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MACROMOLECULAR METAL COMPLEXES WITH MEMORY TO THE CATALYZED SUBSTRATE

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Abstract: A number of complexing polymers containing carboxylic, phosphorylic, amine, imine and pyridine functional groups have been prepared and their complexes with copper, cobalt and nickel have been obtained. The complexes were prearranged for reactions of liquid phase oxidation and hydrogenation of hydrocarbons by means of formation and subsequent fixation in memory of the catalysts the structure of active centres favorable for catalyzed substrate. It has been shown that the prearranged complexes might «remember» the structure optimum for the substrate and this leads to an essential increase in catalytic activity and selectivity of the catalysts.

INTRODUCTION

Interest in solid supported metal complexes has largely grown in the last two decades (Ref.1). These catalytic systems can combine the advantages of heterogeneous catalysts, such as simplicity of separation from the reaction media and high stability with the advantages of homogeneous catalysts, such as high activity and selectivity and possibility of handling more exact information about the structure of active centres. The use of polymer complexons as solid supports opens up new possibilities to vary ligand surrounding and to control catalytic properties of complexes (Ref.2).

This paper summarizes our results on synthesis, investigation and use of macromolecule-metal complexes with memory to the catalyzed substrate.

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RESULTS AND DISCUSSION

Earlier we have developed a principle of preparation of complexing polymers based on use of memory of polymer composition (Refs.3-6). The principle consists in conformational prearrangement of macromolecules of noncrosslinked complexing polymers to a favorable for complexing metal and catalyzed substrate position followed by fixation of conformations optimum for the complex formation by means of intermolecular crosslinking. Crosslinked macromolecules might keep in mind conformations favorable for complexing substrate and this leads to an essential improvement of complex-forming ability of polymers. It has been also shown that prearranged complexes are efficient catalysts for various chemical reactions in comparison with nonprearranged complexes.

Using this principle a number of crosslinked complexing polymers and metal polymer complex catalysts were prepared and used in oxidation and hydrogenation reactions of hydrocarbons.

As an example, reaction of liquid-phase oxidation of ethylbenzene (EB) has been chosen for investigation. Copolymer of diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) has been synthesized, prearranged for complex formation with cobalt and used as catalyst. Copolymerization of DEVPA with AA and preparation of complex forming polymers with three-dimensional structure has been described in more detail in our earlier paper (Ref.3).

The catalytic activity of the catalyst was evaluated according to the oxygen absorption rate and the yield of the reaction products - ethylbenzene hydroperoxide (EHP), methylphenylcarbinol (MPC) and acetophenone (AP). It has been shown that the reaction in the presence of nonprearranged complexes does not practically take place. It should be noted that prearranged complexes can accomodate up to 4,2 meq of cobalt/g whereas in nonprearranged complexes cobalt content does not exceed 1,2 meq/g (Ref.6).

To determine the effect of the amount of catalyst on the reaction proceeding, catalyst concentrations have been ranged from 0.25 to 0.75 g/l which corresponds to cobalt content from 1.05 to 3.15 meq/l. The temperature of

reaction was 90^{0}C - at this temperature the amount of oxygen consumed had been found to be maximum. The results are shown in Fig.1.

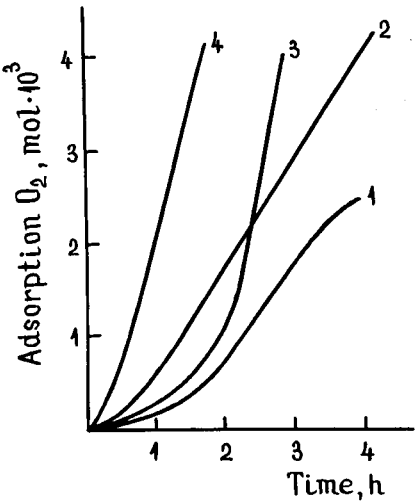

Fig. 1. Kinetic curves for oxidation of ethylbenzene in the presence of cobalt complexes with copolymer of DEVPA and AA. Concentration of the catalyst, g/l: 1 - 0.25; 2 - 0.5; 3 - 0.75; 4 - 1.0 (cobalt benzoate)

It can be seen from the Figure that the highest rate of the reaction is achieved at catalyst concentration between 0.5 and 0.75 g/l which corresponds to cobalt content in the range of 2.1 - 3.15 meq/g. The rate of oxidation is comparable with that in the presence of homogeneous cobalt-containing catalyst - cobalt benzoate which has been taken in an amount of 1g/l to provide maximum reaction rate. This amount corresponds to cobalt content of 8.2 meq/l. The results also show an essential advantage of prearranged cobalt polymer catalyst over cobalt benzoate. First, about three times less amount of cobalt is needed to achieve approximately the same activity of the catalyst. Second, cobalt polymer complexes can be separated and used repeatedly, practically without loss of catalytic activity.

As the next example, complexes of copper with the polymer prepared from polyethylene polyamine (PEPA) and epichlorohydrin-ammonia oligomer (ECHA) have been studied. Molar ratio of PEPA to ECHA was 1:1. They have also been prearranged for the complex formation with copper and both nonprearranged and prearranged complexes have been used in the same

reaction. Preparation and prearrangement of PEPA and ECHA based polymers are described in our paper (Ref.7). The catalyst was taken in an amount of 1 g/l. The content of copper in nonprearranged and prearranged complexes was the same - 1.7 meq/g. Results are presented in Table 1.

Table 1. Oxidation of ethylbenzene in the presence of nonprearranged and prearranged PEPA based copper complexes.

Catalyst	Conversion, % mol	Yield, % mol		
		EHP	MPC	AP
Nonprearranged copper complexes	10.5	3.4	2.1	5.0
Prearranged copper complexes	18.3	6.4	2.9	9.0

It can be seen that prearranged complexes demonstrate higher catalytic activity in comparison with nonprearranged ones, even with similar compositions of both catalysts.

Obviously the improvement of catalytic properties of the prearranged complexes is related not only to higher content of metal but also to essential structural changes of the complexes.

We investigated nonprearranged and prearranged copper complexes with polymers based on PEPA and their low molecular weight analogues using ESR.

It has been shown that the prearrangement provides formation in the polymer phase of complexes with uniform structure similar to their low molecular weight analogues in solution (Ref.8). This is especially important when using metal polymer complexes as catalysts. It is well known that formation of uniform active centres of similar structure is an important condition for preparation of active and selective catalysts.

An attempt has been made to a further increase of activity of metal polymer complexes by means of formation and subsequent fixation in memory of the catalyst of the structure of active centres favorable for hydrocarbon substrate.

Above mentioned complexes of cobalt with the copolymer of DEVPA and AA have been chosen first for such treatment and liquid-phase oxidation of ethylbenzene was taken as a model reaction. The method is based on interaction of noncrosslinked metal polymer complexes with the hydrocarbon substrate or an intermediate product of its transformation in fairly dilute solution, i.e. under conditions when macromolecules are still sufficiently mobile, followed by fixation of the structure by crosslinking and removal of the template substrate from the crosslinked catalyst (Ref.9).

Kinetic curves for the ethylbenzene oxidation in the presence of nonprearranged and prearranged for ethylbenzene and isopropylbenzene complexes of cobalt with the crosslinked copolymer of DEVPA and AA are given in Fig.2.

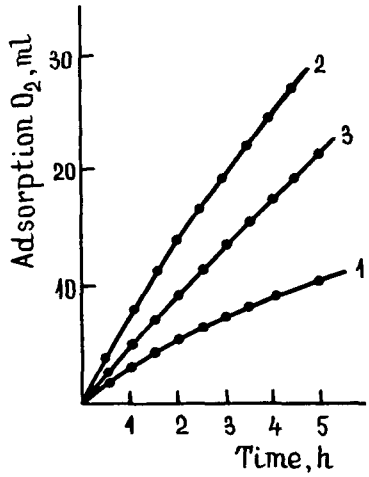

Fig.2. Kinetic curves for oxidation of ethylbenzene in the presence of nonprearranged (1) and prearranged for ethylbenzene (2) and isopropylbenzene (3) complexes of cobalt with copolymer of DEVPA and AA

It can be seen from the Figure that the rate of reaction in the presence of prearranged complexes is much greater than that in the presence of

nonprearranged complexes. Prearrangement for isopropylbenzene also leads to an increase of the reaction rate but less marked than in the case of prearrangement for ethylbenzene.

The next step was preparation of prearranged for n-decane PEPA and ECHA based copper complexes. Catalytic properties of nonprearranged and prearranged for n-decane complexes were investigated in reaction of liquid-phase oxidation of n-decane. Both catalysts contained 1.7 meq of Cu/g. The amount of the catalysts taken in both cases was 0,8 g/l.

Kinetic curves for the oxidation of n-decane in the presence of nonprearranged and prearranged for n-decane complexes are shown in Fig.3.

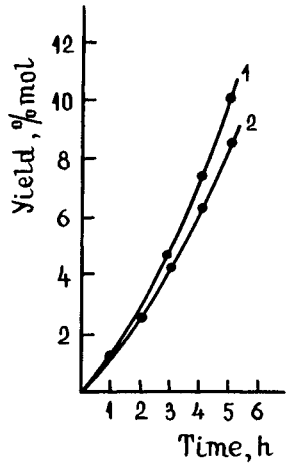

Fig. 3. Kinetic curves for oxidation of n-decane in the presence of nonprearranged (1) and prearranged for n-decane (2) copper complexes

It can be seen from the Figure that in this case prearrangement does not lead to increase in the reaction rate. On the contrary, complexes prearranged for n-decane are less active in oxidation reaction than nonprearranged ones.

It is known that catalytic oxidation of hydrocarbons might proceed by two mechanisms. In the first case, hydrocarbon is adsorbed on the active centres of

catalysts and activated. The activated hydrocarbon reacts with oxygen and is oxidized.

The oxidation reactions previously mentioned proceed according to this mechanism. Prearrangement of complexes for hydrocarbons results in easier adsorption of the substrate on the active centres which in turn improves catalytic activity of the catalyst. In case of the second mechanism oxygen molecules are adsorbed on the active centres of catalysts and activated. The activated oxygen then oxidizes the hydrocarbon. Presumably, the oxidation of n-decane proceeds according to the second mechanism. Thus, the prearrangement for hydrocarbon creates hindrances to adsorption of oxygen instead of facilitating it. That is why in this case decrease in catalytic activity of complexes is observed.

We also carried out hydrogenation of allyl alcohol using poly-4-vinylpyridine (PVP) nickel complexes prearranged for allyl alcohol and for the reaction product - propyl alcohol.

The procedure of preparation of nonprearranged and prearranged for allyl alcohol and propyl alcohol PVP nickel complexes was described earlier (Ref.5). Crosslinked PVP nickel catalyst was taken in the amount of 1,4 g/l. Content of nickel in all catalysts was 4 meq/g.

Kinetic curves for hydrogenation of allyl alcohol to propyl alcohol in the presence of both nonprearranged and prearranged for allyl and propyl alcohol PVP nickel complexes with different degrees of crosslinking are given in Fig.4.

It can be seen from the Figure that the rate of hydrogenation in the presence of complexes prearranged for allyl alcohol, is much higher in comparison with nonprearranged complexes. On the contrary, the rate of the reaction in the presence of complexes prearranged for propyl alcohol is lower than that in the presence of nonprearranged complexes due to blocking of active centres from complexation with allyl alcohol.

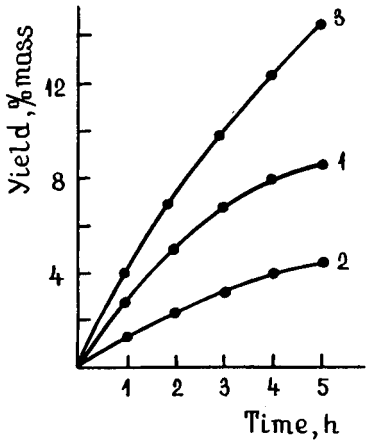

Fig. 4. Kinetic curves for hydrogenation of allyl alcohol into propyl alcohol in the presence of nonprearranged (1) and prearranged for propyl alcohol (2) and allyl alcohol (3) complexes.Crosslinking degree -15%

Kinetic data on hydrogenation of allyl alcohol in the presence of nonprearranged and prearranged for allyl and propyl alcohols complexes were treated in terms of Henri equation (Ref.10).

$$\frac{X}{t} = V + \frac{K_m}{t} \ln \frac{A_0 - X}{A_0}$$

where A_o - substrate concentration at t=0;

X - decrease of substrate concentration due to formation of reaction product;

V - theoretical ultimate rate at infinite substrate concentration;

K_m - constant characterizing enzyme and reaction system (Michaelis constant).

The data in Fig.5 for catalysts nonprearranged and prearranged for propyl alcohol represent straight line with a higher slope than for the catalyst prearranged for allyl alcohol. This line passes through the origin of coordinates, whereas in case of the catalyst prearranged for allyl alcohol this line intersects the ordinate axis in a point of 0.3 mol/min.l which corresponds to the theoretical ultimate reaction rate at infinite concentration of the substrate. This fact confirms that the reaction

of formation of the intermediate catalyst-substrate complex takes place first. After that the hydrogenation reaction proceeds.

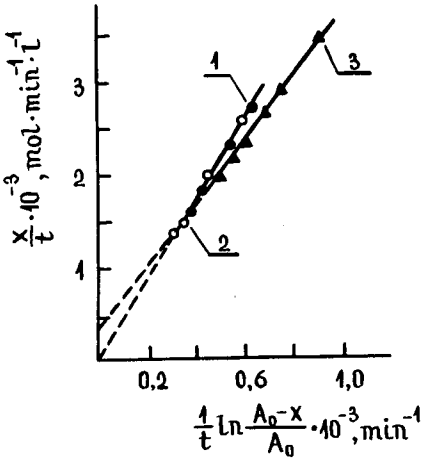

Fig. 5. Kinetic curves for hydrogenation of allyl alcohol into propyl alcohol in the presence of nonprearranged (1) and prearranged for propyl alcohol (2) and allyl alcohol (3) complexes in terms of Henri equation. Crosslinking degree - 15%

CONCLUSION

The results obtained show that the special prearrangement of active centres of macromolecule-metal complexes for the hydrocarbon substrate leads to an essential increase in activity and selectivity of the catalysts prepared on their base. The prearrangement can also be used as an additional instrument for investigation of mechanism of catalytic processes with the use of macromolecule-metal complex catalysts.

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