 1977, 5: 95
2. Hartley, F R and Vezey, P N *Adv. Organomet. Chem.*, 1977, 15: 189
3. Pittman, C U., Jr Catalysis by polymer-supported transition metal complexes. In: Hodge, P and Sherrington, D C (eds), *Polymer Supported Reactions in Organic Synthesis*, Wiley, New York, 1980, p 249

4. Holy, N L Polymer-bound phosphine catalysts. In: *Homogeneous Catalysis of Metal Phosphine Complexes*, Plenum, New York, 1984, p 443
5. Carlini, C and Sbrana, G Catalysis by transition metal derivatives bound to structurally ordered polymers. In: *Advances in Organometallic and Inorganic Polymer Science*, C T Carraher, Jr, Sheets, J E and Pittman, C U, Jr (eds), Wiley, New York, 1982, p 323
6. Ciardelli, F, Braca, G, Carlini, C, Sbrana, G and Valentini, G *J. Mol. Catal.*, 1984, 14: 1
7. Hartley, F R *Supported Metal Complexes. A New Generation of Catalysts*, Riedel Publishing Co., Cordrecht, 1985, p 318
8. Ford, W T Polymeric reagents and catalysts. An overview. (eds), American Chemical Society, ACS Symp. Ser. No. 308, (Polym. Reag. Catal.), Washington DC, 1986, 308: 1
9. Erkerdt, J G The role of substrate transport in catalyst activity *ibid.*, p 68
10. Bergbreiter, D E Soluble polymer-bound reagents and catalysts, American Chemical Society, *ibid.*, p 17
11. Bayer, E and Schuring, V *Angew. Chem., Int. Ed. Engl.*, 1975, 14: 493
12. Ohkudo, K, Fujimoro, K and Yoshinada, K *Inorg. Nucl. Chem. Lett.*, 1979, 15: 231
13. Wilson, M E and Whitesides, G M *J. Am. Chem. Soc.*, 1978, 100: 306
14. Nuzzo, R G, Haynie, S L, Wilson, M E and Whitesides, G M *J. Org. Chem.*, 1981, 46: 2861
15. Bergbreiter, D E and Chandran, R *J. Chem. Soc., Chem. Commun.*, 1985, 1396
16. Bergbreiter, D E, Chen, Z and Chandran, R *Macromolecules*, 1985, 18: 1055
17. Bergbreiter, D E and Chandran, R *J. Am. Chem. Soc.*, 1985, 107: 4792
18. Bergbreiter, D E and Chandran, R *J. Am. Chem. Soc.*, 1987, 109: 174
19. Hirai, H and Nakamura, Y *Chem. Lett.*, 1974, 645
20. Hernandes, L and Nord, F F *J. Colloid Sci.*, 1948, 3: 363
21. Rampino, L D and Nord, F F *J. Am. Chem. Soc.*, 1941, 63: 2745
22. Rampino, L D, Nord, F F and Kavanagh, K E *Proc. Natl. Acad. Sci. USA*, 1943, 29: 246
23. Hirai, H *J. Macromol. Sci.-Chem.*, 1979, A13(5): 633
24. Hirai, H., Nakao, Y and Toshima, N *J. Macromol. Sci.-Chem.*, 1978, A12(8): 1117
25. Hirai, H, Chawanya, H and Toshima, N *React. Polym., Ion Exch., Sorbents*, 1985, 3(2): 127
26. Hirai, H, Nakao, Y and Toshima, N *J. Macromol, Sci.-Chem.*, 1979, A13(6): 727
27. Hirai, H, Nakao Y and Toshima, N *Chem. Lett.* 1978, 545
28. Hirai, H, Chawanya, N and Toshima, N *Macromol. Chem., Rapid Commun.*, 1981, 2: 99
29. Nakao, Y and Kaeriyama, H *Sen'i Kobunshi Zairyo Kenkyusho*, 1984, 39; *Chem. Abstr.* 102: 220390s
30. Hirai, H, Chawanya, N and Komiyama, M *Chem. Lett.*, 1986, 269
31. Hirai, H and Ohtaki, M *Chem. Lett.*, 1987, 149
32. Frolov, V M, Parenago, O P and Shuikina, L P *Kinet. Katal.*, 1978, 19(6): 1608
33. Shuikina, L P, Alnatanova, L I, Kovaleva, L S, Parenago, O P and Frolov, V M *Kinet. Katal.*, 1981, 22(1): 177
34. Abubakirov, R S, Sytov, G A, Perchenko, V N, Omaraliev, T O and Nametkin, N S *Dokl. Akad. Nauk SSSR*, 1983, 272(6): 1379
35. Perchenko, V N, Mirskova, I S and Nametkin, N S *Neftekhimiya*, 1980, 20(4): 518
36. Abubakirov, R S, Sytov, G A, Perchenko, V N, Omaraliev, T O and Nametkin, N S *Dokl. Akad. Nauk SSSR*, 1983, 272(1): 113
37. Perchenko, V N, Sytov, G A, Abubakirov, R S, Omaraliev, T O and Nametkin, N S *Dokl. Akad. Nauk SSSR*, 1985, 282(1): 109
38. Savinova, E R, Kochubei, D I, Kozlov, M A, Chernov, V A, Bogdanov, S V, Moroz, E M, Zaikovskii, V I, Shepelin, A P and Parmon, V N, *J. Mol. Catal.*, 1985, 32: 145
39. Bradley, J S, Hill E, Leonowicz, M L and Witzke, H *J. Mol. Catal.*, 1987, 41: 59
40. Karakhanov, E A, Dedov, A G, Loktev, A S, Pshegetski, V S and Lebedeva, T S *Dokl. Akad. Nauk SSSR*, 1984, 275(5): 1098
41. Karakhanov, E A, Dedov, A G, Loktev, A S, Pshegetski, V S and Stepanova, I P *Khim. Geterotsikl. Soedin*, 1984, 1032
42. Neimerovets, E B, Tshay, L E, Dedov, A G, Subbotin, O A, Egazaryants, S V and Karakhanov, E T *Vestn. Mosk. Univ., Khimiya*, 1989, 30(4): 403
43. Dedov, A G, Zelenkina, O A, Zefirov, N S, Karakhanov, E A, Neimerovets, E B, Tshay, L E, Samoshin, V V and Subbotin, O A, *Dokl. Akad. Nauk SSSR*, 1989, 306(4): 876
44. Dedov, A G, Loktev, A S, Pshegetski, V S and Karakhanov, E A *Neftekhimiya*, 1985, 429
45. Dedov, A G, Loktev, A S, Pshegetski, V S and Karakhanov, E A, *Neftekhimya*, 1985, 176
46. Karakhanov, E A, Neimerovets, E B and Dedov, A G *Vestn. Mosk. Univ, Khimiya*, 1985, 26(4): 429
47. Karakhanov, E A, Neimerovets, E B, Pshegetski, V S and Dedov, A G *Khim. Geterotsikl. Soedin*, 1986, 303
48. Neimerovets, B B, Pshegetski, V S, Riybov, A B, Baranov, V T, Dedov, A G and Karakhanov, E A *Vestn. Mosk. Univ., Khimiya*, 1987, 28(4): 388
49. Karakhanov, E A, Neimerovets, E B, Grishina, I A and Dedov, A G In: *Voprosy Kinet. Katal., Ivanovo, IKHTJ*, 1985, 50
50. Dedov, A G, Evseev, A M, Kalinina, O V, Karakhanov, E A, Linkov, V M, Neimerovets, B B and Syshekova, I G *Vestn. Mosk. Univ., Khimiya*, 1989, 30(5): 505
51. Dedov, A G, Kalinina, O V, Neimerovets, E B and Karakhanov, E A *Vestn. Mosk. Univ., Khimiya*, 1989, in press