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Abstract

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CATALYTIC PROPERTIES OF CHELATE (INTRACOMPLEX) POLYMERS

The search for new types of solid catalysts, intermediate between inorganic catalysts and enzymes, led us to study the catalytic activity of organometallic chelate (claw-like, or intracomplex) polymers. The very first results obtained indicated the promise of using this type of compound as catalysts ([1]).

The purpose of this study was to trace the influence on the catalytic properties of: 1) the metal included in the polymer, 2) the chemical composition of the donor atoms included in the chelate unit, and 3) the organic part of the polymer in the main and side chains. We studied metal polychelates of Cu, Ni, Fe, Pd, Co, Zn, and Cd ([3–8]). As donor atoms entering into the chelate unit, atoms of sulfur, nitrogen, and oxygen were used. The composition of the chelate unit of the polymers investigated may be represented by the schemes

S S	N S	O O	O O
Me	Me	Me	Me
S S	S N	N N	O O
(1)	(2)	(3)	(4)

In what follows, in accordance with the above notation, we shall call the polymers structures 1, 2, 3, and 4 according to the composition of their chelate unit. Table 1 presents the structure and composition of the polymers studied. In polychelates with the same chelate unit, the organic part of the polymer was varied by changing the organic radicals R and r in the main and side chains of the polymer. Organic radicals of the aliphatic and aromatic series were introduced. This enabled us to trace the influence on catalytic activity of the organic part of the polymer at an unchanged composition of the chelate unit.

Experimental Part

The decomposition of hydrazine was studied in the greatest detail. This reaction is sensitive to the electronic state of the contact ([2]) and proceeds in two directions:

$$N_2H_4 \rightarrow N_2 + 2H_2, \quad (1)$$

$$3N_2H_4 \rightarrow 4NH_3 + N_2. \quad (2)$$

The influence of the structure of the polymer and its chemical composition on the direction of hydrazine decomposition makes it possible to evaluate the selectivity of its action—an extremely important characteristic of a catalyst. Among other reactions, the decomposition of isopropyl alcohol and formic acid, which proceed by the dehydrogenation route, was investigated. Oxidation of carbon monoxide on the polymers studied is absent up to 200°.

a) **Influence of the metal.** Table 2 gives experimental data characterizing the specific rate of hydrazine decomposition at 108°, and indicates the percentage of hydrazine decomposition by the first and second pathways for the polychelates studied. From a comparison of the data in Table 2 it follows that only

Table 1

Chelate polymers studied

Polymer designation	Organic compound from which the polychelate was obtained	Chelate unit	Composition of the polychelate
1	Sodium bis-dithiocarbamate	—S S— \ Me \ —S S— [3] R_5—C_6H_4—C_6H_4; R_2—$(CH_2)_2$—; R_3—$(CH_2)_6$—; R_4—(C_6H_4)—	Polymeric dithiocarbamate complex structure shown: ... [R—NH—C(=S)—S—Me—S—C(=S)—NH]$_n$ ...

Polymer designation	Organic compound from which the polychelate was obtained	Chelate unit	Composition of the polychelate
2a	α-Thioalkylpyridineamidodiphenyl $^{(4)}r_1$ H; r_2—CH_3—R_5— biphenyl fragment	—N N— Me S— S—	Polymeric chelate structure shown with two substituted pyridine rings, $C=N$ linkages to a biphenyl group R, sulfur coordination, terminal Me centers, and repeating unit $[\cdots]_n$.
2b	Rubianic acid	—N N— Me S— S—	Polymeric rubianic-acid chelate structure shown: repeating units containing NH, $C=S$, C, S, and Me centers, $[\cdots]_n$.
2c	Poly-(4,4′-bis)-α-thio-2,6-lutidineamidodiphenyl $^{(5)}R_5$— biphenyl fragment; R_6— dimethyl-substituted biphenyl fragment; R_7— dimethoxy-substituted biphenyl fragment	—N N— Me —S S—	Polymeric chelate structure shown with pyridine rings, thioamide fragments $C(=S)$—$N(R)$, Me coordination centers, and a repeating bracketed fragment $[\cdots]_n$.

Polymer designation	Organic compound from which the polychelate was obtained	Chelate unit	Composition of the polychelate
3a	5,5′-Methylene-bis-salicylaldehyde [6]	r_1 H; r_2—$(CH_2)_2$—; r_3—$(CH_2)_6$—; r_4	Polymeric Schiff-base chelate structure shown: phenylene units connected by CH_2, salicylidene $HC=N$ groups, O,N-coordination to Me, and repeating unit $[\cdots]_n$.
3b	Diacetylresorcinol [8]		Polymeric chelate structure shown with resorcinol rings, $C=N$ groups, CH_3 substituents, O,N-coordination to Me, and repeating unit $[\cdots]_n$.
4a	5,5′-Methylene-bis-salicylaldehyde [7]		Polymeric O,O-chelate structure shown: phenylene units connected by CH_2, aldehyde fragments $HC=O$, Me centers, and repeating unit $[\cdots]_n$.

Polymer designation	Organic compound from which the polychelate was obtained	Chelate unit	Composition of the polychelate
4b	Dinitrosoresorcinol	—*O* *O*— *Me* —*O* *O*—	Polymeric *O*,*O*-chelate structure shown with resorcinol rings, nitroso groups *ON* / *NO*, *Me* centers, and repeating unit $[\cdots]_n$.

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Table 2

Catalytic activity of the investigated polychelates in hydrazine decomposition reactions

Polymer	Sample weight, g	S, m^2	S_{sp}, m^2/g	W, $cm^3/m^2 \cdot min$	Amount of hydrazine decomposed, %, reaction (1)	Amount of hydrazine decomposed, %, reaction (2)
$1Cu(R_5)$	0,16	0,16	0,98	0,023	100	0
$1Cu(R_2)$	0,06	0,10	0,19	0,066	54	46
$1Cu(R_4)$	0,11	0,16	0,51	0,004	100	0
$1Cu(R_3)$	0,13	0,01	–	( )0,03	–	–
$1Ni(R_5)$	0,31	0,08	0,27	0,075	60	40
$1Ni(R_2)$	0,22	0,03	0,14	0,005	40	60
$1Ni(R_3)$	0,06	0,10	0,19	0,066	54	46
$1Co(R_5)$	0,22	0,50	2,22	0,014	50	50
$1Co(R_2)$	0,23	0,12	0,53	0,010	50	50
$1Co(R_3)$	0,05	0,01	0,14	0,010	15	85
$1Zn(R_5)$	0,05	0,27	5,75	0,000	–	–
$1Zn(R_2)$	0,10	0,53	5,38	0,000	–	–
$2aCu(r_1, R_5)$	0,14	0,01	0,07	0,200	80	20

Polymer	Sample weight, g	S, m^2	S_{sp}, m^2/g	W, $cm^3/m^2 \cdot min$	Amount of hydrazine decomposed, %, reaction (1)	Amount of hydrazine decomposed, %, reaction (2)
2aCu(r_2, R_5)	0,06	0,12	1,82	0,044	89	11
2cCu(R_6)	0,05	0,05	1,05	0,008	57	43
2cCu(R_7)	0,12	0,04	0,35	0,080	92	8
2cCu(R_7)	0,03	0,08	2,37	0,045	87	13
2aCu(R_7)	0,09	0,38	4,34	0,030	88	12
2aCo(R_5)	0,10	0,88	8,40	0,0001	10	90
2cPd(R_7)	0,03	0,08	2,37	0,005	42	58
2bCu	0,12	0,12	0,99	0,043	12	88
2bNi	0,11	0,11	0,96	0,018	0	100
3aCu(r_1)	0,01	0,12	11,2	0,005	2	98
3aCu(r_2)	0,05	0,03	0,66	0,012	37	63
3aNi(r_1)	0,03	0,06	2,02	0,0000	–	–
3aNi(r_2)	0,05	0,08	1,57	0,0000	–	–
3aNi(r_3)	0,06	0,27	4,69	0,0000	–	–
3aFe(r_1)	0,05	0,38	7,15	0,0020	17	83
3aFe(r_2)	0,04	0,14	3,81	0,0010	70	30
3aFe(r_3)	0,05	0,88	16,60	0,0006	43	57
3aZn(r_1)	0,02	0,01	0,58	0,0000	–	–
3aZn(r_2)	0,06	0,56	9,40	0,0000	–	–
3bCu()$_2$	–	–	0,39	0,0020	66	34
3bCu(r_3)	–	–	0,29	0,4000	53	42
3bNi(r_2)	0,05	0,08	1,31	0,0000	–	–
3bNi(r_3)	0,06	0,27	4,90	0,0000	–	–
3bZn(r_3)	–	–	0,93	0,0000	–	–

polychelates containing transition metals (copper, nickel, cobalt, iron, and platinum) possess catalytic activity. Zinc and cadmium polychelates are catalytically inactive in the temperature range investigated. The highest decomposition rate was observed on copper, palladium, and nickel polychelates of structures 1, 2a, and 2c. In terms of catalytic activity, the metals may be arranged in the series Cu > Ni, Pd > Co, Fe ≫ Zn, Cd. Fig. 1 illustrates the validity of this conclusion.

b) **The influence of addends entering the chelate unit.** Catalytic activity depends very strongly on the nature of the addends in the chelate unit and on the organic part of the polymer. Fig. 2 presents the change in the rate of hydrazine decomposition on copper polychelates with different

Figure 1

Figure 1: Figure 1

compositions of the chelate unit, as a function of the composition of the organic radicals in the main and side chains. It can be seen that curve 1 for polychelates with the chelate unit Cu (N, S) lies considerably higher than the others. This means that, for no composition of the organic part of the polymer, in structures 1, 3, and 4 can the decomposition rate obtained for structure 2 be attained. On the basis of the results of studying the catalytic activity of copper polychelates with different compositions of the chelate unit, they may be arranged in the following order according to the strength of the catalytic action: Cu (N, S) > Cu (S, S) > Cu (N,O) > Cu (O, O). In the same Fig. 2, curve 4 shows the specific catalytic activity of oxides and sulfides of nickel and of monovalent and divalent copper. It can be seen that the catalytic activity of chelate polymers exceeds by two orders of magnitude the activity of inorganic copper semiconductors. For nickel polychelates, an analogous-

logical regularity. The catalytic activity of nickel polychelates was found only for polychelates with chelate-ring structures 1 and 2, containing Ni(S, S) and Ni(N, S). In structure 3, Ni(N, O), nickel becomes catalytically inactive.

On the basis of the study carried out, one may also conclude that the organic part of the polymer, both in the main chain and in the side chain, has a strong influence on catalytic activity (Fig. 2).

Influence of the structure and chemical composition of the polymer on selectivity. Selectivity can be assessed by the ratio of the rates of hydrazine decomposition by the first and second pathways (see reactions (1) and (2)). For the copper polychelates studied, the decomposition varies from 100% by reaction (1), to nitrogen and hydrogen, to 100% decomposition to nitrogen and ammonia by reaction (2), depending on the composition of the addends in the chelate ring of the polymer. When the organic radicals in the polymer are changed, all intermediate values are obtained. Figure 3 presents the dependence of the selectivity of the copper polychelates studied on their chemical composition and structure.

Comparison of the catalytic activity of polychelates with the catalytic activity of the corresponding monomeric analogs. The question arises as to how specific the observed regularities of catalytic activity are for the polymer: will complex compounds of the same composition, i.e., monomeric analogs of the polymers studied, possess analogous properties. The catalytic

Fig. 1. Influence of the metal on catalytic activity. Kinetic isotherms of hydrazine decomposition on polychelates of different metals that showed maximum activity at 108°, hydrazine pressure 1 mm Hg, p. 1 –2a Cu($R_5\eta$); 2 –2c Pd(R_7); 3 –2b Ni; 4 –1 Co(R_2); 5 –3a Fe(r_3)

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. Rate of hydrazine decomposition on copper polychelates differing in the composition of the addend atoms in the chelate ring as a function of the structure and composition of the organic part of the polymer. For polychelates with chelate ring: 1 –Cu(N, S); 2 –Cu(S, S); 3 –Cu(N, O); 4 –for copper and nickel sulfides and oxides.

the specific catalytic activity of the monomeric analogs representing one unit of six polychelates 2aCu(R_5, r_2); 2cCu(R_7); 2cCu(R_6); 3aCu(r_1); 3aCu(r_2); 3aNi(r_1). Only the monomer which does not differ in its high catalytic activity from the polychelate 3aCu(r_1) possessed catalytic activity close to that of the polymer. The remaining monomers, including the monomer of the most active polymer 2aCu(R_5, r_1), had very low catalytic activity, which in a number of cases was practically absent, despite the comparatively high specific surface area of these preparations.

Fig. 3. Selectivity of catalytic decomposition of hydrazine on copper polychelates. *I*–for reaction No. 1; *II*–for reaction No. 2. Along the abscissa are plotted the sample numbers. 1–1Cu(R_4); 2–1Cu(R_5); 3–3bCu(r_3); 4–2bCu(R_7,r_1); 5–2bCu(R_7,r_1); 6–3bCu(r_2); 7–3aCu(r_2); 8–2bCu; 9–3bCu(r_1)

The following regularities were found: catalytic activity and selectivity are determined by: 1) the metal entering into the polychelate; 2) the nature of the addends entering into the chelate unit; 3) the organic part of the polymer has a strong influence on the catalytic properties of polychelates.

The regularities found are similar to the regularities determining the catalytic properties of enzymes. Comparison of the electrical conductivity and catalytic activity of individual polychelates gives no indication of the presence of any interrelation between them. At the same time, adsorption of hydrazine is sometimes accompanied by an increase in electrical conductivity by 1-2 orders of magnitude, which indicates the electronic character of the chemisorption stage. Judging from the change in electrical conductivity, the chelate polymers investigated belong to electronic semiconductors, since hydrazine, on nickel black and other organic semiconductors, being adsorbed, exhibits the properties of an electron donor. The absence of a catalytic relation with electrical conductivity is apparently due to the fact that chemisorption and catalysis are mainly determined not by the semiconducting properties of the polymer as a whole, but by the electronic state of the metal in the chelate unit. The high catalytic activity exhibited exclusively by chelate polymers of transition metals makes it probable that concepts of crystal-field theory may be used to interpret the mechanism of

catalytic action (9).

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Note: Figure translations are in progress. See original paper for figures.