## Catalytic Behavior of Copper(II) Chelate Complexes Sterically Held in Zeolite Large Cavities and Fixed on Its Outer Surface by a Topological Anchor

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**Abstract**—Catalytic properties of copper(II) tricyclic chelate compounds based on enamino ketone of 3-acetyl-2,4-pentanedione and 1,6-hexametylenediamine fixed on NaY and CaA zeolites by the methods of topological and topologically-anchor retention, respectively, were compared. The mode of fixation of chelates on a support affects the character of the liquid-phase catalytic oxidation of cyclohexene by molecular oxygen. At the topological fixation by a steric retention of a chelate compound in a large cavity of NaY zeolite, the reaction rate related to one reaction center of a metal complex is not proportional to the filling degree that points to inaccessibility for a substrate of catalyst molecules localized in inner cavities of crystallites. In an alternative mode of the catalyst topologically-anchor fixation, when only a ligand fragment is held in CaA zeolite, and catalytically active metal center is turned to the side of the reaction medium, the linear dependence of the cyclohexene oxidation rate on the amount of the chelate on the support is retained within the whole studied range of the surface catalyst concentrations. The catalytic activity of the topologically-anchor fixed Cu(II) chelate compound coincides with its activity in the zeolite absence, which points to a pseudo-homogeneous mode of cyclohexene oxidation. At topologically-anchor fixation of a Cu(II) chelate compound on CaA zeolite diffusion limitations characteristic for the fixation by steric retention are completely eliminated.

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Chelate compounds of transition metals with organic ligands are used in various fields of preparative chemistry and chemical technology as effective homogeneous catalysts of organic reactions. At the same time, fixation of metal chelates on a solid support makes it possible to carry out the process in a heterogeneous-catalytic mode more favorable technologically.

However, the deposition of metal complexes on a solid phase encounters significant obstructions, as chelates, in particular of nonionic type, are poorly held on a surface. For some substances (polymeric compounds and silica gels) this problem is solved by fixing metal chelate compounds due to chemical bonding with "grafted" surface functional groups (anchor fixation) [1]. The anchor fixation on metal oxides or on aluminosilicates possessing more favorable chemical-mechanical properties is extremely problematic.

A special case is represented by alkaline forms of crystalline aluminosilicates (for example, synthetic

zeolites of the faujasite type) with their unique structure, chemical inertness, thermal stability, and rather high mechanical strength. The fixation of metal chelate compounds on alkaline forms of zeolite supports has been realized by so-called topological (steric) retention [2], the sense of which consists in the steric hindrances arising because of differences in sizes of chelate complexes and effective diameters of entrance windows (Fig. 1a). Metal chelates synthesized *in situ* in zeolite pores and having sizes greater than the effective diameter of entrance windows cannot leave the support without destruction and are sterically held inside large cavities, not forming chemical bonds with their "walls."

As zeolites are molecular sieves, the arrangement of catalyst molecules in their hollows do not help to solve the problem of diffusion to a catalytically active center, but even more aggravates this problem owing to the appearance of the secondary sieve effect [3] arising due to additional blocking of pores with the "help" of synthetically injected molecules of coordination compounds. Bulk reagents or reaction products are especially sensitive to the secondary sieve effect. In the latter case a chelate compound is immediately removed from the catalysis, as the conversion products are irreversibly held in large zeolite cavities in the same way as the catalyst itself is captured at its own synthesis *in situ*.

To eliminate the negative secondary sieve effect, we offered a topologically-anchor mode of fixing metal chelate compounds on synthetic zeolites X and Y and on zeolite A [4]. The essence of the topologically-anchor fixation consists in the fact that not the whole chelate compound molecule suffers the steric retention, as is the case with the topological fixation, but only its part belonging to a ligand and practically not affecting the catalytic properties of the complex (Fig. 1b). In this case catalytically active metal centers of a chelate compound are forced out of zeolite matrix pores and become accessible to substrates of any sizes. Thus, molecules of reagents can contact with catalytically active centers, not penetrating into zeolite pores.

At present direct quantitative evidences confirming advantages of the topologically-anchor homogeneous catalysts are scarce. Therefore in this work we have



Fig. 1. (a) Scheme of topological (steric) retention (1) of complex I in (2) large cavity of NaY zeolites; (b) schematic diagram of (1) fixing chelate metal complex in CaA zeolite by means of (3) anchor fragment topologically kept in (2) large cavity; (4) entrance windows.





studied the catalytic behavior of heterogenized chelate compound I as a function of the mode of its deposition on zeolite. The aim of the work was to compare catalytic activities of thus prepared heterogeneous catalysts and to confirm quantitatively the existence of the secondary sieve effect for the case of compound I sterically held in large zeolite cavities and also the absence of reaction inhibition when a topological anchor is used for fixing chelate compound I. To reach these aims, we have chosen the reaction of the liquidphase cyclohexene oxidation by molecular oxygen, which we have earlier studied in detail in homogeneous conditions in the presence of related copper(II) chelates [5–7].

To fix chelate compound I, we used NaY (sample A) and CaA (sample B) zeolites. Sample A was obtained by a steric retention of complex I in large

cavities of zeolite NaY [2] (Fig. 1a). In sample **B** complex I is fixed on zeolite CaA by means of a topological anchor [4] (Fig. 2).

Effective sizes of large cavities of zeolites NaY and CaA are approximately equal (~1.1 nm), whereas effective diameters of entrance windows are essentially different and equal 0.7–0.8 and 0.5 nm, respectively [8]. The maximal size of complex I does not exceed the effective diameter of large cavities of NaY and CaA zeolites and hence for topological (steric) fixation any of them is suitable. However, in this case it is more expedient to use zeolite NaY (sample A) with wider entrance windows (~0.8 nm). For the matrix synthesis of complex I, chelate compound II was inserted as a predecessor in large cavities of zeolite NaY, as the size of compound II is smaller than the effective diameter of entrance windows of zeolite



Fig. 2. Topologically-anchor fixation of a Cu(II) chelate compound on zeolite CaA. (a) Phase of CaA support and (b) liquid phase.

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NaY, but exceeds the effective diameter of entrance windows of zeolite CaA. Thus, according to geometrical reasons, zeolite CaA is not suitable for the topological fixation, as compound **II** cannot penetrate from solution into pores of the support. Therefore zeolite CaA was chosen for the alternative topologically-anchor fixation, as narrow entrance windows of this zeolite guarantee more effective retention of a topological anchor (Fig. 1b, position 2) and, consequently, chelate **I**. Furthermore large cavities of zeolite CaA with less wide entrance windows are impermeable for cyclohexene, which makes senseless the arrangement of catalyst molecules in its cavities.

Below the composition and the main characteristics of samples **A** and **B** containing chelate compound **I** sterically held in large cavities of zeolite NaY and fixed on zeolite CaA by means of a topological anchor, respectively, are presented (m is the weight of dehydrated zeolite and y is Cu(II) specific concentration in a sample).

Sample	Carrier	<i>m</i> , g	Cu(II) content, mg	y, µmol g <sup>-1</sup>
Α	NaY	5.55	1.012	2.87
В	CaA	5.01	0.385	1.21

The procedure of fixing a copper(II) chelate compound on zeolite CaA has been considered in detail in [3]. Here we present the main characteristics of samples **A** and **B**, which were used for comparison of their catalytic activity in the reaction of cyclohexene liquid-phase oxidation by molecular oxygen.

**Homogeneous oxidation.** Catalytic activity of homogeneous catalyst I and heterogeneous samples A and B (see above) was studied in the reaction of cyclohexene liquid-phase oxidation by molecular oxygen. It was found beforehand that zeolite NaY or CaA and their decationated forms are inactive in the liquid-phase cyclohexene oxidation under the experimental conditions.

The liquid-phase oxidation of cyclohexene (RH<sub>2</sub>) by molecular oxygen in the presence of cyclohexenyl hydroperoxide (HROOH) was studied in detail earlier [5–7] for copper(II) chelates close in the chemical structure. It is convenient as a model reaction for studying catalytic behavior of chelate compound **I**, as

in all considered cases it proceeds by a common mechanism.

Chelate compound I is sparingly soluble in nonpolar and low-polar organic solvents (benzene, toluene, etc.) and in their mixtures with cyclohexene. In the course of the homogeneous-catalytic  $RH_2$ oxidation the following products are formed: 2cyclohexen-1-one (RO), 2-cyclohexen-1-ol (HROH), and epoxycyclohexane ( $RH_2 > O$ ) in the molar ratio RO : HROH :  $RH_2 > O = 2$  : 1: 1, which corresponds to stoichiometric Eq. (1).



A similar ratio between products of the liquid-phase cyclohexene oxidation by molecular oxygen was observed for related Cu(II) chelates [5–7], which confirms the similarity of reaction (1) mechanisms in these catalytic systems. The identity of the mechanisms of cyclohexene oxidation in various catalytic systems allows us to eliminate a possible influence of this factor (mechanism) on the catalytic effect on passing from one catalyst to another.

Let us note the main singularities of the behavior of the system under consideration in the liquid-phase RH<sub>2</sub> oxidation. First, O<sub>2</sub> absorption by cyclohexene does not occur (exclusive of the background reaction) if at least one of reagents, HROOH or complex I, is absent from the system. In this case HROOH in the presence of chelate I is only consumed. Second, in the case of the liquid-phase cyclohexene oxidation in the presence of chelate compound I, free radicals were not detected in the bulk liquid phase, which agrees with the assumption about the role of HROOH as a mediator of molecular oxygen transfer on a substrate molecule as a result of the coordination with a metal atom of the catalyst. The assumed mechanism of the cyclohexene liquid-phase oxidation in the presence of chelate compound I is shown in the following scheme.



It is known [9] that the coordination of HROOH with a metal atom in coordination compounds occurs through the O atom bound to a radical, therefore we can consider the formation of adducts **H** and **C** (see the scheme) as the key moment in the cyclohexene oxidation by molecular oxygen in the presence of chelate compound **I**. The distinctive feature of the adduct structure is the two-center HROOH coordination with the formation of a strongly distorted five-membered cycle, in which the axial extraligand is bound to the metal atom and to the coordinated O atom of the chelating ligand by a hydrogen bond. A cyclic transition state of a similar type was considered, for example, when studying the oxygen transfer on an alkene from an oxovanadate complex with HROOH [10].

The assumed scheme reflects not only the qualitative catalyst composition taking into account the formation of three main products of the liquid-phase cyclohexene oxidation by molecular oxygen, but also the above-enumerated singularities of the process. For example, it considers the possibility of the catalytic cyclohexene oxidation directly by cyclohexenyl hydroperoxide (route **H**–**C**–**D**–**E**–**G**), though, according to the experimental data, the contribution of this route seems to be insignificant.

It is shown in the considered scheme that the absorption of molecular oxygen, which is possible only under conditions of formation of the above-named adducts H and C, becomes "involved" in the process in

the stage of the complex **E** formation. Thus, the minor cycle (E-G) of the oriented graph presented by the scheme can be considered as the conjugate process of the catalytic cyclohexene oxidation by molecular oxygen and cyclohexenyl hydroperoxide.

The observed rate of the catalytic cyclohexene oxidation in the presence of chelate complex **I** is independent of the partial pressure of oxygen in the range of 0.006–0.06 MPa and linearly depends on the analytical concentration of homogeneous catalyst **I** and concentrations of substrate  $RH_2$  and cyclohexenyl hydroperoxide HROOH. Kinetic curves of the oxygen absorption at the liquid-phase  $RH_2$  oxidation in the presence of chelate compound **I** are given in Fig. 3. In all considered cases the observed initial rate  $r_0$  of the homogeneous cyclohexene oxidation by molecular oxygen agrees with empirical Eq. (2).

$$r_0 = k_{\text{hom}} [\text{RH}_2]_0 [\text{I}] [\text{HROOH}]_0.$$
(2)

Here  $k_{\text{hom}}$  is the effective rate constant of the homogeneous oxidation,  $[RH_2]_0$  and  $[HROOH]_0$  are initial concentrations of cyclohexene and cyclohexenyl hydroperoxide, respectively, and [I] is the analytical concentration of a homogeneous catalyst.



**Fig. 3.** Absorption of O<sub>2</sub> (*n*, mmol) by cyclohexene solutions (20 ml) in toluene as a function of time in the presence of: (*1*) chelate **I** ( $1 \times 10^{-4}$  M) at [HROOH] 0.05 M, [RH<sub>2</sub>] 1 M, and (2) heterogeneous catalysts **A** (*m* = 1.1 g; *y* = 2.87 µmol g<sup>-1</sup>) and (3) **B** (*m* 1.89 g; *y* 1.21 µmol g<sup>-1</sup>) at [HROOH] 0.2 M, [RH<sub>2</sub>] 4.94 M, normal atmospheric pressure, and 293 K.

The observed initial rate  $r_0$ , effective rate constant  $k_{\text{eff}}$  of the liquid-phase cyclohexene oxidation in toluene (1:1) by molecular oxygen in the presence of 0.2 M HROOH, chelate compound I (0.51 M), and samples A and B are given below; the volume of solution 0.02 l; T 293 K; m is the weight of a sample, and y is the specific Cu(II) concentration in the sample; the constant was calculated by Eqs. (3)–(5).

Catalyst	$r_{\rm obs} \times 10^6$ , mol l <sup>-1</sup> s <sup>-1</sup>	т,	y, µmol g <sup>-1</sup>	$k_{\rm eff}$ , $l^2  {\rm mol}^{-2}  {\rm s}^{-1}$	
		g		$k_{ m hom}$	k <sub>het</sub>
I	7.50	_	_	$3.0 \times 10^{-2}$	_
A	0.39	1.10	2.87	_	$2.5 \times 10^{-3}$
В	1.48	1.89	1.21	_	$2.6 \times 10^{-2}$

Heterogeneous oxidation. Now we shall consider how the catalytic activity of chelate compound I varies after its fixation on zeolite during the liquid-phase oxidation of cyclohexene. In the absence of chelate compound I zeolites NaY and CaA are inactive under conditions of this experiment. Therefore the observed catalytic effect, which was detected in the presence of heterogeneous catalysts A and B (Fig. 3), is connected exclusively with the catalytic activity of the fixed chelate compound.

Kinetic curves of the  $O_2$  absorption by cyclohexene solutions in toluene in the presence of samples A and **B**, and also in the presence of homogeneous catalyst **I**, are shown in Fig. 3. In both cases after heterogenization of homogeneous catalyst **I** absorption of  $O_2$ on the solid support occurs with a rate exceeding the rate of the background process by several orders. Therewith in the presence of heterogeneous catalysts **A** and **B** the mechanism of cyclohexene oxidation does not change. It is confirmed by the qualitative and quantitative catalysate composition, in which 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and epoxycyclohexane in the molar ratio 2:1:1 were detected.

The initial rate of  $O_2$  absorption by cyclohexene in a heterogeneous system containing catalysts **A** or **B** is described by Eq. (3).

$$r_0 = k_{\text{het}}^* [\text{RH}_2]_0 [\text{HROOH}]_0. \tag{3}$$

Here  $k^*_{het}$  is the effective rate constant of the heterogeneous oxidation of cyclohexene in the presence of samples **A** and **B**;  $[RH_2]_0$  and  $[HROOH]_0$  are initial concentrations of cyclohexene and cyclohexenyl hydroperoxide, respectively. The effective rate constant  $k_{het}^*$  depends on the content of an active component in the solid catalyst support, sample weight, and the technique of depositing complex I on zeolite. It was found that the length of a linear section of the rate of cyclohexene oxidation by molecular oxygen in the presence of samples A and B is different. An apparent decrease in  $k_{het}^*$  depending on time of the catalyst operation takes place first for sample A. The time of "working-out" of the catalysts B and I is much longer, and an apparent decrease in their activity takes place at high conversion degrees.

Thus, the interval of the cyclohexene stationary oxidation by molecular oxygen in the presence of sample **B** is retained for higher conversion degrees as compared to sample **A**. It seems to be connected with a diffusion inhibition of reaction (1) due to selective adsorption of water formed upon cyclohexene oxidation. Zeolite wetting results in the displacement of a reagent from large cavities and to the apparent decrease in the effective rate constant.

**Catalytic behavior of** sample **A.** Let us assume that all molecules of chelate compound **I** fixed on zeolite participate in the catalytic process. We shall assume also that the concentration of chelate **I** in a heterogeneous system ( $[I]_{het}$ ) can be presented as ratio (4) of the compound **I** content in a solid phase (*a*, mol) to the total volume of liquid and solid phases (*v*, 1).

$$[I]_{het} = a/v. \tag{4}$$

When a solid phase is used in a volume comparable with a solution volume, the system is intensively stirred, and also rather effective permeability of zeolite for reagents is taken into account, we can neglect the concentration gradient on the surface of crystallites. In this case we can consider the solid phase as a peculiar quasi-solution with boundaries moved apart conventionally up to the total volume of the heterogeneous system. Furthermore, the above-mentioned assumptions also do not contradict the common sense because sterically fixed metal chelates in large zeolite cavities are in the state of monomolecular dispersion. Then the effective rate constant  $k_{het}$  can be presented by Eq. (5).

$$k_{\text{het}} = k_{\text{het}}^* / [\mathbf{I}]_{\text{het}}.$$
 (5)

By physical meaning the value  $k_{het}$  is the heterogeneous analog of the constant  $k_{hom}$  and represents the effective rate constant of the heterogeneous cyclohexene oxidation related to one catalytic center of sample **A**. By definition,  $k_{het}$  should not depend on the

amount of a homogeneous catalyst fixed on zeolite. However this assertion is not valid practically for any catalyst concentrations in zeolite.

Let  $\theta$  be a degree of pores filling of the catalyst support by molecules of compound **I**. Then  $\theta = N_1/N_2$ , where N<sub>1</sub> and N<sub>2</sub> are the amounts of catalyst molecules and large cavities, respectively, in a sample of dehydrated zeolite NaY. The dependence of the effective rate constant of cyclohexene heterogeneous oxidation  $k_{het}$  (1) calculated by Eqs. (3)–(5) on the degree of the sample **A** filling by the catalyst is shown in Fig. 4. The effective rate constant  $k_{het}$  is calculated for an initial time instant. It is seen that only at low filling degrees  $k_{het}$  is almost independent of the chelate compound concentration in zeolite. In this case the maximal value of  $k_{het}$  (~2.5×10<sup>-3</sup> mol<sup>-2</sup> l<sup>2</sup> s<sup>-1</sup>) does not coincide with the value of  $k_{hom}$ . As the filling degree increases further, the effective rate constant of cyclohexene heterogeneous oxidation  $k_{het}$  decreases.

The maximal concentration of chelate compound **I** in a sample, at which  $k_{het}$  is conditionally constant, corresponds to filling of no more than 1–3% of large cavities of NaY zeolite with chelate compound. For geometrical reasons the molecule of chelate compound **I** can be arranged only in one large cavity of zeolite, in



**Fig. 4.** Dependence of effective rate constant  $k_{het}$  of liquidphase cyclohexene oxidation on specific density of filling large cavities *y* of sample **A** by chelate compound **I** in the system: cyclohexene–toluene, 1:1; [HROOH] 0.2 M: (1) "direct" run and (2) "inverse" run. T = 293 K.

1 g of which the number of large cavities is ~0.61 mmol. Therefore the specific concentration of copper(II) chelate compound in sample **A**, at which  $k_{het}$  continues to be conventionally independent of the degree of filling large cavities with the catalyst, does not exceed ~0.02 mmol g<sup>-1</sup> NaY.

The constancy of the effective rate constant in the interval of low degrees of filling zeolite ( $0.01 < \theta < 0.02$ ) points to the fact that in this case all molecules of the chelate compound deposited on zeolite are accessible to molecules of reagents and consequently take part in the heterogeneous catalytic process.

The decrease in the effective rate constant with increasing filling degree of large zeolite cavities by catalyst molecules, which is observed at high filling degrees, can be caused by different reasons. As the effective rate constant was calculated for an initial time instant, deactivation of the catalyst is improbable. The decrease in the effective rate constant  $k_{het}$  is probably connected with increasing diffusion resistance of a sample with respect to cyclohexene molecules.

The concentration dependence of the effective rate constant  $k_{het}$  is a typical evidence of the secondary sieve effect, which is caused by the fact that catalyst molecules localized in large cavities inside crystallites are removed from the catalytic process. At a high filling of zeolite large interior cavities become inaccessible for the reagent RH<sub>2</sub> owing to blocking pores by catalyst molecules. Therefore, when we use chelate compound I topologically fixed on zeolite, a self-screening of an active component due to blocking pores and increasing diffusion resistance is observed. Thus, the increase in the fraction of chelate I molecules fixed on the zeolite and taking no participation in the catalytic cyclohexene oxidation because of steric hindrances, leads to the fact that the effective constant  $k_{het}$  becomes dependent on the total amount of the catalyst in a solid phase.

This explanation of the effect of the inhibition of the liquid-phase cyclohexene oxidation by molecular oxygen with increasing specific concentration of the catalyst in a solid phase is confirmed by a rise of the catalyst A activity after partial destruction of chelate compound I by a dilute acid solution and extraction of destruction products from the sample. In this case only the trend to "recovery" of the effective rate constant  $k_{het}$  value is retained as the active component is extracted from zeolite. No adequate recovery of  $k_{het}$ takes place even at a very high extraction degree. This dependence is presented in Fig. 4 by curve 2. It is seen from Fig. 4 that the "reverse" run of  $k_{het}$  does not coincide with the "direct" run and lays lower for all values  $0.01 < \theta < 0.09$ .

The incongruity of the  $k_{het}(\theta)$  dependences seems to be connected with several reasons. First, with the fact that the molecules of the catalyst obtained by the "direct" and "inverse" modes are differently arranged in cavities. The extraction of an active component from sample A by the destruction of the complex begins from opening cavities on an outer surface of crystallites. This is the place where catalyst molecules accessible to a reagent are arranged. In the course of all subsequent extraction procedures the large cavities disposed further from the external surface of crystallites are sequentially depleted of catalyst molecules. Compound I is extracted from sample A nonuniformly over the volume of crystallites, and the most screened molecules of chelate compound I are extracted from zeolite in the latest time. As chelate compound I is extracted from a sample, i.e. as the total amount of copper in zeolite decreases, the fraction of the most hardly accessible molecules of the catalyst can decrease also due to a redistribution of catalyst molecules in the volume of crystallites and due to more uniform filling of large cavities on the border with the solid phase outer surface.

Thus, the apparent increase in the activity of the heterogeneous catalyst in the course of the extraction of copper(II) chelate compound is caused by the increase in the fraction of accessible catalyst molecules on the background of the decrease in the total concentration  $[I]_{het}$  [relation (4)].

So, in the case of the topological (steric) fixation of catalyst **I** in zeolite NaY the maximal activity is reached at low  $\theta$  degrees of filling large cavities. At the same time the reaction rate depends on the value of  $\theta$ , the decrease of which is extremely inexpedient as it results in a drop in the catalyst efficiency. Though  $k_{\text{het}}$  is independent of a sample weight for any filling degree by definition, the rate  $r_0$  of the heterogeneous cyclohexene oxidation at a fixed filling degree depends linearly on the sample weight **A** (Fig. 5).

**Catalytic properties of sample B.** Sample **B** contains chelate compound **I** fixed on zeolite CaA by the method of topologically-anchor retention. The concentration of complex **I** in a heterogeneous system and the effective rate constant  $k_{het}$  were calculated by Eqs. (3)–(5) in the same manner as before. The value

of the effective rate constant of cyclohexene oxidation by molecular oxygen in the presence of sample  $\mathbf{B}$  is given above.

First of all it is necessary to note that the values of effective rate constants  $k_{het}$  for samples **A** and **B** do not coincide. The values of  $k_{het}$  calculated for sample **B** is not only higher than the maximal  $k_{het}$  value for sample **A**, but within the limits of an experimental error coincides with the effective rate constant  $k_{hom}$  of the liquid-phase cyclohexene oxidation in the presence of homogeneous catalyst **I**.

The difference in properties of samples **A** and **B** is not limited only to the formal incongruity of effective rate constants  $k_{het}$ . In the case of the liquid-phase cyclohexene oxidation involving sample **B** the observed reaction rate linearly depends on specific concentration (y) of chelate compound **I** in a solid phase (Fig. 6), whereas the effective rate constant  $k_{het}$ is practically constant within the experimental error limits.

Thus, the catalytic behavior of chelate compound **I** depends on the mode of applying the catalyst on a solid phase. The coincidence of kinetic parameters

(effective rate constant) for homogeneous and heterogeneous processes points to the fact that in the presence of heterogeneous catalyst **B** the liquid-phase cyclohexene oxidation occurs in a mode close to homogeneous. Therefore, when we use sample B, in which catalytically active centers of copper(II) chelate compound are taken away from zeolite pores and turned to the side of the reaction medium, the behavior of the heterogeneous system reminds the behavior of homogeneous catalyst I. In other words, in the presence of sample **B** the pseudo-homogeneous mode is realized. In sample **B** complexes **I** are not adsorbed on the outer surface of crystallites, but are in the liquid phase volume, not losing a topological connection with the catalyst support, and are completely accessible to reagents. Therefore at effective solution stirring the cyclohexene oxidation in the presence of sample B occurs in the kinetic mode. The dependence of the initial rate r<sub>0</sub> of cyclohexene liquid-phase oxidation in toluene (1:1, 0.02 l) by molecular oxygen on the specific density y of chelate compound I fixed on zeolite CaA is given below; [HROOH] 0.2 M; T =293 K, the presented data were calculated from the parameters of dependences l-3 (Fig. 6).



**Fig. 5.** Dependence of initial rate  $r_0$  of cyclohexene oxidation on weight *m* of sample **A** in the system cyclohexene–toluene (1:1, 0.02 l); at [HROOH] 0.2 M, T = 293 K, and various filling degrees: (1) 0.005, (2) 0.047, and (3) 0.07.



**Fig. 6.** Dependence of initial rate  $r_0$  of cyclohexene oxidation on specific concentration (*y*) of chelate compound **I** fixed by topologically-anchor retention in zeolite CaA. System cyclohexene–toluene (1:1, 0.02 l); [HROOH] 0.2 M; T = 293 K, samples *m*, g: (*I*) 0.5, (*2*) 1.0, and (*3*) 1.5.

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<i>m</i> , g	$dr_0/dy$ , g l <sup>-1</sup> s <sup>-1</sup>	$k_{\text{het}},$ $l^2 \text{ mol}^{-2} \text{ s}^{-1}$
0.5	0.64	0.0267
1.0	1.28	0.0259
1.5	1.91	0.0257
	<i>m</i> , g 0.5 1.0 1.5	m, g $dr_0/dy,$ g $\Gamma^{-1}$ s <sup>-1</sup> 0.50.641.01.281.51.91

The same complexes in sample **A** are fixed in zeolite pores, and the realization of the kinetic mode is impossible even at infinitesimal concentration of chelate **I** in the catalyst support, as is indicated by a low limiting value of  $k_{het}$ .

Coincidence of the  $k_{het}$  value in the presence of sample **B** with the  $k_{hom}$  value for the liquid-phase cyclohexene oxidation in the presence of compound **I** confirms the independence of the catalytic activity from a detailed structure of distant substituents in  $\gamma$ position of a quasi-aromatic chelate metal cycle detected earlier [11] for the instance of related copper(II) chelate compounds. In fact, the topologically-anchor fixation of chelate compounds on zeolites is impossible without a ligand modification that generally does not guarantee the conservation of catalytic properties of the initial chelate compound. However, as our data show, the topologically-anchor fixation of chelate compound **I** practically does not affect its catalytic properties.

In conclusion it is necessary to note that the comparison of two related methods (steric and topologically-anchor fixation of chelate compounds of metals on zeolites) points to the fact that the latter method has a number of advantages. The matrix synthesis yielding a catalytically active copper(II) chelate compound sterically held in zeolite is connected with the appearance of a secondary sieve effect and, hence, with a decrease in the effectiveness of using a heterogenized catalyst. The secondary sieve effect and self-screening of a catalyst negatively influence the value of the effective reaction rate constant.

At the same time the effective rate constant of cyclohexene oxidation in the presence of chelate compound I fixed on zeolite CaA within the experimental error limits coincides with the value of  $k_{\text{hom}}$  that allows us to consider the method of the retention of metal coordination compounds by topological anchor as one of ways for solving the actual problem of connections between homogeneous and a heterogeneous catalyses.

## EXPERIMENTAL

Chelate compound I was synthesized by the method described in [12] from freshly prepared copper(II) hydroxide and a corresponding ligand. The heterogenization of complex I in synthetic zeolite NaY (fraction of 0.5–1 mm, SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> = 5.1) (sample A) was carried out by a matrix synthesis from copper(II) triacetylmethanate complex and hexametylenediamine fixed in large cavities [2, 13]. Sample B was prepared by topologically-anchor retention on zeolite CaA [4]. The samples were characterized by diffuse reflection spectra and elemental analysis.

Zeolite CaA (ALDRICH) was used in the form of a commercial granular preparation with size of granules of 1-1.5 mm. Zeolite CaA was calcinated in air by a standard technique within 5 h at 550°C before the synthesis of the catalyst.

Chelate compound I was partially extracted from a matrix by a dilute solution of an acid with the subsequent determination of copper(II) in the extract by the iodometric titration. After partial extraction of copper(II) from a sample, zeolite was multiply washed out with water and held in a sodium sulfate solution for the inverse ion exchange to restore the cationic form.

Cyclohexene was obtained by a dehydration of cyclohexanol, purified from cyclohexenyl hydroperoxide by boiling with metal sodium, and stored in an argon atmosphere. The concentration of cyclohexenyl hydroperoxide was determined by the iodometric titra-tion in an alcohol solution.

The kinetics of liquid-phase oxidation of cyclohexene were studied by a static method in a thermallycontrolled glass reactor at atmospheric pressure and room temperature. Toluene, which relatively readily dissolves homogeneous catalyst **I**, was used as a solvent. The qualitative and quantitative composition of the catalysate was determined by the TLC method and by the use of a Chrom-5 Separon gas chromatograph (column 1.5 mm  $\times$  3m).

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