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Copper Catalysts Based on Fiberglass Supports for Hydrocarbon Oxidation Reactions with the Participation of Hydrogen Peroxide

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Abstract—Copper-containing catalysts were prepared by the adsorption of the ammonia complexes of Cu(II) on the surface of a silicate fiberglass material followed by the thermal and oxidative treatment of the samples. The states of copper after the adsorption of ammonia complexes and in the prepared samples were characterized using electronic diffuse reflectance spectroscopy. The catalytic activity of the samples in hydrogen peroxide decomposition and cyclohexane oxidation reactions was studied. It was found that molecular oxygen can be involved in the radical process of hydrogen peroxide oxidation. Based on spectroscopic data, it was hypothesized that partially reduced Cu(I)–Cu(0) compounds are active species in the catalysts of this type.

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INTRODUCTION

Hydrogen peroxide is the most promising reagent for a number of oxidation processes in terms of cost and environmental safety. The oxidative functionalization of hydrocarbons is a problem to be solved frequently by hydrogen peroxide oxidation. In this area, a great body of data on catalysis by transition metal ions and complexes, in particular, copper compounds, has been accumulated.

Copper complexes with various mono-, bi-, and tridentate organic ligands, such as pyridine, bipyridine, tripyridine, tris(pyrazolyl)borate, tris(pyrazolyl)methane [1], and porphyrins, are used in the oxidation of organic substrates. In the presence of these complexes, the hydrogen peroxide oxidation of saturated and unsaturated hydrocarbons, alcohols, and alkylbenzenes occurs with the formation of corresponding alcohols, ketones, and hydroperoxides [1].

Under conditions of homogeneous liquid-phase catalysis, the ligand environment of copper ions, on the one hand, retains them in solution and, on the other hand, forms the structure of active sites. The oxidation reactions of saturated [2, 3] and unsaturated aromatic hydrocarbons [3] analogous to homogeneous reactions occur on the surface of solid copper complexes, which are insoluble in the reaction mixture. Thus, the oxidation of cyclohexane by hydrogen peroxide occurs intensively in the presence of heterogeneous mononuclear and tetranuclear porphyrin complexes of copper [2]. The corresponding alcohol and ketone, cyclohexyl hydroperoxide, and adipic acid are the oxidation products. Other complexes, such as copper(II) *trans*-1,4-cyclohexanedicarboxylate, oxidize various alcohols to corresponding ketones with selectivity higher than 99% in a 20-fold excess of hydrogen peroxide [3].

Copper complexes with organic ligands immobilized on solid support surfaces belong to another category of heterogeneous systems. Metal oxides [4, 5]; silicon oxides [6–8]; and zeolites X, Y [9, 10], MCM-41 [8, 11], ZSM-5 [12, 13], and HMS [14] are most commonly used as supports. The examples of a sufficiently high activity of heterogenized copper complexes are well known. Thus, the conversion of phenol in an aqueous solution by hydrogen peroxide oxidation on heterogeneous catalysts of this type was higher than 36%; the total selectivity for catechol and hydroquinone was higher than 95% [14]. Aromatic unsaturated hydrocarbons (toluene and benzene) were completely oxidized to CO_2 and H_2O in the presence of the most active catalysts 5 wt % Cu/ZrO_2 [4] and 1.5 wt % Cu/SiO_2 [7].

Several problems appear in the use of heterogeneous catalysts for peroxide oxidation. The majority of heterogeneous systems described in the literature, like homogeneous systems, contain organic components. The degradation of organic ligands occurs in an oxidizing medium, and the support is also often affected. In addition, many supports, particularly zeolites, exhibit high porosity. Therefore, a portion of an active component becomes inaccessible to reactants or the desorption of oxidation products from the catalyst surface into a solution is hindered [8–14].

In this study, copper catalysts were prepared by the immobilization of inorganic copper complexes on a fiberglass support, which was characterized previously [15]. The important properties of the fiberglass used are the following: (i) a low specific surface area and the absence of pores; (ii) the presence of a great number of surface silane and siloxane groups, which serve as immobilization sites for complex copper cations; and

(iii) stability to degradation upon high-temperature treatments to 900°C [15].

In this work, we were the first to study heterogeneous copper-containing catalysts prepared by the adsorption of copper(II) acetate and copper(II) tetraammoniate on a fiberglass support in the liquid-phase oxidation reaction of cyclohexane. Catalytic systems based on fiberglass materials were used only in gas-phase reactions [16, 17], and they were not used previously in liquid-phase oxidation catalysis.

EXPERIMENTAL

Chemicals

The silica fiberglass support used in this study was characterized in detail previously [15]. The material consisted of threads slightly less than 1 mm in diameter, which were weakly spun from thin fibers with d ~7–10 μm; the threads easily disintegrated into individual fibers. The fibers consisted of nonporous amorphous SiO_2 with $S_{sp} = 1$ m^2/g.

The following chemicals were used in this study: cyclohexane of analytical grade, reagent-grade hydrogen peroxide (30%), aqueous ammonia (25%) of analytical grade, acetonitrile from Kriokhrom with a water content of 0.005% (was used without preliminary purification), distilled water, and 95% ethanol.

Synthesis of Cu/SiO$_2$ Samples

The Cu/SiO_2 samples were prepared by the adsorption of copper from solutions of cationic ammonia complexes of Cu(II) on a fiberglass support.

To prepare impregnating solutions, copper chloride ($CuCl_2 \cdot 2H_2O$) or copper acetate ($Cu(CH_3COO)_2$) was dissolved in water with the addition of 25% NH_4OH at the molar ratio $Cu(II)/NH_4OH = 1 : 10$.

Adsorption was performed in a thermostated shaken glass reactor with a volume of ~50 ml at a fiberglass-to-solution-weight ratio of ~1 : 20 and at a fixed solution temperature. The adsorption temperature and time were varied over the ranges 30–70°C and 10–120 min, respectively. After the adsorption, the sample was removed from the reactor, repeatedly washed with distilled water at room temperature, and dried on a filter in a flow of warm air.

For the reductive treatment of the samples, they were placed in a glass reactor, which was initially blown with helium at a rate of 80 ml/min for 5 min and then with hydrogen at a rate of 70 ml/min. The sample was heated to a specified temperature at a rate of 10 K/min in a flow of hydrogen and kept for 1 h at this temperature. The main treatment temperature was varied from 100 to 400°C for different samples. The treatment was finished by cooling the sample to room temperature in a flow of hydrogen and purging with helium.

Physicochemical Methods

The concentration of copper was determined by X–ray fluorescence spectroscopy after the complete dissolution of the sample.

The electronic diffuse reflectance spectra of copper-containing fiberglass Cu/SiO_2 samples and the UV transmission spectra of the solutions of copper complexes were measured with reference to $BaSO_4$ over the range 11000–54000 cm^{-1} on a UV-2501 PC spectrophotometer (Shimadzu, Japan) with an ISR-240 A diffuse reflectance attachment. The electronic diffuse reflectance spectra were plotted in the wavenumber–Kubelka–Munk function ($F(R)$) coordinates. The transmission spectra of solutions of copper(II) complexes were measured with reference to water using a quartz cell with an optical path length of 2 mm.

The cyclohexane oxidation products were analyzed by gas chromatography on a Kristall 2000m instrument equipped with a DB-1701 capillary column (30 m in length and 0.53 mm in i.d.) and a flame ionization detector.

Catalytic Tests

The catalytic reactions of cyclohexane oxidation and hydrogen peroxide decomposition were performed in a thermostated glass reactor with a volume of ~30 ml, which was connected to a graduated glass gas burette. As a rule, the catalyst (0.1 g), the solvent acetonitrile (3.8×10^{-2} mol), and the cyclohexane substrate (1.85×10^{-3} mol) (some experiments on hydrogen peroxide decomposition was performed in the absence of cyclohexane) were loaded in the reactor. The reactor was thermostated ($T = 60$°C) for several minutes and connected to the gas burette, and atmospheric pressure was maintained in the system. In order to perform the cyclohexane oxidation reaction in an atmosphere of oxygen or nitrogen, the reactor was purged with an appropriate gas. Hydrogen peroxide (8.53×10^{-3} mol) was introduced into the reactor through a special nozzle without depressurization; thereafter, a magnetic stirrer was turned on (500 rpm). Changes in the gas-phase volume in the course of the reaction were monitored using the gas burette.

The catalytic activity of the samples in the reaction was evaluated as the total amount of products formed in a specified time interval.

RESULTS AND DISCUSSION

UV Spectra of Impregnating Solutions and the Cu/SiO$_2$ Samples Prepared from Them

As can be seen in Fig. 1, the spectrum of a solution of $CuCl_2 \cdot 2H_2O$ in water changed upon the addition of ammonia. Even at the concentration ratio $[CuCl_2 \cdot 2H_2O]/[NH_4OH] = 1 : 4$, a tetracoordinated ammonia complex of copper was formed, as evidenced by absorption at 16 500 cm^{-1} (curve *5*) [18]. Moreover, this

solution exhibited absorption over the range 28000–33000 cm^{-1} due to polynuclear hydroxo complexes of Cu(II). At a higher concentration of ammonium hydroxide (the concentration ratio $[NH_4OH]/[CuCl_2 \cdot 2H_2O]$ increased from 4 to 50), the absorption characteristic of hydroxo complexes became less intense and practically disappeared (curves *4*, *3*, and *2*), whereas the absorption band intensity of ammonia complexes increased. Because the treatment of the support with highly concentrated ammonia solutions could cause the degradation of the material, a solution containing a tenfold amount of ammonia with respect to Cu(II) was subsequently used for impregnation. As judged from the UV spectrum (Fig. 1, curve *4*) and published data [18], Cu(II) ions occur in this solution as $[Cu(NH_3)_6]^{2+}$ cations, whereas hydroxo complexes are almost absent.

In the case of copper acetate, the solutions exhibited analogous spectra. Therefore, a solution with a tenfold amount of ammonium hydroxide with respect to copper acetate was also used in this case for impregnation.

The samples containing from 0.05 to 0.08 wt % copper were obtained by the treatment of the fiberglass with a solution of the ammonia complex of copper. Table 1 summarizes the treatment temperatures and the support–solution contact times. As judged from the data in Table 1, the adsorption equilibrium of the ammonia complexes was rapidly established, so that changes in the temperature and time of fiberglass treatment with the ammonia solution of copper over the specified ranges only slightly affected the metal content of the final sample. Nevertheless, higher copper contents of the samples after more intense treatments (at higher temperatures and longer contact times) can be noted. Thus, the subsequent experiments were performed with catalyst sample no. 7 (Table 1).

The diffuse reflectance spectra of support samples after contact with solutions of the ammonia complex of copper $[Cu(NH_3)_6]Cl_2$ were characterized. The band

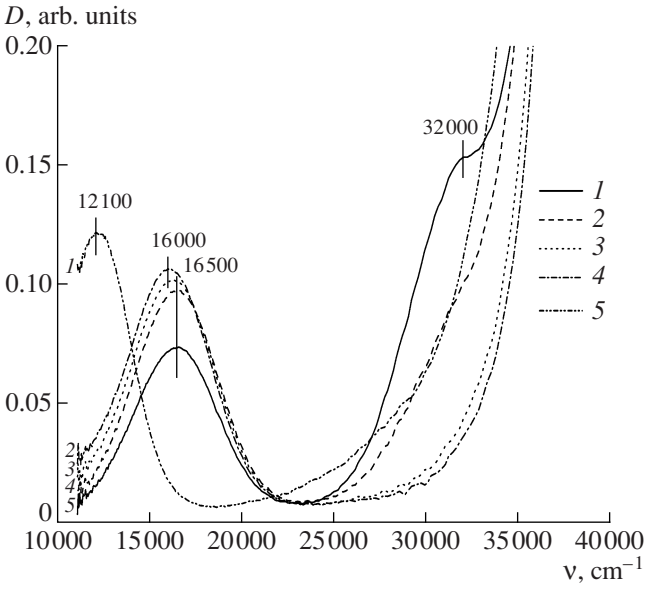

Fig. 1. UV spectra of the ammonia complexes of copper(II) in water: (*1*) $CuCl_2 \cdot 2H_2O$, (*2–5*) with the addition of $NH_3 \cdot H_2O$ to the molar ratios Cu/NH_3 = (*2*) 1 : 50, (*3*) 1 : 30, (*4*) 1 : 10, and (*5*) 1 : 4.

due to the ammonia complex on the fiberglass surface shifted to 14900 cm^{-1}, as compared to an analogous band for the solution (16000 cm^{-1}). This suggests the chemical interaction of the ammonia complex with the support surface, because of which the composition of the coordination sphere of copper ions changed. The band due to hydroxo complexes shifted to the long-wavelength region (to 30600 cm^{-1}); this band was much more intense than that in the spectrum of the solution. As judged from the intensity ratio between the bands due to the ammonia complex and hydroxo complexes, the major portion of surface copper occurred as hydroxo complexes, unlike the starting solution con-

Table 1. Conditions of the adsorption of the ammonia complexes of copper on fiberglass and the copper contents of the resulting samples

Sample	Treatment conditions			[Cu], wt %
	temperature, °C	time, min	impregnating solution	
1	50	60	$[Cu(NH_3)_6]Cl_2$	0.06
2		120		0.07
3	60	10		0.05
4		60		0.07
5		120		0.08
6	70	10		0.07
7	50	120		0.07
8	50		$[Cu(NH_3)_6] \cdot (CH_3COO)_2$	0.08

Note: The impregnating aqueous solution contained $[CuCl_2 \cdot 2H_2O] = [Cu(CH_3COO)_2] = 1.52 \times 10^{-2}$ mol/l and $[NH_3 \cdot H_2O] = 1.52 \times 10^{-1}$ mol/l.

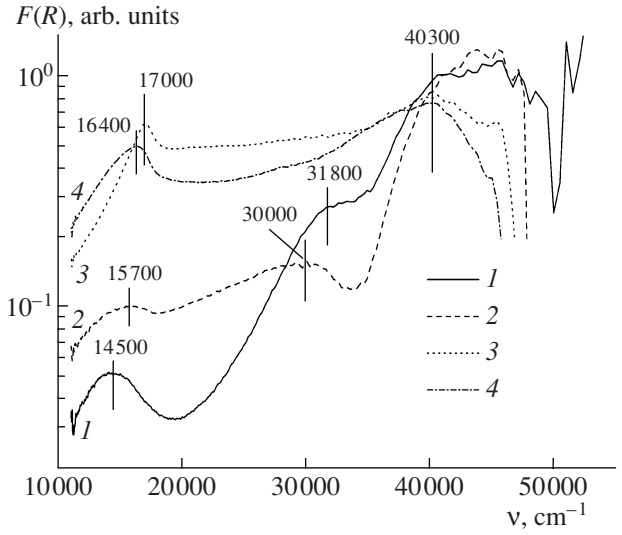

Fig. 2. Diffuse reflectance spectra of fiberglass samples prepared by impregnation from a solution of $Cu(NH_3)_6Cl_2$ and reduced in a flow of hydrogen at (*1*) 100, (*2*) 200, (*3*) 300, or (*4*) 400°C.

taining only the ammonia complex. The intensities of both of the bands were somewhat higher in the samples treated under more severe conditions: at a higher temperature and a long time of contact between the fiberglass and the solution.

In the course of adsorption, support threads partially separated into thin fibers; therefore, the threads were specially divided into fibers in the subsequent experiments. This resulted in a more uniform wetting of the sample with the impregnating solution and had a weak effect on the spectra of the samples after adsorption.

After the reductive treatment with hydrogen from the gas phase, intense absorption in the region 20000–25000 cm^{-1}, which corresponds to mixed-valence Cu(I)–Cu(0) compounds [19–21], appeared or increased in the spectra of the samples. In the next series of samples, the adsorption of the copper complex was performed at 50°C for 120 min followed by treatment in a flow of hydrogen. Figure 2 shows the diffuse reflectance spectra of the samples thus prepared. After the treatment of the samples at the highest temperatures (300 and 400°C), absorption bands at 17000 and 16400 cm^{-1} (curves *3* and *4*), which were attributed to copper metal [19], appeared in the spectrum in addition to absorption characteristic of Cu(I)–Cu(0) compounds. As the reduction temperature was increased from 300 to 400°C, the absorption characteristic of the mixed-valence compounds decreased, whereas the absorption band due to the metal became more intense.

An analogous change in the spectrum resulted from the reductive treatments of catalysts prepared from copper acetate.

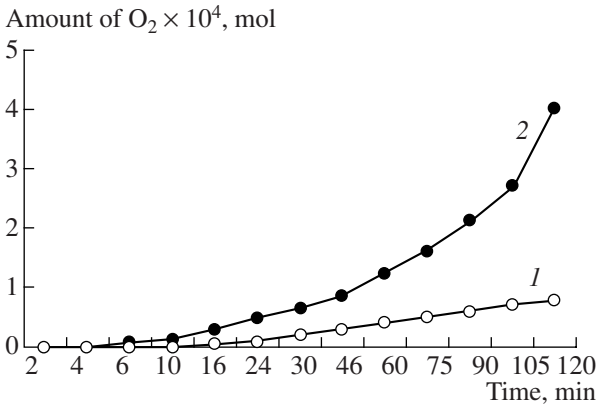

Fig. 3. Kinetics of O_2 release in the decomposition of H_2O_2 in the presence of (*1*) 0.05 or (*2*) 0.10 g of the catalyst.

Hydrogen Peroxide Decomposition

The samples subjected to reductive treatment catalyzed the decomposition of aqueous hydrogen peroxide in an acetonitrile solution.

The initial portion of the kinetic curves is characterized by an induction period, which is related to the development of a chain process. The rate of decomposition subsequently increased with time (Fig. 3).

The rate of reaction and the shape of hydrogen peroxide decomposition curves depended on both catalyst weight (Fig. 3) and the initial amount of hydrogen peroxide in solution. The dependence exhibited a complicated character; however, the curves were similarly shaped. As the catalyst weight and the amount of hydrogen peroxide were increased, the induction period shortened; in this case, the rates of hydrogen peroxide decomposition and reaction product formation increased with time.

Cyclohexane Oxidation in the Presence of Fiberglass Samples

The oxidation of cyclohexane occurred under the reaction conditions of hydrogen peroxide decomposition. Cyclohexanol, cyclohexanone, and minor amounts of cyclohexyl hydroperoxide were the main oxidation products. Note that the fiberglass samples that were dried in air after the adsorption of $[Cu(NH_3)_6]Cl_2$ were found to be almost inactive. Catalytic activity in cyclohexane oxidation, as well as in hydrogen peroxide decomposition, developed only after the reductive treatment of the samples. Figure 4 shows the amounts of cyclohexane oxidation products formed upon the addition of copper-containing fiberglass prepared by adsorption from an ammonia solution of the copper complex $[Cu(NH_3)_6]Cl_2$ and reduced in hydrogen at various temperatures from 100 to 400°C. As the reduction temperature was increased, the catalytic activity increased and reached a maximum after reduction at 300°C. As the catalyst reduction tempera-

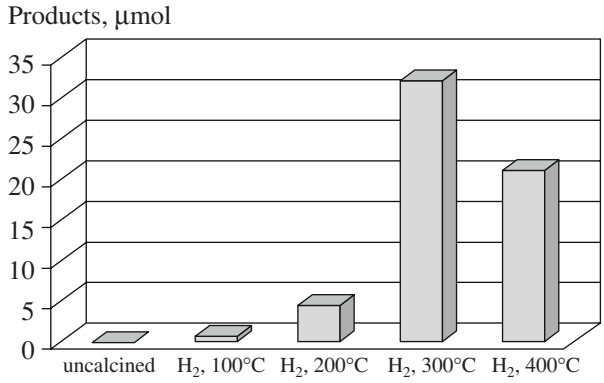

Fig. 4. Amounts of cyclohexane oxidation products (cyclohexanol + cyclohexanone) formed in the presence of copper-containing fiberglass prepared by adsorption from an ammonia solution of $Cu(NH_3)_6Cl_2$ and reduced at various temperatures. Time: 120 min. Atmosphere: O_2.

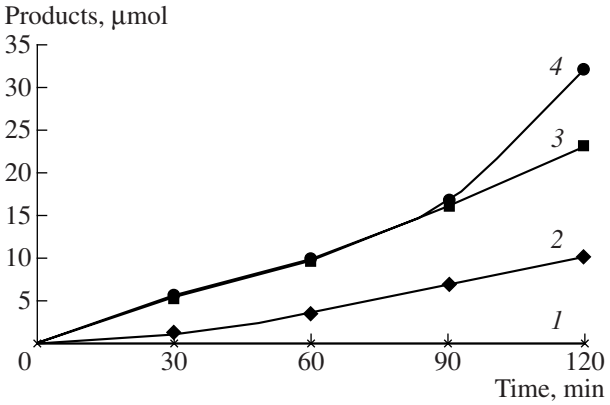

Fig. 5. Effect of the gas atmosphere on the rate of cyclohexane oxidation: (*1*) O_2, (*2*) $N_2 + H_2O_2$, (*3*) air + H_2O_2, and (*4*) $O_2 + H_2O_2$.

ture was further increased to 400°C, a smaller amount of cyclohexane oxidation products was obtained. At the same time, as the calcination temperature was increased, the diffuse reflectance spectra exhibited more intense absorbance in the region 20000–25000 cm^{-1} (Fig. 2), which corresponds to mixed-valence Cu(I)–Cu(0) compounds.

An analogous behavior in cyclohexane oxidation was observed in the samples prepared from copper acetate. An unreduced sample did not exhibit activity. As in the previous series of samples, activity appeared only after reductive treatment; the activity of the samples from $Cu(CH_3COO)_2$ was lower than that of the samples prepared from a solution of $[Cu(NH_3)_6]Cl_2$ by a factor of ~2. This can be due to the following reasons: (i) a positive effect of Cl^- anions, which can be minor constituents of the samples prepared from a chloride-containing solution of $[Cu(NH_3)_6]Cl_2$, on catalysis and (ii) different concentrations of mixed-valence compounds, as evidenced by different absorption intensities in the region 20000–25000 cm^{-1}.

Note that the fiberglass samples exhibited sufficiently high catalytic activity in the reaction of cyclohexane oxidation even at a low copper content. Comparing the results of catalytic tests with the spectroscopic characteristics of the catalysts, we found that the catalytic activity of the samples correlated with the intensity of absorption in the region that is characteristic of Cu(I)–Cu(0) compounds. These compounds formed in the partial reduction of the initial ammonia complexes of Cu(II).

The composition of the gas phase in the reactor and the temperature of the reaction solution, as well as the amounts of the catalyst and hydrogen peroxide added, affect the rate of buildup of the main oxidation products: cyclohexanol and cyclohexanone. The effects of these factors are considered below.

The oxidation reaction was performed in various gas atmospheres: air, oxygen, and nitrogen (Fig. 5). In the latter two cases, the reactor with the loaded reactants was purged with O_2 or N_2 and connected to a burette filled with the corresponding gas.

In the interaction of cyclohexane with oxygen in the absence of hydrogen peroxide, the formation of oxidation products was not detected (curve *1*). Nevertheless, oxygen positively affected the rate of cyclohexane oxidation in the presence of peroxide. Figure 5 shows that, in the presence of oxygen (curve *4*), oxidation occurred much more rapidly than in nitrogen or air (curves *2* and *3*, respectively).

Oxygen was consumed in the course of the reaction with hydrogen peroxide. It is likely that oxygen reacted with radicals formed by the decomposition of hydrogen peroxide to result in chain branching. In accordance with the reactions given below, this increased the rate of cyclohexane oxidation (R is cyclohexane).

$$RH + OH^\bullet \longrightarrow R^\bullet + H_2O, \quad \text{(I)}$$

$$R^\bullet + O_2 \longrightarrow ROO^\bullet, \quad \text{(II)}$$

$$ROO^\bullet + RH \longrightarrow R^\bullet + ROOH, \quad \text{(III)}$$

$$ROOH \longrightarrow RO^\bullet + OH^\bullet, \quad \text{(IV)}$$

$$RO^\bullet + RH \longrightarrow ROH + R^\bullet. \quad \text{(V)}$$

In air, the oxidation reaction occurred more slowly than in oxygen, whereas the buildup of products in nitrogen occurred only because of hydrogen peroxide decomposition. The cyclohexanol/cyclohexanone product ratio remained almost the same regardless of the composition of the gas mixture (air, oxygen, or an inert gas—nitrogen). This product ratio suggests the simultaneous formation of cyclohexanol and cyclohexanone from a common precursor, cyclohexane, whereas the oxidation of cyclohexanol to cyclohexanone did not occur.

The temperature of the reaction atmosphere also considerably affected the rate of cyclohexane oxidation (Fig. 6). We found that cyclohexane oxidation occurred very slowly over a range from room temperature to

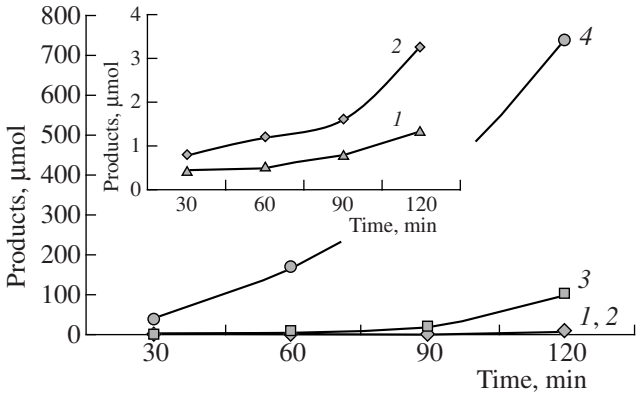

Fig. 6. The temperature dependence of the rate of cyclohexane oxidation in an atmosphere of oxygen: (*1*) 40, (*2*) 50, (*3*) 60, and (*4*) 65°C.

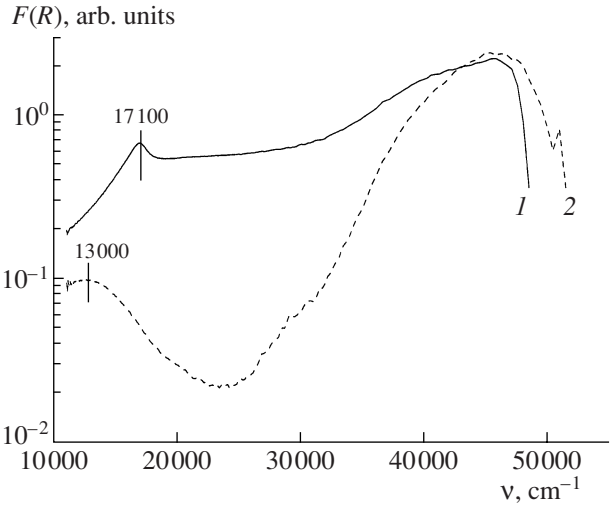

Fig. 7. Diffuse reflectance spectra of fiberglass samples (*1*) before and (*2*) after cyclohexane oxidation. T = 65°C; oxygen atmosphere.

50°C (curves *1*, *2*). The rapid buildup of the oxidation products cyclohexanol and cyclohexanone came into play at 60°C (curves *3*, *4*).

In the presence of copper-containing fiberglass samples, an insignificant growth of cyclohexane oxidation products was observed in the first minutes of reaction; this is consistent with the analogous shape of hydrogen peroxide decomposition curves. The rate of the oxidation reaction increased with time with increasing catalyst sample weight and the amount of hydrogen peroxide in solution.

After completion of the reaction of cyclohexane with hydrogen peroxide, the catalyst was removed and used repeatedly. In the repeated test, the sample exhibited a negligibly low activity, as compared with that of the fresh catalyst. The amount of detected products was 35 μmol, which is smaller than that in the first cycle by a factor of 20. As judged from the spectra of a sample recorded before and after the catalytic reaction (Fig. 7), deactivation was related to the oxidation of reduced Cu(I)–Cu(0) compounds to Cu(II). A band at 13000 cm^{-1} corresponds to a Cu(II) compound [21]. For comparison, a band due to CuO lies at 15400 cm^{-1} [19]. We found that the reductive treatment of the sample allowed us to reactivate it to an insignificant extent.

CONCLUSIONS

The silica fiberglass support is promising for liquid-phase reaction catalysts because of its low surface area, the absence of a pore structure, and chemical resistance over a wide range of pH. The adsorption of the ammonia complexes of Cu(II) from a weakly alkaline solution results from coordination bonds with functional groups on the support surface. Mixed-valence Cu(I)–Cu(0) compounds are formed on the surface by the subsequent treatments. Although the copper content of the resulting catalysts is low, they exhibit good catalytic activity in the reactions of hydrogen peroxide decomposition and cyclohexane oxidation. Table 2 compares the activity of the resulting catalysts (Cu/fiberglass) with the activities of various copper compounds based on other supports in the oxidation reactions of organic substrates. The amount of oxidation products was 90 mol cyclohexanol + cyclohexanone per mole of copper as a catalyst constituent per hour. It is of importance that, in an oxygen-containing atmosphere, molecular oxygen was involved in the chain radical oxidation process, probably through preactivation, which also occurred on copper compounds. The participation of

Table 2. Comparison of the activity of the prepared catalysts with published data

Catalyst	Oxidized substrate	Reaction rate, mol product × (mol active component)$^{-1}$ h^{-1}	Reference
Copper(II) *trans*-1,4-cyclohexanedicarboxylate	Linear, cyclic, and aromatic alcohols	0.40–0.21	[3]
[Cu(sal-ambmz)(Cl)]Y	Phenol	565.7	[9]
	Styrene	127.4	
Cu/MCM-41	Benzyl alcohol	75.6	[22]
[Cu(sal-oaba)(H_2O)]Y	Cyclohexanol	220.3	[23]
Cu/fiberglass	Cyclohexanol	90	This work

molecular oxygen in cyclohexane oxidation allowed us to decrease the consumption of hydrogen peroxide: 0.08 mol of oxidation products was formed per mole of H_2O_2, whereas a higher peroxide consumption is usually characteristic of chain radical oxidation reactions.

Now, it is clear that copper particles are sufficiently stable to washing off, whereas sample deactivation was mainly related to the reversible oxidation of copper. The repeated use of the catalyst should be further studied in more detail.

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