Allylic isomerization of dichlorobutenes catalyzed by iron-containing nanoparticles stabilized in polymeric matrices

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Iron-containing clusters obtained by the decomposition of iron complexes in a solution—melt of a polymeric matrix exhibit catalytic activity in the isomerization of dichlorobutenes. The activity of the clusters stabilized in the polytetrafluoroethylene and polyethylene matrices depends on the nature of the stabilizing matrix and the content of the metal in it, *i.e.*, on the size and structure of the cluster, and substantially exceeds the activity of supported metals and powders. The clusters in the polytetrafluoroethylene matrix are more active than those in polyethylene. The dependence of the catalytic activity on the metal content has an extreme character, and for the polyethylene matrix it achieves a maximum at a metal content of ~10%. In catalysts with this composition, the particle size increases to 4—5 nm, and the distance between them is shortened, on the average, to 10 nm, which leads to interaction of the cluster particles with each other.

Key words: iron, clusters, polymer matrix, particle size, structure, catalysis, isomerization, dichlorobutenes.

Clusters and metal particles immobilized in polymer matrices attract the attention of researchers as promising catalysts of many processes. Reactions in which the catalytic properties of the metal depend on the size or structure of particles,[1] in particular, allylic isomerization of dichlorobutenes (DCB),[2,3] are of special interest.

$$\underset{\text{3,4-DCB}}{\mathrm{ClCH_2CHClCH{=}CH_2}} \rightleftharpoons \underset{\text{1,4-DCB}}{\mathrm{ClCH_2CH{=}CHCH_2Cl}} \qquad (1)$$

The rate and selectivity of this process in the presence of palladium nanoparticles immobilized in the polyparaxylilene matrix depend on the character of interaction of the particles, which is defined by the size of nanoparticles and the distance between them. The specific activity of the samples prepared by cryochemical synthesis is also related to the average distance between the nanoparticles in the polymer and electroconductivity of the sample. When these factors change, the isomeric composition of 1,4-DCB that formed changes: for isolated nanoparticles and metal powder, the *trans-* to *cis-*isomers ratio in the products is (7—8) : 1, and in the case of nanoparticle ensembles, the ratio decreases to (2—3) : 1.[2,3]

It was of interest to reveal whether the regularities observed can be extended to other catalysts of the cluster type. In this work, we studied allylic isomerization of dichlorobutenes in the presence of iron-containing clusters immobilized in polytetrafluoroethylene (PFE) or polyethylene (PE) matrices. Reaction (1) was chosen as the model because it is catalyzed by several metals, in particular, Fe^0 carbonyl complexes, Fe^{III} compounds, Cu clusters and polynuclear complexes,[4—9] and Pd.[2,3] The activity of the catalysts was assumed to be the ratio of the number of moles of DCB formed during the experiment to the number of g-atoms of iron in a weighed sample of the catalyst and the duration of the experiment in hours (the average catalyst turnover/mol $(\mathrm{mol\ h})^{-1}$).

Experimental

Iron-containing composites in PFE and PE matrices were prepared by monomolecular decomposition of iron carbonyl $Fe(CO)_5$ in a solution—melt of the polymer matrix in an inert atmosphere at a high temperature.[10—12] The prepared metallopolymeric materials were kept in sealed vessels in a dry box. Iron carbonyl and Fe_2O_3 (analytical purity grade) were used without additional purification.

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Reagents and solvents were thoroughly purified by standard methods and additionally dried with molecular sieves. Both 3,4-DCB and 1,4-DCB were used as starting compounds. The purity of reagents was monitored by GLC.

Reaction mixtures were prepared in a box with a dry inert atmosphere and on a vacuum setup. The reaction was carried out in sealed tubes in the absence of oxygen at 70—100 °C. The catalyst (0.01—0.04 g) containing from 7 to 50 wt.% metal and a solution (0.5—3.0 mL) of DCB in benzene in a ratio of 1 : (10—20) were placed in the tube, the DCB concentration being 0.5—0.9 mol L^{-1}. The tubes were thermostatted at the reaction temperature for 20, 40, or 60 min. The composition of products was analyzed on a Chrom-5 chromatograph with a flame-ionization detector on columns with the SE-30 and PEG-2000 stationary phases at 100—120 °C.

Preliminary experiments showed that DCB isomerization in the presence of the Fe-containing catalysts proceeded with a measurable rate only in the absence of oxygen.

Results and Discussion

Table 1 presents the data on DCB isomerization catalyzed by the Fe-containing clusters stabilized in the polymeric matrices (16.6 wt.% catalyst in the reaction mass) and the results obtained under similar conditions in the presence of Fe and Fe_2O_3 powders, supported Fe/SiO_2 catalyst, and platinum black. For correct comparison of the data on the catalytic activity obtained for different DCB isomers (see entries *1* and *4* in Table 1), it should be taken into account that the equilibrium constant of reaction (1) at 70—90 °C is 4.0—4.5. Multiplying this value by the activity value found for the isomerization of 1,4-DCB (6.3 mol (mol $Fe)^{-1}$ h^{-1}), we obtain 28.4 mol (mol $Fe)^{-1}$ h^{-1}, which is comparable with the experimental data on 3,4-DCB isomerization.

As can be seen in Table 1, the activity of the cluster materials in DCB isomerization is higher than that of the supported materials and metal powders. The PFE matrix-stabilized iron-containing clusters catalyze isomerization at 70—90 °C. In the isomerization of 3,4-DCB, the equilibrium concentration of the isomers in the presence of the catalyst in the PFE matrix is achieved at 90 °C within 1 h, whereas in the presence of Pd black (see Table 1, entry *8*), it is achieved for at least 3 h even at 100 °C. The same time is required for the establishment of the equilibrium DCB concentration when Fe carbonyl complexes are used as catalysts.[4]

The clusters in the PE matrix are less active than those in the PFE matrix: the equilibrium DCB concentration is achieved within 1 h only at 100 °C. However, their activity is much higher than that of supported Fe and metal powders and is comparable with that of iron oxide. Since we carried out the experiments in dilute solutions of DCB, it can be assumed that in pure DCB the activities of the catalysts would be much higher. Under the conditions of the first-order reaction, when the initial portions of the kinetic curve can be approximated by a straight line, an increase in the concentration by an order of magnitude on going to the pure substance would result in a corresponding increase in the amount of the product formed, *i.e.*, the activity would also increase by 10 times. It is known that for isomerization with some metal complex catalysts the order with respect to DCB >1 and is close to 2[8,9]; in these cases, the difference should be still higher. The results obtained indicate that in the series of the known catalysts, the Fe-containing systems in the PFE and PE matrices have a high activity.

The catalytic activity of the cluster materials as a function of the metal content is demonstrated in Table 2 for

Table 1. Isomerization of DCB in the presence of the Fe-containing clusters (16.6% catalyst in the sample) stabilized in PFE and PE matrices and of other metal-containing catalysts

Entry	Isomer	Amount of DCB /mol 10^3	Catalyst	Weight of catalyst/mg	Content of metal in catalyst /mol 10^5	Temperature /°C	Time /min	Yield of product (%)	Amount of product /mol 10^3	Activity[a]
1	3,4-DCB	1.46	Fe clusters in PFE matrix	8.3	2.5	80	40	44	0.64	39
2	3,4-DCB	1.46	The same	12.1	3.6	90	20	41	0.60	50
3	3,4-DCB	0.91	The same	19.0	5.6	90	60	82	0.75	13.4
4	1,4-DCB	0.73	The same	8.2	2.4	70	60	21	0.15	6.3
5	1,4-DCB	0.46	Fe clusters in PE matrix	20	5.9	100	60	21	0.10	1.64
6	3,4-DCB	0.91	Powder Fe	9.8	17.5	100	60	12	0.11	0.62
7	3,4-DCB	0.91	Powder Fe_2O_3	14.0	17.5	100	60	61	0.56	3.2
8	3,4-DCB	0.91	12% Fe on silica[b]	48.0	10.3	100	60	20	0.18	1.7
9	3,4-DCB	0.91	Pd black	30	28	100	180	68	0.62	0.74

[a] In moles of product per mole of iron per hour.

[b] The catalyst, prepared by impregnation of silica with iron nitrate followed by reduction with hydrogen, was kindly presented by P. A. Chernavskii (M. V. Lomonosov Moscow State University).

Table 2. Isomerization of 1,4-DCB (100 °C, 1 h) in the presence of Fe-containing clusters stabilized in a PE matrix

Amount of DCB /mol 10^3	Content of Fe in catalyst		Yield of 3,4-DCB (%)	Amount of 3,4-DCB /mol 10^5	Activity*
	%	mol 10^5			
0.55	7	3.3	10	5.5	1.67
0.46	7	2.5	9	4.1	1.65
0.46	10	4.0	20	9.2	2.30
0.55	10	5.5	22	12.2	2.22
0.46	10	3.6	15	6.9	1.92
0.46	16.6	5.9	21	9.7	1.64
0.46	16.6	5.5	15	6.9	1.27
0.46	20	3.9	10	4.8	1.23
1.10	20	18.2	18	19.8	1.09
1.10	30	27.8	16	17.6	0.63
0.46	50	18.3	3	1.4	0.08
0.46	50	17.8	2	0.9	0.05

* In moles of product per mole of iron for hour.

Fe-containing clusters stabilized in a PE matrix. The function has an extreme character. The maximum of activity falls on catalysts containing ~10 wt.% Fe. The activity of clusters with a higher (to 50 wt.%) metal content is low and does not exceed that of iron powder.

To reveal the reasons for the extreme increase in catalytic activity at 10% metal content, let us consider in more detail the known data on the size distribution of metallic particles and their arrangement in the polymeric matrix. Similar systems have previously been described in detail.[10–13] The composition and properties of cluster particles depend on the nature of the matrix and the iron content. The matrices are not inert towards high-activity metal clusters. The PFE matrix is defluorinated by the Fe particles, and in the case of the PE matrix, it is dehydrogenated and chemical bonds are formed due to the interaction of the Fe valence d-electrons with MO of polyethylene. The latter does not prevent the oxidation of the cluster particle: it occurs in air during one to several days, depending on the composition of sample. All cluster particles studied have a multiphase composition, and the main phases can be identified. For the Fe concentration <20—40 wt.%, the clusters contain difluoride (in the PFE matrix) or iron oxide (in the PE matrix) along with the metal; iron carbide additionally forms at a higher metal concentration.

As the metal content increases, the cluster size increases and the distances between the clusters are shortened. Each concentration of the metal is characterized by a specific, rather narrow size distribution of particles and periodicity of their arrangement in the matrix bulk. The typical distribution curves of the particles in catalysts with different concentrations of Fe in the PE matrix obtained by small-angle scattering[11,12] are presented in Fig. 1. The fraction of the clusters with a specific size normalized to the total number of particles corresponds to the *D* values on the ordinate. It is seen that the distribution is narrow; particles of 1.8—2.0 nm predominate at low Fe concentrations, and the admixture of larger aggregates is minor (see Fig. 1, curve *1*). At a metal content ≥7 wt.%, the character of the distribution changes and corresponds to curve *2*, which exhibits a somewhat broader distribution with a predominance of particles ~4 nm in size. Similar measurements at an Fe concentration of 10 wt.% showed that in this case ~80% particles were <4 nm, and the character of distribution remained almost unchanged up to an iron content of 22 wt.%.[11,12]

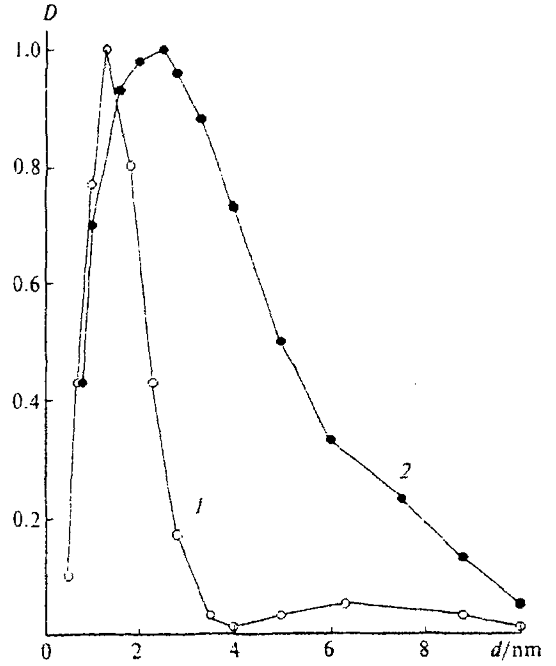

Fig. 1. Diagram of size (*d*) distribution (*D*) of Fe clusters in the PE matrix at a metal content of 1 wt.% (*1*) and 7 wt.% (*2*).

It is seen from the data presented that the average size of nanoparticles slightly depends on the metal concentration. The periodicity of arrangement of clusters in the matrix changes much more strongly in this composition interval. This is indicated by the change in the average distance (*l*) between the clusters (according to the small-angle scattering data)[12]:

Content of Fe (wt.%)	1	3	8	22
l/nm	32	22	11	9

It is seen that an increase in the Fe concentration to 8 wt.% results in shortening of the distance between particular metal aggregates to ~11 nm, and the *l* value changes more weakly with further increase in the metal content. In addition, at a metal concentration equal to ~10 wt.%, the polymeric matrices begin to manifest the properties of cluster ensembles; the thermal resistance of the material increases sharply and its magnetic properties change: composites containing >10 wt.% metal are ferromagnetic. It follows from this that at metal concentrations in the region of 7—10 wt.%, the whole complex of properties of the system changes sharply, which is related to the decrease in the distance between the particles (*l*). Beginning from some *l* value, the properties of the material are determined by those of the whole ensemble of its component-aggregates. The modification of one cluster (for example, a decrease or increase in its charge due to interaction with a reactant molecule) results in a change in the state of other particles, which, according to the published data,[13] may lead to a jumpwise change in the characteristics of the system as a whole. The appearance of new properties in the ensemble of interacting particles can also be due to their mutual overcharging, which appears only when the clusters reach a specific critical distance between them comparable with their sizes (in our case, 5—10 nm).[13] The increase in the activity of Fe-containing clusters related to the increase in the metal content to 10 wt.% and shortening of the distances between them may be a result of similar cooperative effects of interaction of the clusters in catalysis. This effect disappears, the properties of the system approach those of the bulk metal, and the activity decreases with further bringing together and enlargement of the particles that take place when the metal content increases.

In addition to the size distribution of the particles and their arrangement in the matrix, the composition of the particles is also a factor that determines the catalytic activity. The higher activity of the iron fluoride phase than that of iron oxide can, in particular, be the reason for the higher activity of the clusters in the PFE matrix. The strong decrease in the activity with increase in the Fe concentration to 50 wt.% can partly be related to the increase in the less active phase of iron carbide in the metal aggregates.

The results obtained indicate that allylic isomerization catalyzed by Fe-containing clusters stabilized in polymers is a structure-sensitive process. The activity of these systems substantially exceeds that of metal powders and depends on the nature of the stabilizing matrix and the metal content in it, *i.e.*, on the distribution of clusters, their size, and structure. In the PE matrix, the dependence of the activity on the metal content is extreme and reaches a maximum at an iron concentration equal to 10 wt.%, *i.e.*, precisely where the capability of cluster particles to interact with each other begins to appear and many properties of the polymer composite change. These data along with the previous results[2,3] on Pd clusters stabilized in polymeric films suggest that a general size-structural effect determines the behavior of polymer-immobilized cluster particles in catalysis.

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